

DRAGONITE[™]

Halloysite for reinforcement and processing improvement in polymer foams

AMI - PolymerFoam2012 - October 9th Dr. Chris DeArmitt - CTO



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Agenda

- o Applied Minerals
- Halloysite structure & properties
- O Enhancing plastics
- O Case study: Cycle time reduction
- Case study: Injection molded foam
- O Case study: Extruded foam
- O Commercial aspects
- Oconclusions



Applied Minerals at a Glance

- US based publicly traded SEC reporting company
- 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*[™] trade name
- World renowned technical experts in geology, minerals characterization, plastics and materials
- Over \$ 7M invested to date in resource characterization and quantification
- Became commercial in 2010 with 30 000 tons annual capacity and expanding significantly in 2012



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
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Dragonite[™] SEM





Dragonite Chemistry



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



Markets Addressed

Plastics

Productivity +20% Mechanicals +20% Flame retardance

Coatings

UV cure speed +20% Mechanicals +20% Improved adhesion

Environment

Oil clean-up Soil remediation Heavy metal sequestration



Reinforcement Flame retardance Thermal stability



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Dragonite in Plastics

| Plastic Type | Mechanical Enhancement | Cycle Time Reduction | Clear Film | Flame Retardance |
|--------------------|---------------------------|-------------------------|------------------|---------------------|
| PE | v | ~ | v | v |
| PP | v | ~ | ✓ | v |
| EVA | v | TBD | v | v |
| PA6 | v | TBD | TBD | v |
| PA12 | v | ~ | TBD | v |
| PVC | v | TBD | v | v |
| PLA | v | TBD | v | v |
| Ероху | v | TBD | TBD | v |
| EPDM | v | TBD | TBD | v |
| Suggested Grade | Dragonite™ XR or HP | Dragonite™ HP | Dragonite™ HP | Dragonite™ XR |



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



Dispersibility of Halloysite and Polarity



- Halloysite has been shown to disperse well in all types of system, from apolar to very polar
- Wetting through the tubes gives mechanical bonding even in cases where no specific chemical interaction takes place
- In thermosets, thermoplastics and elastomers, effective reinforcement is reported even without dispersants or coupling agents
- Dispersants and coupling agents may also be used



Dragonite in Semi-crystalline Plastics

| Property | HDPE | PP | PVC | PA6 | |
|--------------------|-----------|-----|-----------|-----------|--|
| Modulus (%) | +30 | +27 | +6.5 | +22 | |
| Yield Strength (%) | +15 | +23 | +5 | +13.5 | |
| Notched Izod | No change | +40 | No change | No change | |
| Nucleation | Yes | Yes | * | Yes | |

All at **1 weight % loading** incorporated using standard twin-screw extruder * PVC has very low crystallinity, nucleation not yet investigated



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Case Study #1 Cycle Time Reduction for HDPE Part

PHASE 1:

Drop-in solution: Significant cycle time reduction

| | Virgin HDPE | HDPE + 1% Dragonite HP | Savings |
|--------------------------------|-------------|---------------------------|---------|
| Cycle time per part (seconds) | 107 | 80 | 25% |
| Parts per hour | 34 | 45 | 32% |
| Cost per part (\$) | 8.07 | 7.53 | 7% |
| | | | |
| Effective cost of HDPE (\$/lb) | 0.85 | 0.76 | 11% |

- At 1 wt% Dragonite-HP loading, the customer achieved a 25% reduction in cycle time resulting in significant manufacturing cost reduction
- Results based on actual commercial process of the end user
- The customer was able to reduce the visibility of sink marks by >60%
- A 20% increase in stiffness without affecting impact resistance of the final part
- Also validated in PP copolymer and homopolymer
- Applies to injection molding and extrusion

PHASE 2:

Additional savings through thin-walling

Better mechanicals enables thin-walling:

- 5-10% reduction in wall thickness
- 10% further reduction in cycle time
- 5–10¢ per lb additional savings



Ideal Foam Nucleating Agent

- High surface area
- Irregular shape / anisotropic
- Easily dispersible
- Reinforcing
- Nucleates crystal growth
- o Safe
- Inexpensive
- o Natural
- Available



Foam Mechanical Properties



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Case Study #2 Foamed injection molded HDPE parts

| Property | HDPE 897 | No HNT | 1% HNT | 3% HNT | 1% HNT from MB | 1% HNT from MB |
|------------------------|----------|---------|---------|--------|-------------------|-------------------|
| Pressure (psi) | 1000 | 1000 | 1000 | 1000 | 1000 | 2200 |
| Shot Size (inch) | 2.1 | 1.6 | 1.6 | 1.6 | 1.6 | 1.4 |
| Color | Natural | White | Yellow | Yellow | White | White |
| Mean weight (g) | 4.414 | 4.205 | 4.242 | 4.242 | 4.235 | 4.048 |
| Shrinkage (%) | 4 | 0.8 | 1.2 | 0.4 | 0.8 | 1.2 |
| Density (%) | 0 | 8.25 | 8.8 | 8.25 | 9.3 | 13.6 |
| Flex Modulus (kpsi) | 133 | 139 | 150 | 147 | 151 | 152 |
| Flex Strength (psi) | 3412 | 3373 | 3477 | 3488 | 3468 | 3430 |
| Elongation (%) | 150-450 | 320-475 | 140-325 | 55-225 | 60-190 | 31-360 |
| Notched Izod | NB | 11.62 | 13/HB | 12.75 | 14.6 | 13.6 |

2.2 % KibbeChem AccuLite 250 Endothermic except Sample 1 none used and Sample 6 1.1% Temperature and back pressure kept constant

Case Study #2 Foamed injection molded HDPE parts

- Nucleation of crystallization gives faster solidification
- Nucleation of cell formation leads to better mechanicals and surface finish
 - 10-15% weight reduction and same mechanicals as unfoamed HDPE or
 - Same mechanicals as present foam but at lower density
- In automotive applications opt for lower density
- Or go for the cost advantage



Case Study #3 Foamed extruded HDPE sheet

- Nucleation of crystallization gives faster solidification
- Nucleation of cell formation leads to better mechanicals and surface finish
- 30% less endo-exo blowing agent needed (KibbeChem AccuLite 416)

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- Production speed up by 30-40%
- Cheaper, better products



Next Step: Mesofoam Formation



Tubes hold up to 20 volume % actives Loading well proven and scaled up with QC method in place



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Technology Status



- Dragon Mine Halloysite deposit characterized and proven in 2010
- Time to first commercial sale was less than 12 months
- First commercialization in PE, World market \$1 BN
- Dragonite saves money even in PE so there is a value proposition in the other more expensive plastics from PP through nylons to PEEK
- Sampling and working with hundreds of companies world-wide
- In advanced development stages in e.g. plastics, coatings and adhesives



Availability and Pricing

- Dragonite HP[™] high-purity Halloysite is commercially available from Applied Minerals
- DragoniteHP[™] is shipped directly from the Dragon Mine Utah, USA in powder form
- Dragonite/Foam masterbatch concentrates are available through collaboration with KibbeChem
- Supply is > 30ktons / yr to support large-scale applications
- Samples of Dragonite HP[™] Powder or MB are available
- Technical support is available from Applied Minerals



Conclusions

- Tubular materials have long held great promise
- Due to high aspect ratio, surface area and easy dispersibility, Halloysite provides effective reinforcement with no downside
- Crystal nucleation gives excellent mechanicals and productivity boost
- Foam nucleation improves mechanicals and lowers weight
- Dragonite[™] is 100% natural, safe, cost-effective and abundant enough to support large-scale commercial applications
- The benefits are proven by the rapid development and commercialization of new applications in multiple fields



Thank You For Your Time



