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# 2009 Symposium on Nanomaterials for Flexible Packaging

# 2009 Symposium on Nanomaterials for Flexible Packaging

- Sarah Schirmer is Materials Engineer for the US Army Natick Soldier Research, Development & Engineering Center in Natick, MA
- Sarah develops and tests monolayer and multilayer plastic films for combat ration packaging.
- Sarah works closely with the other members of her team to solve problems with military ration packaging.
- The goal is to develop combat rations packaging systems for the warfighter that feature enhanced survivability, improved acceptability, increased safety/security, reduced weight, improved shelf life and reduced packaging waste.
- Sarah attained her Bs and MS at the University of Massachusetts at Lowell

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2009 Symposium on Nanomaterials for Flexible Packaging

# Nanocomposites for Military Food Packaging Applications


Presented by:

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# Outline

- Introduction
- Background
- Nanocomposites
- Military Applications
- Characterization
- Non-Retort Pouch
- Retort Pouch
- MRE™ Meal Bag
- Conclusions

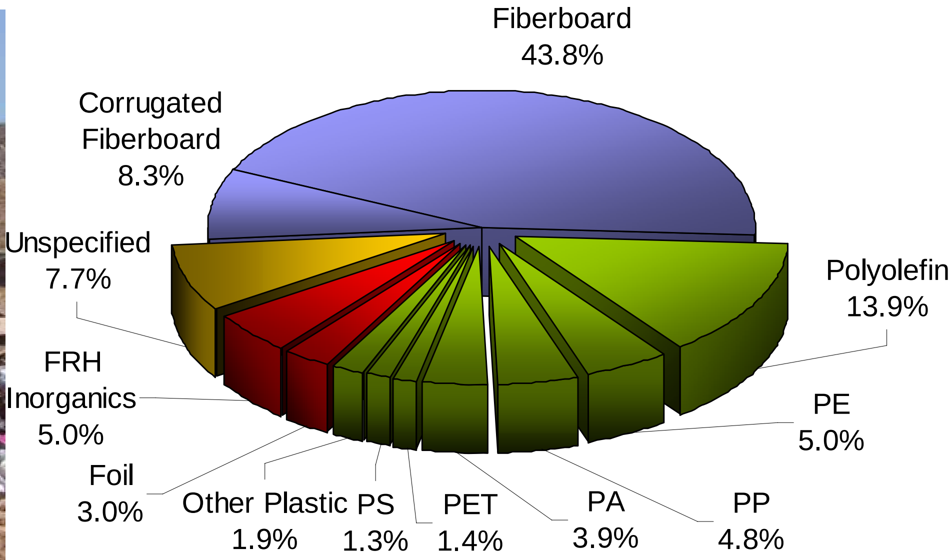
# Introduction


"An army travels on its stomach."

~Napoleon Bonaparte


# Background

- Meal, Ready-To-Eat (MRE™)
  - Contents include individually packaged
    - Entrée, crackers, spread, dessert or snack, beverage, accessory packet, plastic spoon and flameless ration heater
      - 0.3 pounds of packaging waste per MRE
      - 30,000 tons of packaging waste per year

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# Background

- Stringent barrier properties required for the retort entrée:
  - Oxygen transmission rate of 0.06 cc/(m²-day) 50% RH 23°C
  - Water vapor transmission rate of 0.01 g/(m²-day) 90% RH 37.8°C

- Shelf life of three years at 80°F (27°C) or six months at 100°F (38°C)


# Background

MRE$^{TM}$ Meal Bag


LLDPE

MRE$^{TM}$ Retort Pouch Structure

Inner Layer →

Polyolefin
Aluminum Foil
Polyamide
Polyester

Outer Layer →

MRE$^{TM}$ Non-Retort Pouch

Inner Layer →

Polyolefin
Aluminum Foil
Polyester

Outer Layer →

# Background

- Aluminum foil is used for the retort and non-retort structures
  - Excellent barrier to oxygen and water vapor
  - Aluminum foil laminates are not recyclable
  - Pin holes and stress cracking is a problem
  - Can not make use of microwave sterilization
  - Lamination and not co-extrusion must be used
    - Lamination is more expensive and less efficient

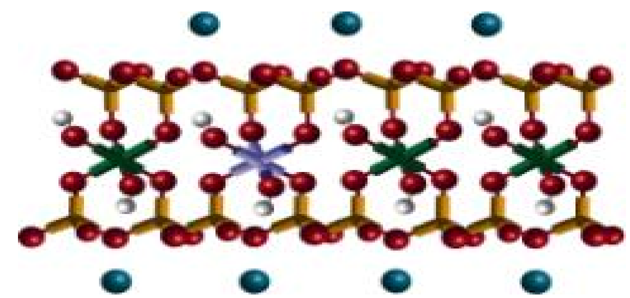
- Retort processing of the MRE™ entrée
  - High temperature water and steam commercial sterilization method
  - 121°C (250°F) for 30 minutes
  - Kills bacteria and microorganisms

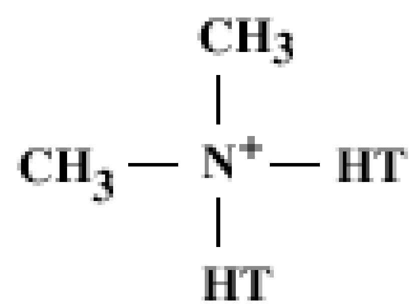
# Nanocomposites

- Nanocomposite films have shown significant improvement in:
  - Barrier Properties
    - Oxygen and Water Vapor
  - Mechanical Properties
    - Young's Modulus and Tensile Strength
  - Thermal Properties
    - Heat Deflection Temperature
    - Heat Resistance
    - Decreased Flammability
- Property improvement is dependent on the level of interaction between the polymer and nanoparticle

# Nanoparticles

- Layered silicate nanoparticles are commonly used in polymer nanocomposites
  - Crystal lattice 1 nanometer thick
  - 100-200 nanometer wide platelets
  - High surface area
  - High aspect ratio
    - Increases interaction with polymer as compared to traditional additives
  - Organically modified to be compatible with polymers






- Nanoparticles investigated include
  - Montmorillonite layered silicate (MLS)

HT = Hydrogenated Tallow
(extended hydrocarbon chain increases compatibility with polymer)

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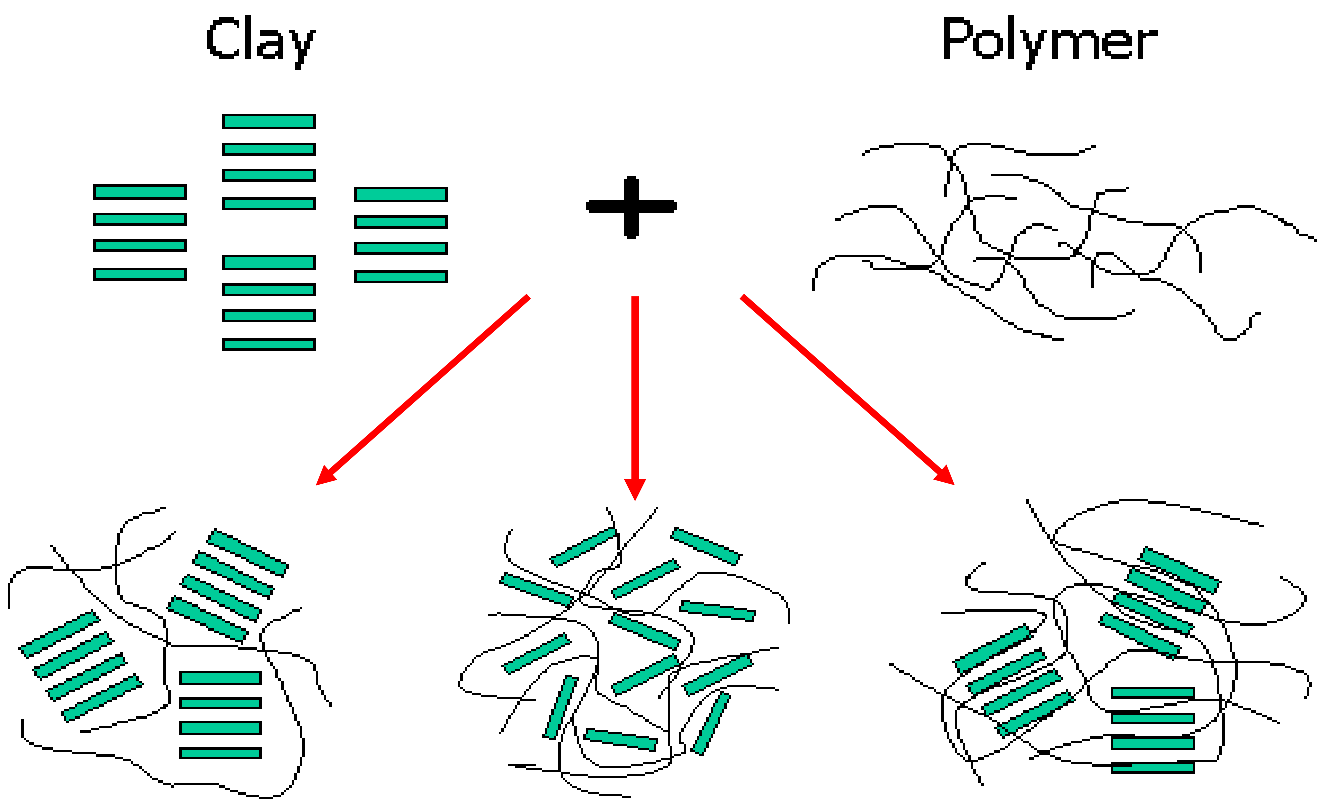
# Nanocomposite Morphology




Conventional Composite

Exfoliated Nanocomposite 80-100 Å separation

Intercalated Nanocomposite 20-30 Å separation

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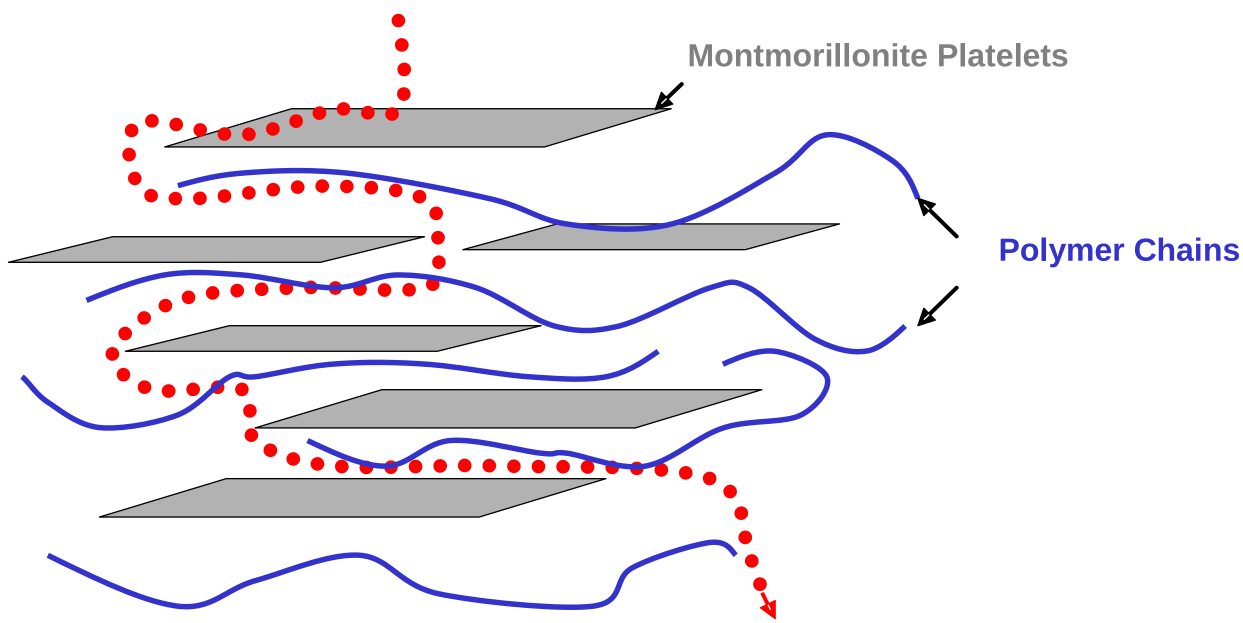
# Nanocomposite Barrier Theory

- Tortuous Pathway Model
  - Created because of the large surface area and high aspect ratio
  - Increased path length of the gas molecule leads to increased barrier properties



# Nanocomposite Food Packaging Applications

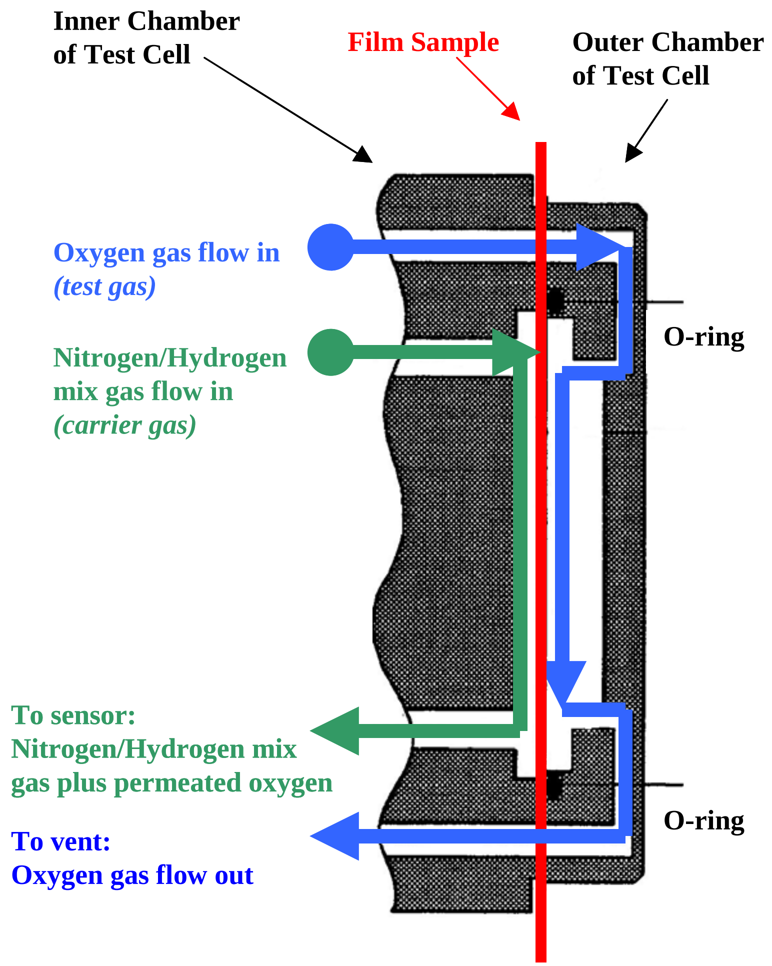
- MRE$^{TM}$ Non-Retort Pouch
  - Develop all polymeric structure to replace the current aluminum foil tri-laminate
    - Must have sufficiently high barrier to oxygen and water vapor
- MRE$^{TM}$ Retort Pouch
  - Develop all polymeric structure to replace the current aluminum foil quad-laminate
    - Must meet stringent barrier requirements
    - Must be retort processed
- MRE$^{TM}$ Meal Bag
  - Down-gauge the current 11 mil (0.28 mm) thick meal bag
    - Attempt to decrease thickness while maintaining mechanical properties and durability

# Characterization

- Oxygen Permeability
  - MOCON® Ox-Tran 2/20
    - 23$^{o}$C and 0%, 60% and 90% RH
    - 50 $cm^2$ Area
      - ASTM D3985

- One side of the sample is flushed with pure oxygen while the other side has a mixture of nitrogen and hydrogen; any oxygen that is able to permeate the sample is carried by the mixed gas to the oxygen sensor which determines the oxygen transmission of the sample in units of cc/$m^2$-day

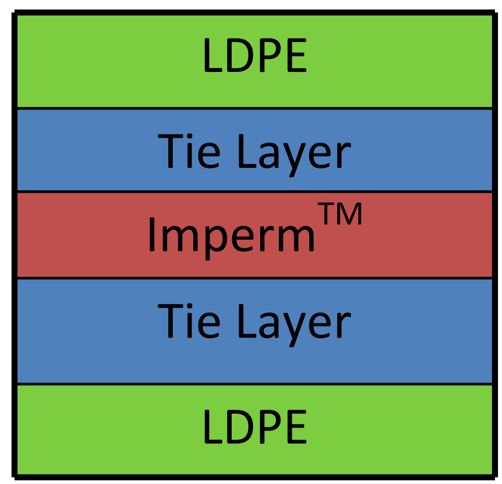
- Oxygen Transmission Rate (OTR) cc/$m^2$-day
- Oxygen Permeation Rate (OPR) cc-mil/$m^2$-day
  - OPR is the OTR normalized to thickness and can only be used for monolayer films



# Experimental Non-Retort Pouch

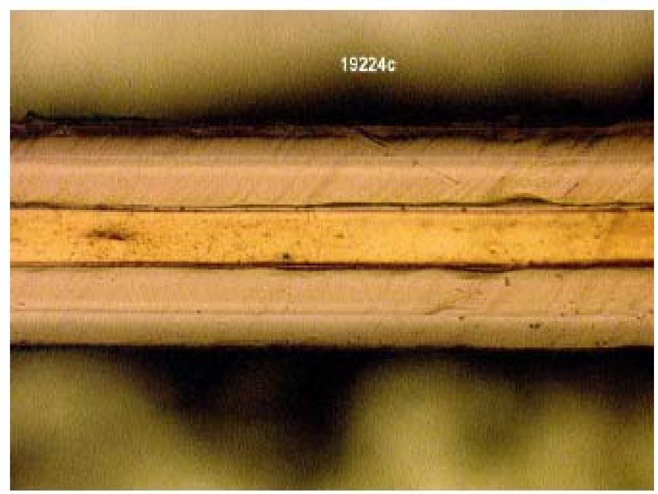
- MXD6 nylon nanocomposite called Imperm$^{TM}$ 105
  - (poly(m-xylylene adipamide))
  - Produced by Mitsubishi/Nanocor
  - Used currently in multilayer PET carbonated beverage bottles
  - Superior oxygen barrier at a wide range of relative humidities
  - Montmorillonite Layered Silicate Content 3.3-3.6% as reported by Nanocor
  - 0.01% ethylene bis-stearamide used in processing
- Low Density Polyethylene Huntsman 1031
  - Provide water vapor barrier and heat sealability
- DuPont Bynel 4125 used as the tie layer
  - Maleic anhydride grafted LLDPE
  - Used as an adhesive to keep polar and non-polar polymers from delaminating

**Multilayer Film Structure ↓**



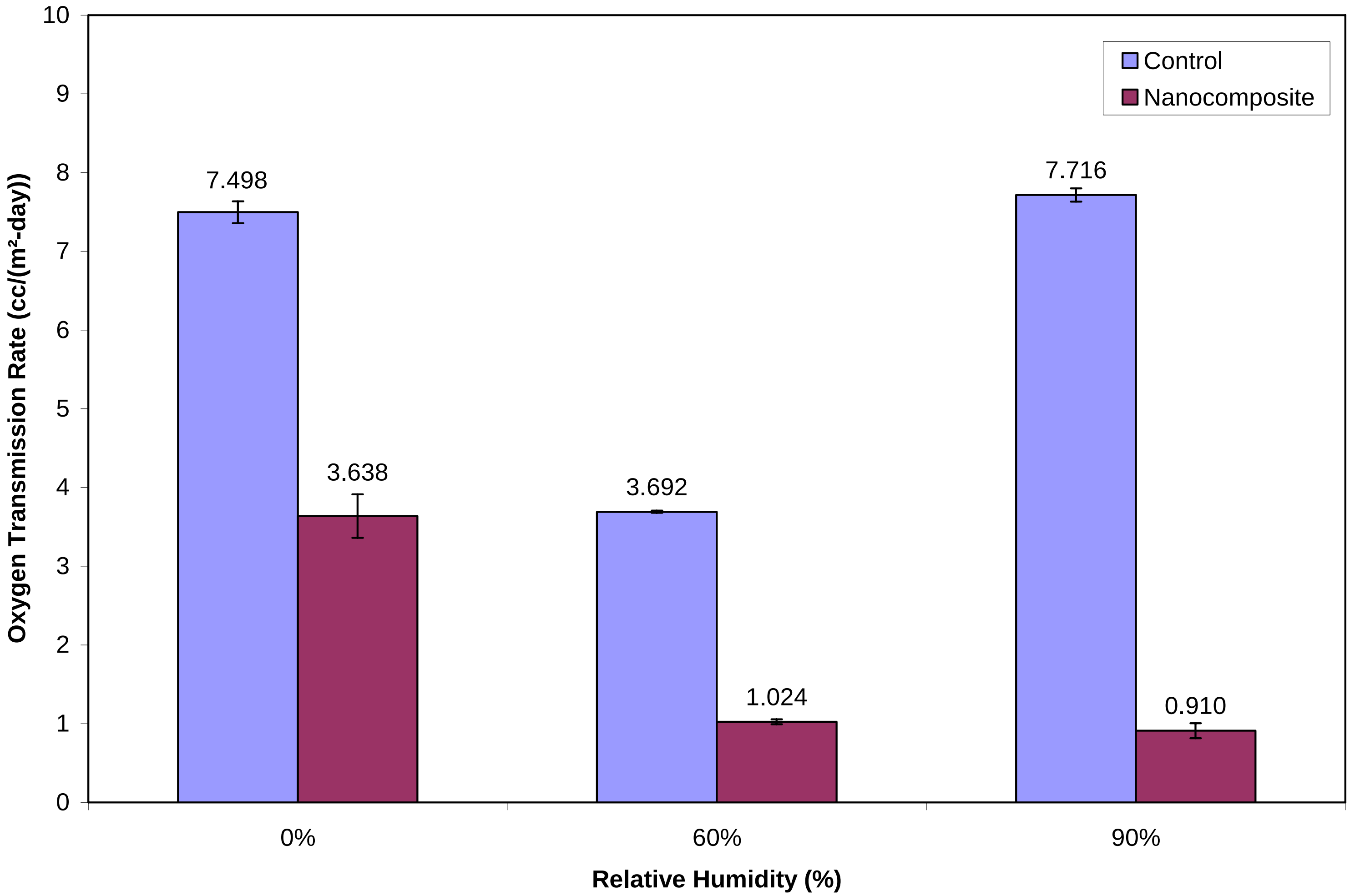
# Non-Retort Pouch: Processing and Characterization

- Davis-Standard Multilayer Extrusion System
  - Imperm core 30:1 L/D
  - LDPE skins 25:1 L/D
  - Tie layers 27:1 L/D
- Optical microscopy used to measure layer thickness
  - Nikon OptiShot2-POL polarized light microscope with an attached digital camera
  - 7 mil film
    - 43% core
    - 7% tie layers
    - 21% skins




Courtesy of Pliant Corporation

# Non-Retort Pouch Oxygen Barrier




Testing Conditions:

Temperature 23°C

100% Oxygen Concentration

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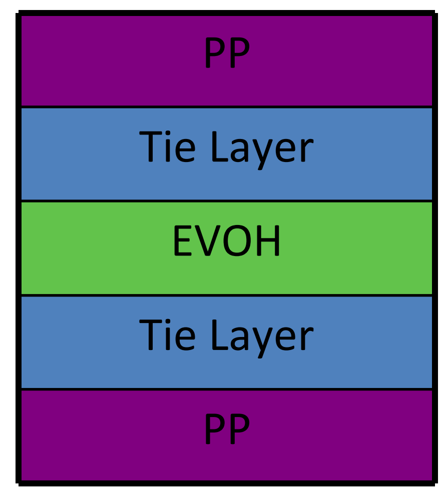
# Summary

- Significant improvement in oxygen barrier properties of the nanocomposite as compared to the neat film
  - 65% decrease in OTR seen at 0% RH
  - 74% decrease in OTR seen at 60% RH
  - 88% decrease in OTR seen at 90% RH
- Nanocomposite showed improved barrier properties with increasing relative humidity
  - 60% decrease in OTR transitioning from 0% to 60% RH
  - 11% decrease in OTR transitioning from 60% to 90% RH
- Storage and sensory studies in progress to determine if barrier properties are sufficient
  - No barrier specifications for the non-retort pouch

# Experimental Retort Pouch

- Ethylene co-Vinyl Alcohol (EVOH) E105B
  - 44 mol% ethylene
  - Produced by EVALCA
  - Excellent oxygen barrier properties, however dependent on relative humidity
  - Used for flexible packaging, bottles, tubes, thermoformed cups and coatings
- Polypropylene Nanocomposite
  - Huntsman P4G2Z-159 Retort grade, FDA Approved
  - Compounded 7.5% Cloisite 20A with 2.5% compatibilizer with polypropylene
    - Cloisite 20A is a montmorillonite layered silicate
    - Epolene G-3003 maleic anhydride grafted polypropylene
- Mitsui Admer QF551A used as the tie layer
  - Maleic anhydride grafted polypropylene

**Multilayer Film Structure ↓**



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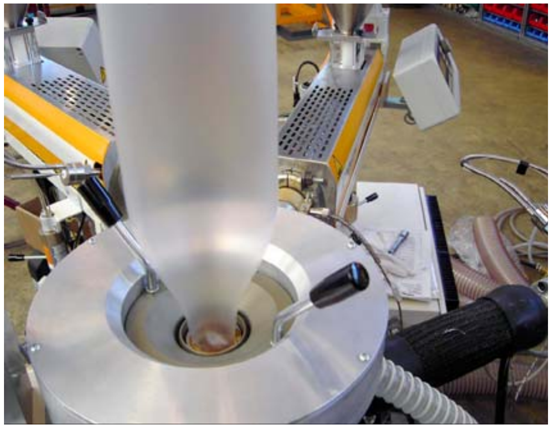
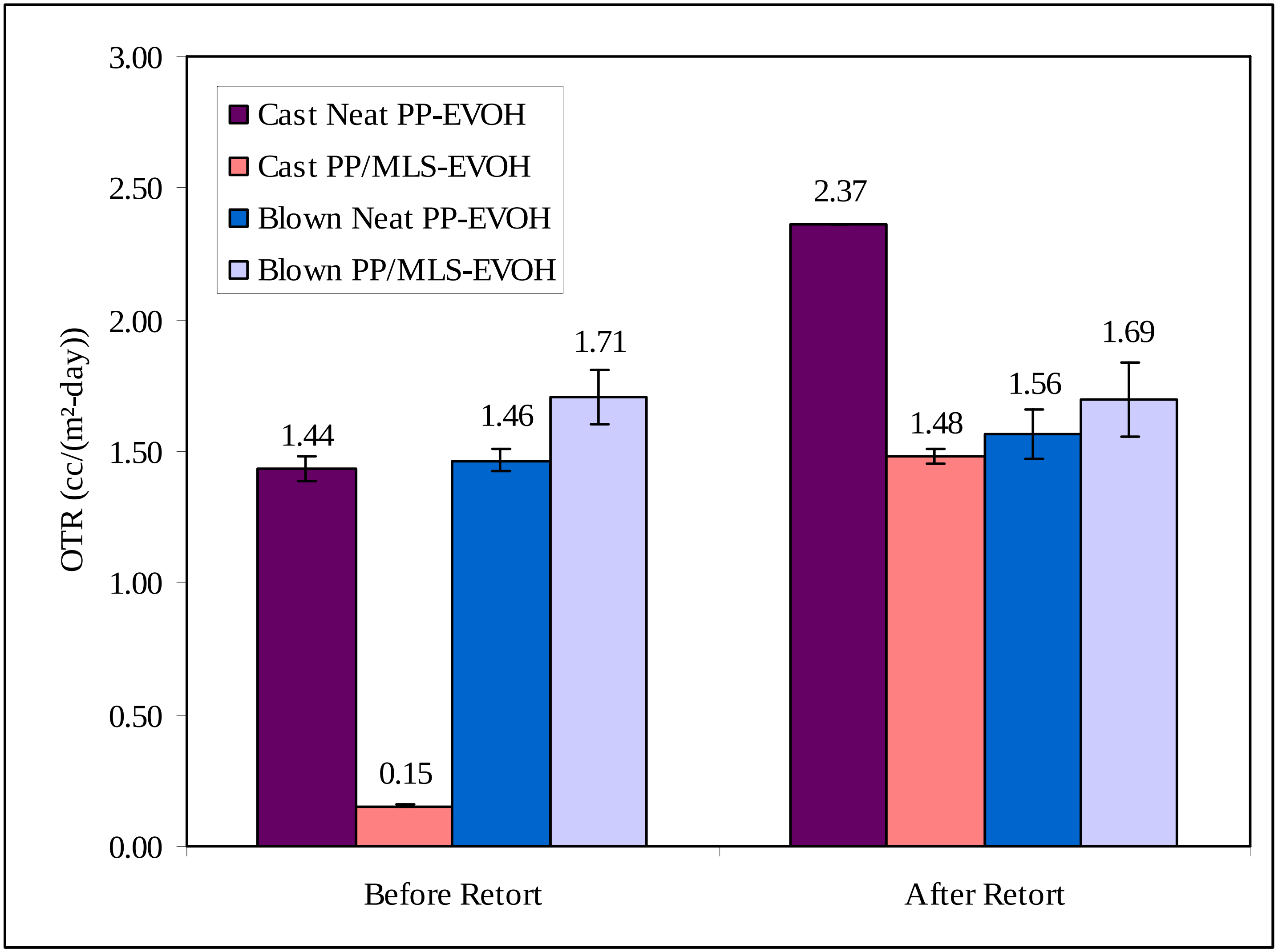
# Retort Pouch: Processing and Retort

- Collin Teach-Line co-Extruder 20 mm screws 25:1 L/D
  - Blown Film
  - 30 mm diameter 0.8 mm die gap
    - EVOH core 40 rpm
    - Tie layers 20 rpm
    - PP skins 60 rpm
  - Cast Film
  - 120 mm wide variable 0.2 to 2.0 mm slot die
    - EVOH Core, Tie layer and PP skins ~60 rpm
      - Visual inspection revealed interfacial instabilities



- Berlin Chapman Vertical Water and Steam Retort
  - 30 minutes at 121°C
    - Pouches 8 x 18 cm, filled with 100 ml water

# Retort Pouch Oxygen Barrier




Testing Conditions:

0% RH

Temperature 23°C

100% Oxygen Concentration

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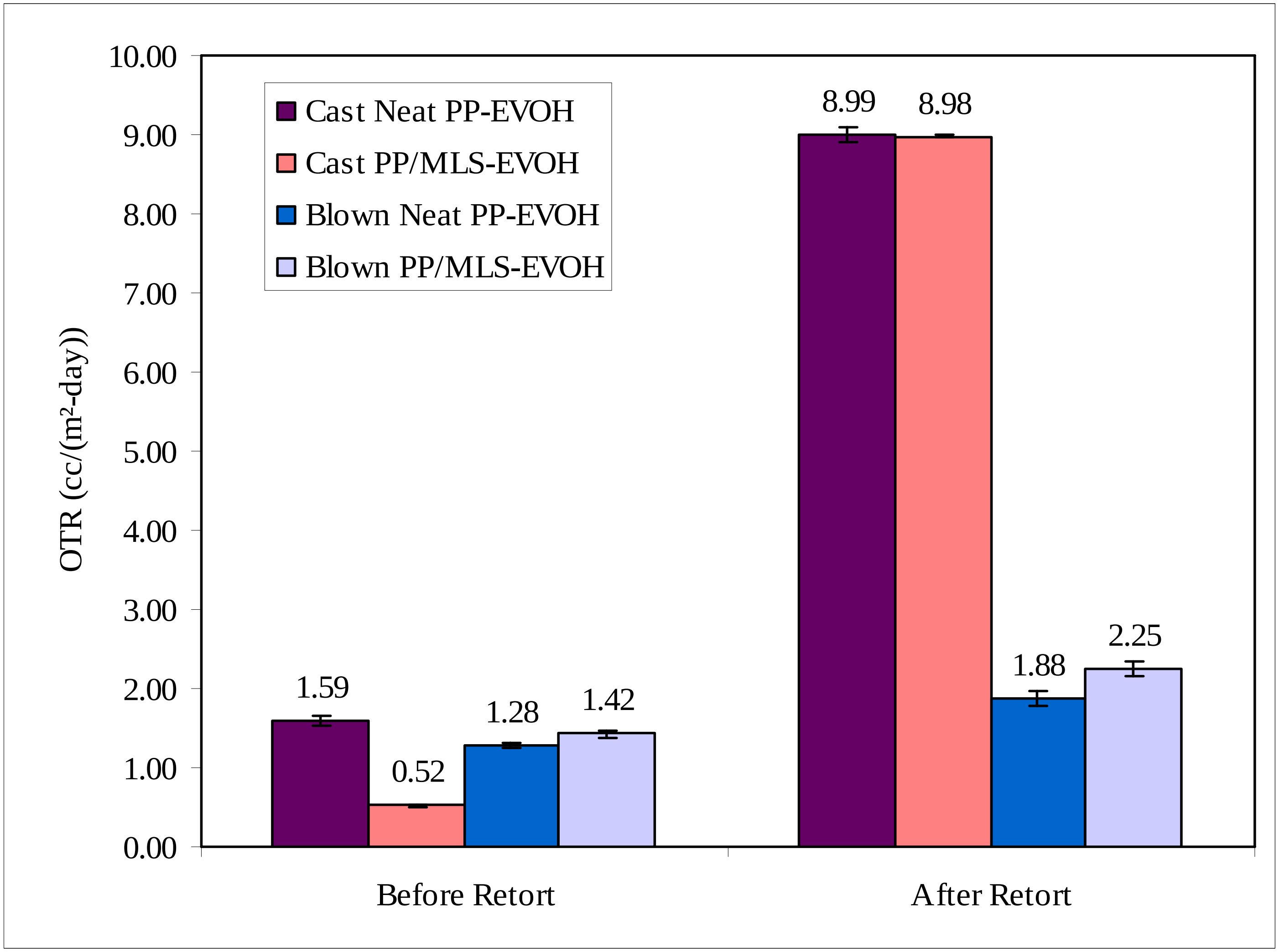
# Retort Pouch Oxygen Barrier




Testing Conditions:

60% RH

Temperature 23°C

100% Oxygen Concentration

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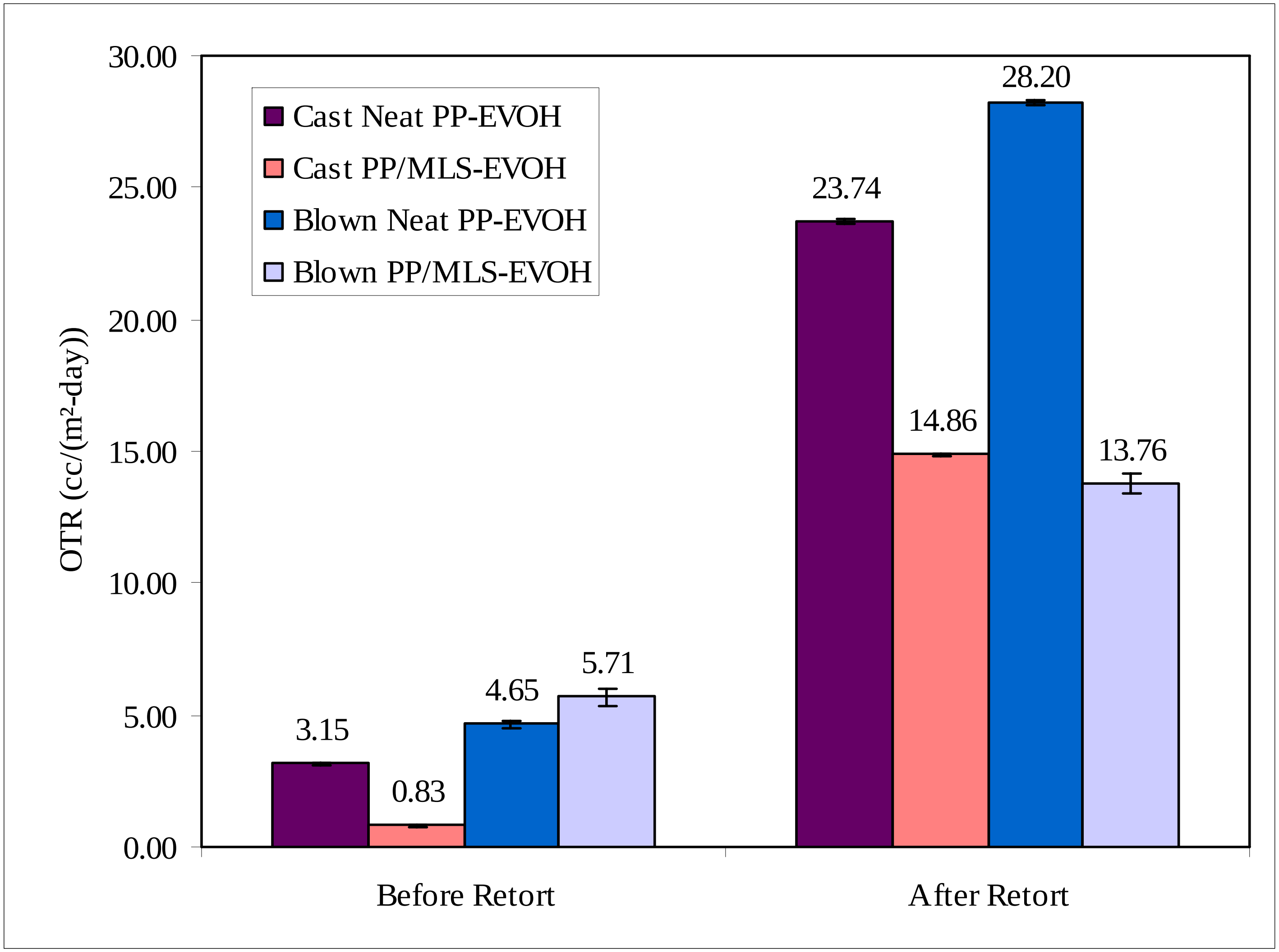
# Retort Pouch Oxygen Barrier



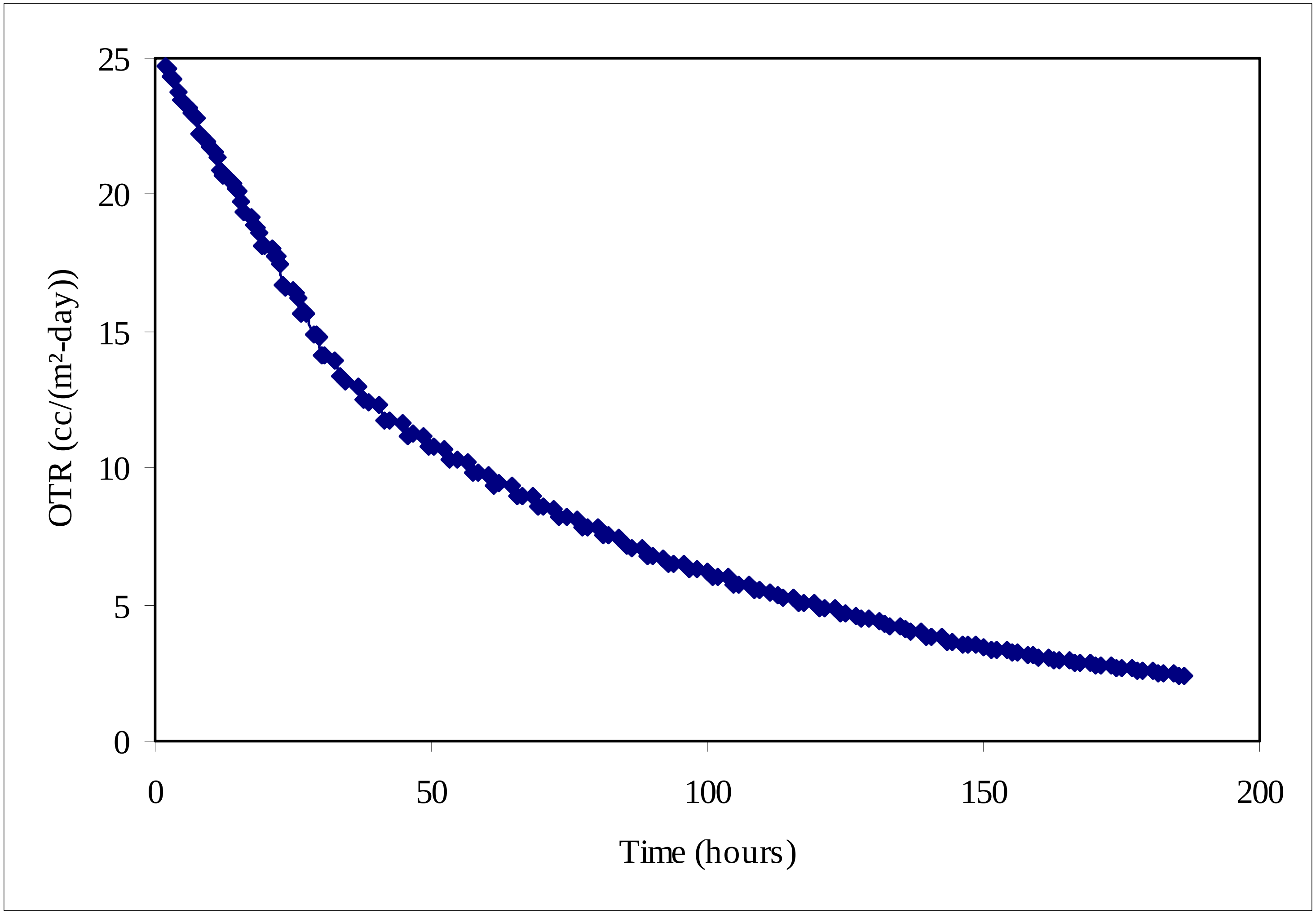

Testing Conditions:

90% RH

Temperature 23°C

100% Oxygen Concentration

# Retort Pouch Drying Out Curve




Testing Conditions:

0% RH

Temperature 23°C

100% Oxygen Concentration

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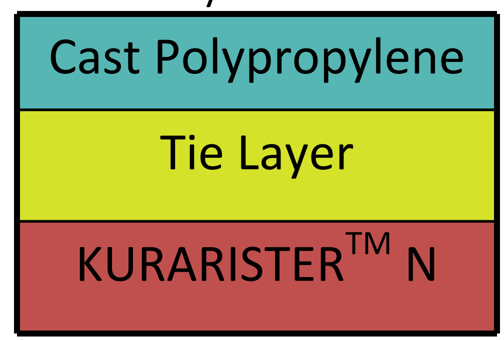
# Summary

- Experimental MRE Retort Pouch
  - Did not meet oxygen barrier requirements before or after retort processing
  - Oxygen barrier properties decreased significantly after retort processing
  - Retort shock was observed
    - Irreversible decrease in barrier properties of EVOH due to the absorption of moisture during retort processing
  - Eliminate EVOH from the multilayer structure
- Multilayer films utilizing KURARISTER™ N
  - Superior barrier properties and excellent retortability

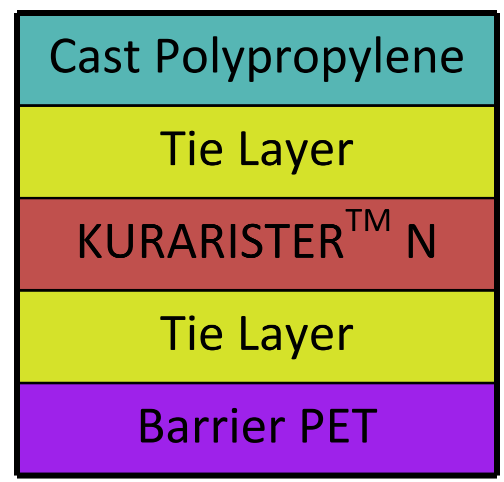
# New Experimental Retort Pouch

- KURARISTER™ N
  - 16 µm biaxially oriented nylon with a nanocomposite barrier coating on both sides of the film
    - Excellent oxygen barrier properties
    - Retortability
    - Not relative humidity dependant
    - Excellent flex crack resistance
- Barrier PET
  - 12 µm PET with an inorganic coating
- Tie Layer
  - Mor Free 225 + C33 solventless retort grade adhesive

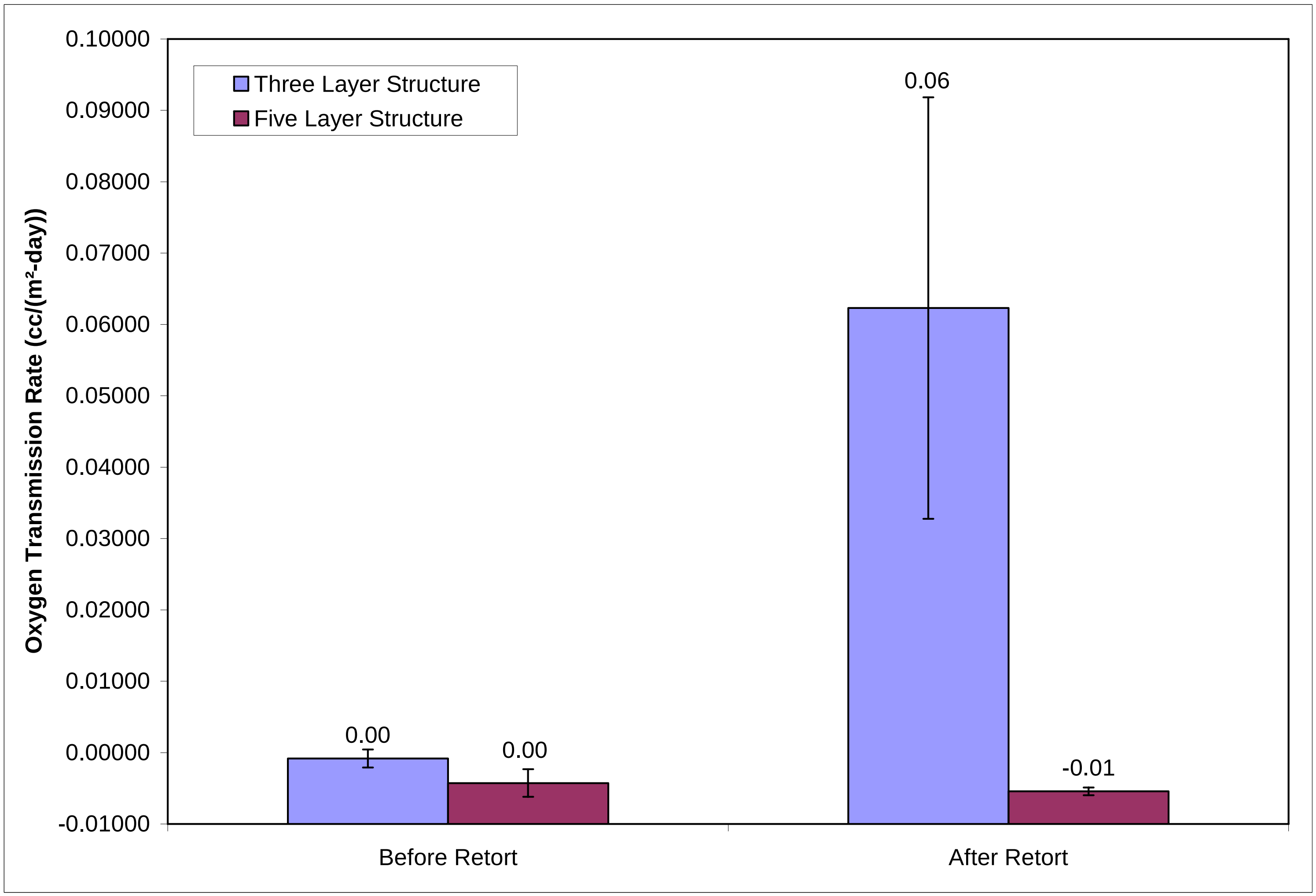
Three Layer Structure




Five Layer Structure



# New Retort Pouch Oxygen Barrier




Testing Conditions:

Temperature 23°C

100% Oxygen Concentration

# New Experimental Retort Pouch

- Oxygen barrier tested at 23°C and 90% RH
  - All samples tested before and after retort processing
  - Before and after retort processing oxygen barrier exceeded the lower limit capabilities of the Ox-Tran 2/20
    - Model L lower limit 0.005 cc/m²-day
  - Retort pouch specifications require an oxygen transmission rate of 0.06 cc/(m²-day) or less
  - Experimental KURARISTER™ pouches meet oxygen barrier specifications

# Summary & Future Work

- 3500 pouches produced and packed into current MRE™ meal bags
  - 1750 three layer pouches
  - 1750 five layer pouches
- Demonstration and Validation
  - Storage studies and sensory analysis
    - Completed at a range of temperatures and relative humidities
  - Demonstrate manufacturability
    - Work with converters and packers
  - Demonstrate durability within the military logistics system
    - Rough handling
    - Storage and distribution studies
  - Field testing and evaluations

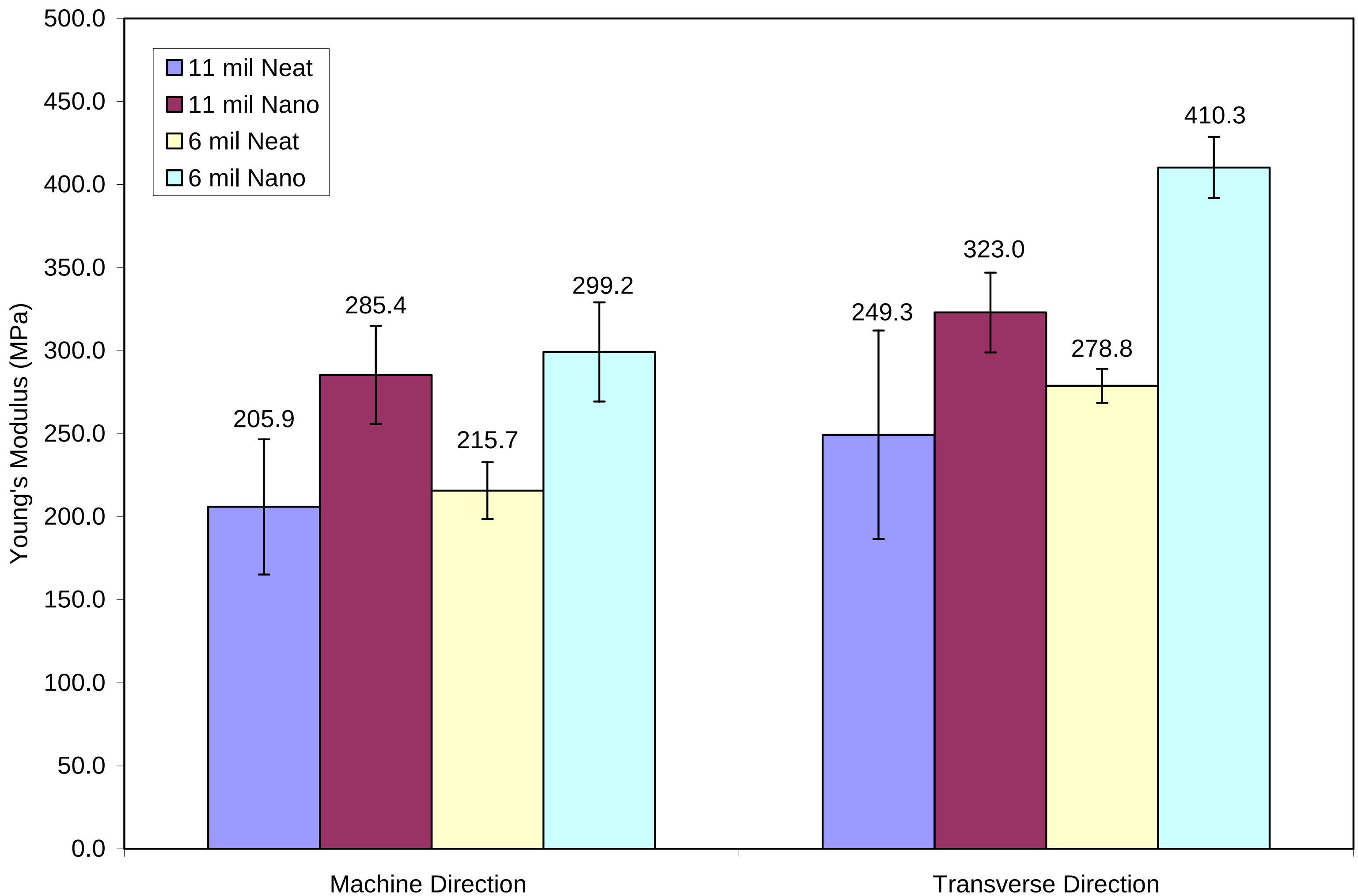
# MRE™ Meal Bag Laboratory Scale

- Monolayer Nanocomposite LDPE
  - LDPE Dow Chemical 683i
  - Montmorillonite Layered Silicate 7.5% Cloisite 20A
    - Zenix ZPT-30 30 mm co-rotating twin screw extruder
  - Compatibilizer Polybond 3109 Crompton Chemical
- Monolayer Nanocomposite LDPE Blown Films
  - Haake PolyLab twin screw extruder
    - Conical, counter-rotating, intermeshing
    - 31.8 mm diameter 300 mm length
  - 25 mm diameter 1.0 mm die gap

# MRE™ Meal Bag Pilot & Production Scale

- Pilot Scale
  - – Alcan Packaging
    - Monolayer neat and nanocomposite LDPE
      - – 2 mil and 6 mil blown films
- Production Scale
  - – Diversapack LLC
    - Monolayer blown films were processed and converted into MRE meal bags
      - – 6 mil neat and nanocomposite
      - – 11 mil neat and nanocomposite
    - 1200 meal bags for each design were produced

# Production Scale Young's Modulus

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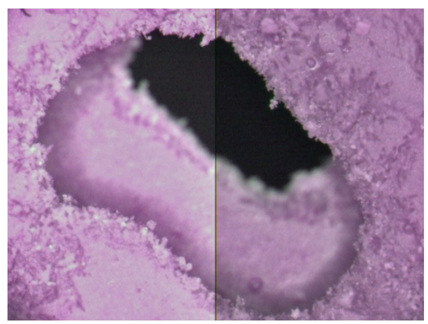
# Production Scale Testing Overview

- Seal Strength Analysis
- Thermogravimetric Analysis
  - Onset Degradation Temperature
  - Clay Content
- Differential Scanning Calorimetry
  - Glass Transition Temperature
  - Melting Temperature
  - Enthalpy
- Tensile Testing
  - Young's Modulus
  - Toughness
  - Strain at Break
  - Stress at Yield
- Propagation of Tear Resistance
- Falling Dart Impact Resistance
  - Room Temperature (25°C)
  - Cold Temperature (10°C)
- Oxygen Transmission Rate
  - 0% RH 23°C
- Water Vapor Transmission Rate
  - 90% RH 37.8°C
- Altitude Testing
  - US Army Research Institute of Environmental Medicine (US ARIEM) High Altitude Research Facilities
  - 5,000 ft increments up to 35,000 ft

# Production Scale Testing Overview

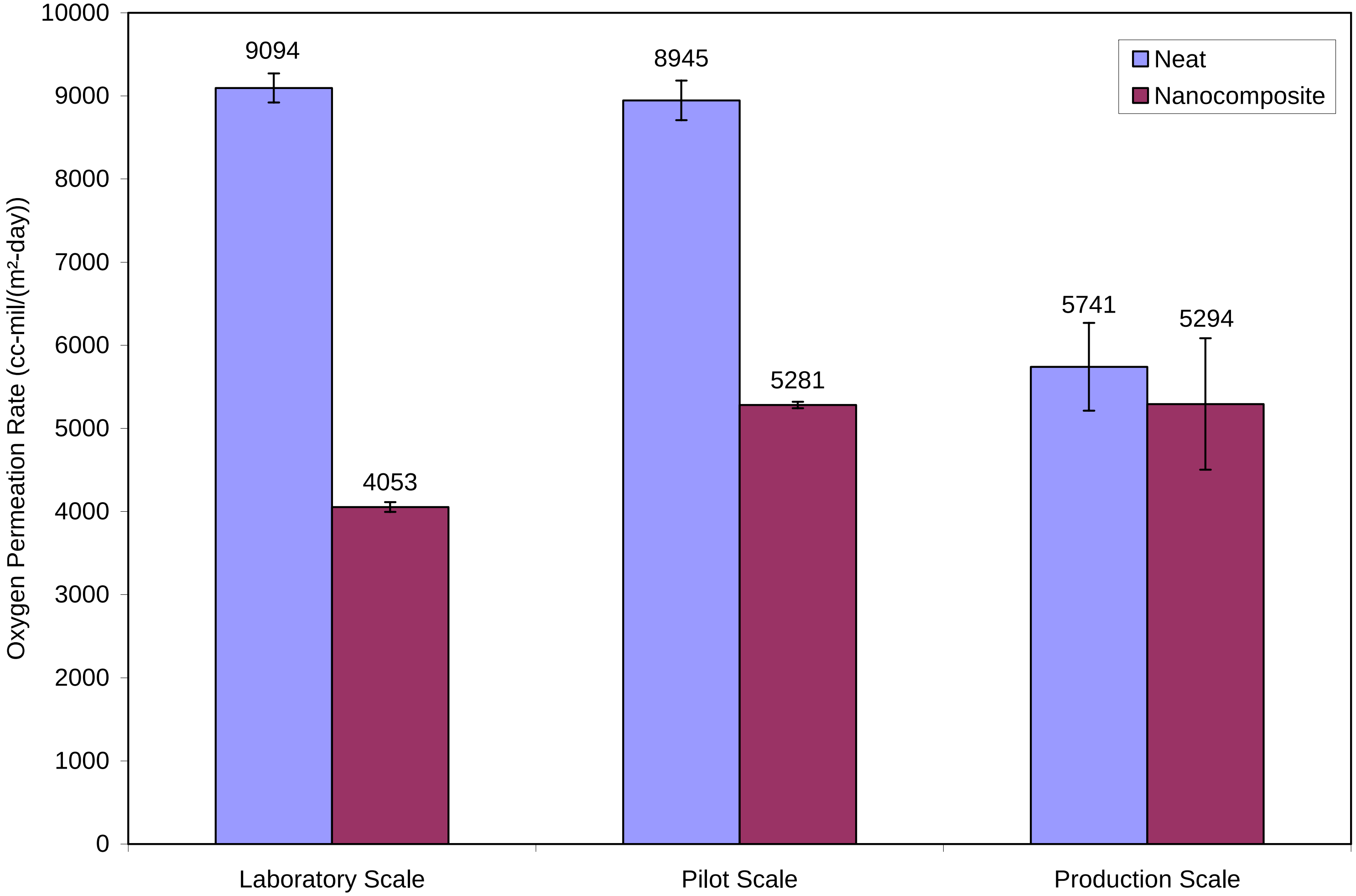
- Air Drop
  - US Army Yuma Proving Grounds in Yuma, AZ
    - Joint Precision Airdrop System (JPADS)
      - High altitude precision airdrop system
    - Containerized Delivery System (CDS)

    A-22 bundle for aerial delivery of 36 cases of MRE’s



- Insect Infestation
  - Cigarette beetles
  - Warehouse beetles
  - Dry dog food, dry milk, Brewer’s yeast
    - Rough texture from nanoparticles facilitated penetration by giving insects a point to gain leverage

# Meal Bag Experimental Monolayer Blown Films
# Oxygen Barrier




Testing Conditions:

0% RH

Temperature 23°C

100% Oxygen Concentration

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# Meal Bag Performance Improvements

| | Current Meal Bag | Neat LDPE | Nanocomposite LDPE |
|---|---|---|---|
| Thickness (mil) | 11 | 6 | 6 |
| Oxygen Permeation Rate (cc-mil/m²-day) | 8264 | 9097 | 3703 |
| Young's Modulus (MPa) | 127 | 93 | 186 |
| Onset of Thermal Degradation (°C) | 351 | 370 | 450 |
| Insect Infestation Test | Pass | Fail | Pass |

# Summary

- Monolayer Scale-Up Results
  - Similar oxygen barrier properties of neat and nanocomposite films were seen when transitioning from laboratory to pilot scale
  - Significant increase in oxygen barrier of the neat film when transitioning from pilot to production scale
  - Similar oxygen permeation of nanocomposite films seen at laboratory, pilot and production scale
- Multilayer Scale-Up Results
  - Slight increase in oxygen barrier of the neat film when transitioning from laboratory to pilot to production scale
  - Decreased oxygen barrier of the nanocomposite films when transitioning from laboratory to pilot scale, increased oxygen barrier when transitioning from pilot to production scale
- Overall the nanocomposite films and prototype meal bags had improved oxygen barrier over the neat films and prototype meal bags

# Review

- Non-Retort Pouch
  - Nanocomposite significantly improved barrier properties of films and prototype pouches
    - Imperm™ 105 3.3-3.6% montmorillonite layered silicate
- Retort Pouch
  - Nanocomposite polypropylene improved barrier properties of multilayer films, however results were inconsistent and films were not able to be retort processed
    - Polypropylene with 7.5% montmorillonite layered silicate
  - KURARISTER™ N multilayer films
    - Provided excellent barrier to oxygen and retortability
  - Meets retort pouch barrier specifications
- MRE™ Meal Bag
  - Nanocomposite significantly improved barrier, mechanical and thermal properties
    - LDPE with 7.5% montmorillonite layered silicate
  - Meal bag thickness decreased by about half, from 11 mil to 6 mil thick

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# Conclusions

- Nanocomposites
  - Improved oxygen barrier properties
  - Improved mechanical and thermal properties
  - Being investigated for military food packaging applications
    - Non-retort pouch, retort pouch, MRE$^{TM}$ meal bag
- Nanocomposites could be included in future military packaging as soon as 2013
  - If 100 million* MRE's are procured the change from the current 11 mil meal bag to the 6 mil nanocomposite meal bag would save approximately 3.5 million pounds!

*Based on annual procurement

# Acknowledgements

- US Army NSRDEC
  - Jo Ann Ratto, Christopher Thellen, Danielle Froio, Jeanne Lucciarini
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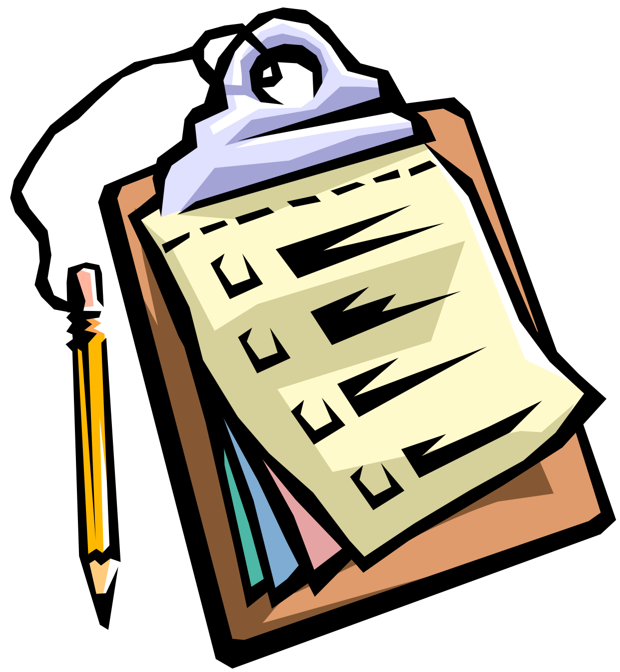
# Thank You


**PRESENTED BY:**

## Sarah Schirmer

**Materials Engineer**

**US Army NSRDEC**

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