COLOURFUL IDEAS: THE LATEST PIGMENTS
EUROPE’S MASTERBATCH MARKET TRENDS
MAKING FILLERS WORK MORE EFFICIENTLY
HOW TO PRODUCE PERFUMED POLYMERS
Introducing Dragonite-HP

DRAGONITE-HP™ is an inorganic, halloysite-based, multi-functional polymer additive designed to provide an unmatched combination of reinforcement and cycle time reduction in polyolefins. Dragonite-HP is available to resin producers, compounders and the molders of polyolefin parts.

- Increases modulus and strength by 20% in a wide range of engineering plastics
- 15-30% cycle time reduction for HDPE and PP
- Lowers CTE and warpage
- Eliminates sink marks
- Fully recyclable while retaining properties
- Flame retardant at higher loadings
- Reduced energy consumption
- Reduced manufacturing cost
- Increased productivity means no need to invest in new injection molding machines
- Carbon credits possible
- Improved mechanicals allow thin-walling for materials saving and further cycle time reduction

Available as masterbatch, free-flowing powder or liquid concentrate to provide easy, accurate dosing.
For additional information and sample contact us: info@appliedminerals.com

<table>
<thead>
<tr>
<th>ACTUAL EXAMPLE</th>
<th>Virgin HDPE</th>
<th>HDPE +1% Dragonite HP</th>
<th>Savings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle time per part (seconds)</td>
<td>107</td>
<td>80</td>
<td>25%</td>
</tr>
<tr>
<td>Parts per hour</td>
<td>34</td>
<td>45</td>
<td>32%</td>
</tr>
<tr>
<td>Cost per part ($)</td>
<td>8.07</td>
<td>7.53</td>
<td>7%</td>
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<tr>
<td>Effective HDPE cost ($/lb)</td>
<td>0.85</td>
<td>0.76</td>
<td>11%</td>
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</table>
Minerals are used in polymers not only as lower-cost fillers but increasingly as modifiers to improve properties such as stiffness, heat deflection temperature, and creep resistance. Examples include talc, kaolin, mica, silica, wollastonite and calcium carbonate. In addition, minerals like alumina trihydrate (ATH) and magnesium hydroxide (MgOH) are used as non-halogenated flame retardants in applications like wire and cable.

Coating the surface of minerals enhances dispersion and compatibility, thus further boosting properties. Surface treatment suppliers see a growing demand for their products driven by requirements for property enhancement and the increasing use of fillers of all types. These include fibres and biomass as well as minerals. In addition, the growing use of non-polar polyolefins, which are not as compatible with fillers as polar polymers like polyamides, is driving demand for dispersants and coupling agents.

Dr John Yun, global technology leader for polymer modifiers at Chemtura, explains: "We see strong growth of coupling agents in automotive, wood plastics composites, and wire and cable applications, but we also see growing activity in building and construction, appliance and other segments where there is an evolution from metal to plastic or from engineering...
Success with silanes

Silanes are used broadly to coat siliceous mineral fillers, such as talc, silicates and aluminates, to promote bonding between or dispersion of inorganic fillers and organic polymers. Dow Corning offers its Xiameter brand organo functional and alkyl/aryl functional silanes used for coupling and dispersion.

Gelest notes that its dipodal silanes have seen strong growth in use in many applications, including mineral surface treatments, over the past two years. Dipodal silanes have two trialkoxy silane units, doubling the sites for bonding to the substrate and greatly increasing hydrolytic stability. Dipodal silanes can form a thicker film on the filler surface than can traditional silanes, claims Professor Janis Matisons, senior manager of R&D at Gelest.

While calcium carbonate fillers do not typically form stable bonds with silane coupling agents, mixed silane systems containing a dipodal silane in combination with a conventional silane can increase adhesion, says Gelest. In these systems, the low molecular weight and low surface energy of the silanes allows them to form thin films on various fillers, which can then crosslink to form a "coupled silica-rich encapsulating network".

Matisons says that the company has seen interest in coating minerals such as calcium carbonate fillers and that Gelest now offers specific grades for various resin systems. He explains, "We can coat any mineral, but we must choose the correct silane(s); it is not a 'one silane fits all' situation. The silane must bind to both the filler and the host resin, as well as have the heat stability needed for a given process temperature."

Gelest’s newest silane coupling agent family is the cyclic azasilanes that adhere to the mineral surface during treatment without releasing by-products such as chlorine, methanol, or ethanol, which must be carefully removed from the process. In addition to being safer and easier to process, the cyclic silane adheres to a wider range of fillers, notes Matisons.

Gelest, which has produced silanes for minerals and other applications for the past 20 years, began offering pre-treatment of minerals about four years ago and is currently expanding its capacity for pre-treatment. Matisons says, "We see more customers wanting pre-treated minerals rather than doing the treatment themselves. In particular, customers are looking for a quality-control process and a guarantee of a specific percentage of the right silane on the particles."

Functionalized polyolefins

Chemtura, which produces Polybond MA or acrylic acid-grafted polyolefin coupling agents, recently developed Polybond3149 to both aid dispersion and compatibilize high grade resins to filled polyolefins."

Common surface treatments include stearates, silanes, and functionalized polymers like maleated polyolefins, which act as either dispersants or coupling agents in the polymer-filler system. Dispersants, which adhere to the mineral particles but not to the polymer, enhance the process of breaking up agglomerated particles and dispersing them throughout the polymer, and can help reduce viscosity in highly loaded systems. Coupling agents are similar and usually act as dispersants, but form strong bonds with both the mineral and the polymer, which reduces water absorption and helps improve physical properties such as tensile strength.

Dispersants and coupling agents can be added to the system either by the mineral supplier as a pre-treated surface, or during the compounding step. According to suppliers, a certain level of expertise is required to accurately dose the treatment and obtain a uniform coating, and pre-treated fillers are easier to handle. However, coupling agents and dispersion aids can be more effective when added in situ versus pre-treating, says Norm Kanar, Xiameter global product market manager at Dow Corning. Others caution that while some treatments can be added directly in a twin-screw compounding extruder, some have a boiling point lower than that of the melt temperature and should be premixed before adding to the extruder.
### Additives Feature | Fillers and Coupling Agents

**Luzenac is targeting its Jetfine talcs at automotive applications, including front bumpers and dashboards. It is using a proprietary coating to improve scratch and mar resistance.**

Loadings of inorganic filler and non-halogenated flame retardants like ATH and MgOH in wire and cable applications. The new product is a maleic anhydride-modified LLDPE that, compared to Chemtura’s maleic anhydride-modified HDPE Polybond coupling agents, improves the pliability of polyolefin-based wire and cable compounds. Chemtura has several other development projects in coupling agents underway, and expects to commercialize more new products in the next 12 to 18 months.

Jeremy Austin, business development manager at Cray Valley, notes that every mineral has a different surface chemistry, and thus a different optimal surface treatment. Cray Valley supplies a wide range of chemistries and seeks to match the chemistry to the mineral’s surface.

For example, maleic anhydride end-groups are effective for filler types like ATH and MgOH, while carboxylic acid anchors with dolomite. For ATH and MgOH used as non-halogenated flame retardants, Cray Valley identified its anhydride-functional butadiene as an optimal dispersant. "While mineral loadings of more than 60% in these flame retardant formulations can cause a significant drop in physical properties, surface-treated minerals reintroduce ductility and prevent this physical property drop by improving the dispersion of the mineral and preventing agglomerates. We see this as a growing need due to the increasing use of non-halogenated flame retardants," comments Austin.

The company plans to investigate alternative surface treatments for calcium carbonate; although traditionally seen as a low-cost filler mineral, Cray Valley sees growing interest in adding value through surface treatments.

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**Talc Talk**

Demand for talc-filled compounds is growing, particularly in automotive applications where talc-filled polyolefins continue to replace metal or engineering thermoplastics. Increasingly finer talc grades, from micronized grades down to smaller ultrafine particle sizes, are desired as functional or reinforcing fillers that improve physical properties such as dimensional stability.

Frederic Jouffret, global director for polymers and paint development at talc supplier Luzenac, which was recently acquired by Imerys from Rio Tinto, sees growing use of the company’s Jetfine talcs, which have very small particles produced with a unique ultrafine milling technology, for high performance polypropylene and engineering thermoplastics. He explains that ultrafine talcs yield high performance at lower addition levels, resulting in parts with lower weight to meet the ever-important weight-savings goals of the automotive industry.

Although talc does not typically need surface treatments for coupling with polyolefins, surface-treated grades are used to improve coupling in engineering thermoplastics such as PC, ABS, or PA and to improve scratch and mar resistance (SMR) performance.

Luzenac’s R7 grade, a micronized talc with a proprietary coating, improves SMR in TPOs and impact copolymer PP for visible automotive parts such as instrument panels. Luzenac R7 is also being used to solve moulding appearance issues like weld lines in some filled engineering thermoplastic applications. Current research is investigating proprietary surface treatments to further optimize SMR and cost-performance, notes Jouffret. The company is also developing surface treatments for Jetfine grades.
Halloysite Clay has a Hollow Nanotubular Structure

Mica and Nanoclays

Mineral supplier Imerys notes that mica, which adds stiffness, thermal resistance, and dimensional stability, is growing in use in automotive applications. Surface-treatments are used to increase durability and improve dispersion, which enhances properties. For example, surface-treated mica increases the impact and tensile strength of PP, which in some instances can allow the material to replace engineering thermoplastics.

Montmorillonite-based layered silicate nanoclays, when exfoliated or separated into nano-scale platelets and dispersed in polymer systems, provide greatly improved properties at low loadings. These nanoclays are challenging to disperse and most require surface treatments as well as advanced compounding techniques in order to be used.

Applied Minerals produces Dragonite halloysite, an aluminosilicate clay that, unlike layered silicate nanoclays, has a hollow nanotubular structure. Halloysite has traditionally been used in applications like fine china, catalysts and food extension, but is now finding use as an advanced functional filler for plastics.

Dr. Chris DeArmitt, Applied Minerals’ CTO, notes, “High aspect ratio minerals like talc generally improve modulus and strength at the cost of losing impact, and spherical minerals like silica improve impact but not strength. In contrast, halloysite improves strength and modulus by 20% or more with no loss (and in some cases even an improvement) in impact, at a loading of just 1% Dragonite.” He adds that halloysite can reduce cycle times by 15-25% through nucleation of crystal growth in PP, and also in HDPE.

Halloysite is significantly different from other nanoclays in that it has a naturally exfoliated morphology that results in easy dispersion without surface treatments or other dispersant aids. “We compound 40% halloysite masterbatches on a twin-screw extruder with no need for surface treatment,” explains DeArmitt.

In addition to pelletized masterbatches, Applied Minerals’ Dragonite products are available commercially as a powder or in a low-dust wax concentrate.

While halloysite does not need surface treatments for most plastics applications, researchers have found surface agents that may provide unique advantages for certain systems. For example, it has been found that a silane coupling agent enhanced properties of halloysite nanotubes (HNT) to a greater extent than silica coupled with the same silane in natural rubber.

Halloysite Research

In another project, researchers at the South China University of Technology in Guangzhou, China, treated HNT with a complex of resorcinol and hexamethylene-triamine (RH) used as an adhesive in the rubber industry. The study found that RH facilitated dispersion and orientation of HNT in styrene-butadiene rubber (SBR) and formed interfacial hydrogen bonds, substantially improving compound properties.

DeArmitt comments that this type of system could be used in energy-efficient automotive tyres, in which systems of precipitated silica and coupling agents have almost replaced carbon black in the past two decades. Halloysite also benefits from additives such as maleated PP when used at higher loadings, up to 60% by weight, as a halogen free flame retardant. Dragonite’s advantage over ATH and MDH is that its bound water is not released until over 400°C, so it can be compounded into high performance polymers like PEEK, says DeArmitt. Cray Valley is also working with Dragonite halloysite to optimize coatings that could enhance properties at lower loadings.

Minerals in Compounding Conference

The next AMI Minerals in Compounding conference will take place on 30 November to 1 December 2011 in Atlanta, Georgia, USA. The full programme has recently been published – click here for more details.

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