



#### **DRAGONITE**<sup>™</sup>

Halloysite: Reinforcing halogen free fire retardant for plastics from PE to PEEK

AMI – Fire Retardants in Plastics Denver Colorado June 14<sup>th</sup> 2012



## Agenda

- Applied Minerals
- Halloysite structure & properties
- Enhancing plastics
- Case study: PET pallets
- Commercial aspects
- Conclusions

#### Applied Minerals at a Glance

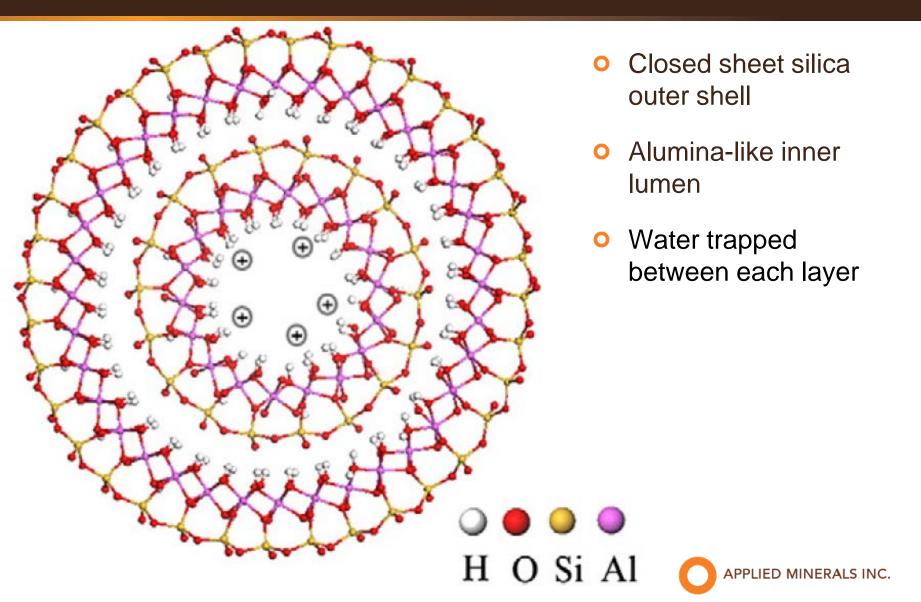
- US based publicly traded SEC reporting company. Ticker: AMNL
- Owner and operator of the Dragon Mine Halloysite Clay Deposit in Utah USA
- Over 30 years of proven reserves
- Product grades marketed under the *Dragonite<sup>™</sup>* trade name
- World renowned technical experts in geology, minerals characterization, plastics and materials
- Completed a \$ 6M geologic evaluation of the Dragon Mine including Halloysite and Goethite nano iron oxide pigment
- Became commercial in 2010 with 30 000 tons annual capacity and expanding

## Technology Description - What is Halloysite?



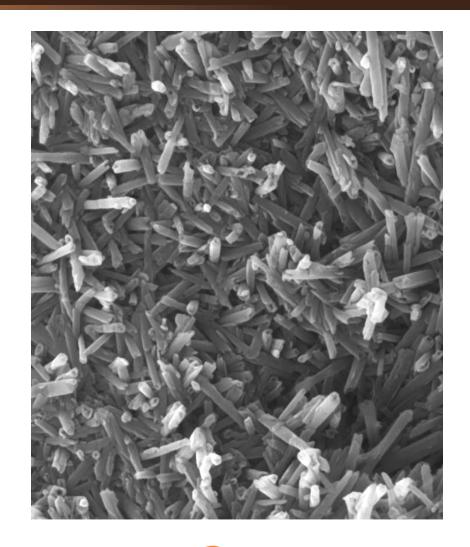
- Halloysite is a natural aluminosilicate clay with a hollow tubular morphology
- Naturally exfoliated morphology means no need to chemically separate particles and makes for easy dispersion
- Halloysite nanotubes typically have diameter ~50nm with lengths ranging from 1 to 2 microns giving an aspect ratio of ~20
- Traditional uses include fine china, fillers in paints and paper, food extenders, catalysts and molecular sieves

## Dragonite Chemistry



#### Characterization

- XRD Mineralogy
- XRF Major element chemistry
- ICP-MS range of trace elements
- FTIR
- Surface area
- Porosity
- Brightness and colour
- Particle size distribution
- SEM and TEM morphology



### Halloysite Property Overview

- Aluminosilicate mineral: Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>. nH<sub>2</sub>O
- Molecular weight: 294.19
- CAS: 1332-58-7
- Density: 2.60 ± 0.03 gcm<sup>-3</sup>
- Refractive index at room temperature: 1.534, dried at 100°C 1.548
- Specific heat capacity: 0.92 kJkg<sup>-1</sup>K<sup>-1</sup>
- Thermal conductivity: 0.092 WK<sup>-1</sup>m<sup>-1</sup>
- Thermal diffusivity: 5.04 x 10<sup>-4</sup> cm<sup>2</sup> sec<sup>-1</sup>
- CTE: 10.0 ± 1.5 perpendicular to the layer, 6.0 ± 2.0 parallel
- Colorless and UV transparent
- pH in water 6.4-7.2
- Particle shape: 1-2 microns long, 50nm across, 15nm diameter hole
- Modulus ~130 GPa
- Surface area: 65-120 m<sup>2</sup>g<sup>-1</sup>
- O Dragonite™ purity: 95-100%



## Dragonite™ Intrinsic Properties and Applications

#### High aspect ratio

Reinforcement of plastics, elastomers, coatings etc.

#### High surface area

 Catalysts, adsorbents, carrier, elastomers, immobilization, nucleation of crystal growth and foam cell formation

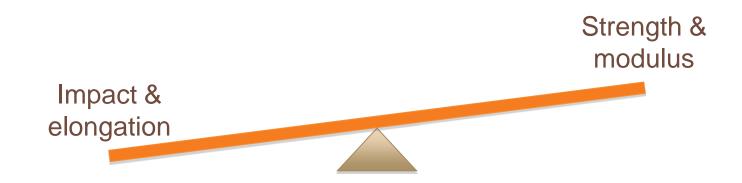
#### **Hollow**

 Controlled release, thermal insulation, light-weighting, wicking, membranes, reverse osmosis

#### **Bound water**

Fire retardance, temperature indicator, foaming agent

#### **Property See-Saw**



- Isotropic fillers retain impact but do not reinforce
- Reinforcing fillers ruin impact resistance and elongation to break
- Halloysite reinforces and retains or improves impact and elongation
- This is possible due to shape, surface area and easy dispersibility

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### The Challenge

Customer target is for a high-performance pallet:

- •Flexural Modulus ~1000 kpsi
- •Flexural Strength ~1800 psi
- ONotched Izod Impact resistance ~1 J/cm²
- OMFI ≥15 g/10 min due to existing mold
- Fire retardance to UL 2335
- Safe, non-migrating and halogen free FR requirement
- Starting point is Rynite 35% GF filled PET but unable to achieve mechanicals and UL 2335 with existing FR packages

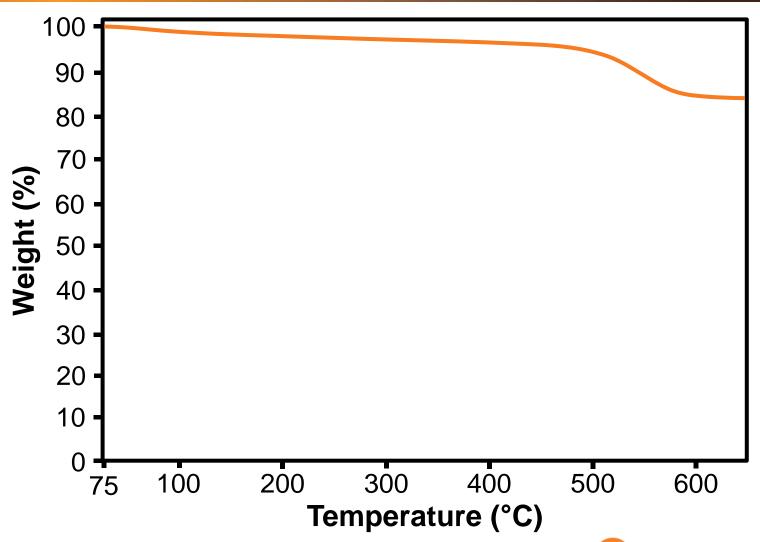
### Why Dragonite?

- Other solutions had failed to provide the answer
- Phosphorous-based systems plasticize
- Halogenated products not acceptable
- Mineral based FR like ATH and MDH not appropriate for PET
- Dragonite known to reinforce while retaining impact and providing FR

### **Experimental Plan**

- Prepare a highly loaded Dragonite masterbatch in recycled PET copolymer that can be combined with commercial Rynite GF PET
- Pre-drying the Dragonite and good dispersion essential
- Selected Americhem due to their experience with hydrolytically unstable polymers, excellent dispersion ability and QC
- Dragonite has some reactivity so adding a surfactant or stabilizer can be beneficial
- In this case 2% RDP was chosen due to proven affinity to Dragonite and previously reported results (BCC 2011)
- The aim was to add the Dragonite masterbatch in the minimum amount needed to pass UL 2335

### Dragonite Thermal Stability by TGA

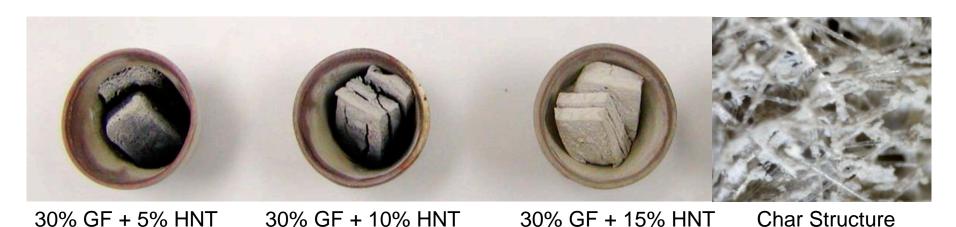


# **Dragonite Solution**

Property	PET 35%GF	PET 28%GF + 10% HNT	PET 23%GF + 16% HNT	PET 21%GF + 18% HNT
Flexural Modulus (kpsi)	1577	1115	1085	1026
Flexural Strength (psi)	31112	19849	19417	17643
Notched Izod (ft-lb/in)	1.58	0.75	0.89	0.71
Unnotched Izod (ft-lb/in)	13.4	8.1	9.2	7.2
MFI (g/10 min)	7		20	24
Char Density				1.485
Seconds to burn 5cm (need >180)	135	150	165	229

### PET FR Development

- Reinforcing, halogen free flame retardant
- Good mechanicals in combination with glass fiber
- High water release temperature > 400°C means Dragonite is ideally suited to polymers processed at high temperature
- Char strength boosted with Dragonite<sup>™</sup> plus glass fiber
- Synergistic fluxing effect



#### Conclusions

- All mechanical targets met
- Dragonite is reinforcing so it was possible to replace a portion of the glass fiber and still have good strength and modulus
- Impact resistance was retained at an acceptable level
- By adding the Dragonite in recycled PET copolymer the flow was increased by 3 fold, essential for injection molding
- Fire retardance to UL 2335 certification anticipated (underway)
- Safe, non-migrating and halogen free FR requirement
- Working closely with the customer and using in-house testing with fast turn-around time we were able to meet the targets
- We continue to optimize this formulation while also extending this reinforcing FR masterbatch approach to PP, PA6 etc.

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#### **Commercial Status**



- Dragon Mine Halloysite deposit characterized and proven in 2010
- Commercialization status:
  - Nucleation of HDPE and PP for better mechanicals and reduced cost in injection molded parts and extruded profiles
  - The only reinforcing and halogen-free mineral fire retardant for engineering plastics (recent Samsung press release)
  - Reinforces foams, improves productivity and helps surface appearance
  - Several new developments in the pipeline

### Availability

- Dragonite<sup>™</sup> brand high-purity Halloysite is commercially available from Applied Minerals
- Dragonite<sup>™</sup> is shipped directly from the Dragon Mine in Utah, USA
- Masterbatch concentrates are available as well as neat powder
- Supply is plentiful (>30 ktons) to support large-scale applications
- Samples are available to interested parties
- Technical support is also available

# **Thank You For Your Time**

Q&A

