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July/August 2010

ORGANIC GROWTH: WPCs TAKE OFF

NEW OPTIONS FOR PLASTICS FILLERS

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Filled with success

Companies are working hard to develop new fillers that can enhance the performance and economics of plastics compounds. Industry expert **Dr Chris DeArmitt** picks out some recent developments that have caught his attention

Plastics are an irreplaceable part of our everyday lives due to their excellent properties, processability and versatility. That versatility comes, to a large extent, from the use of additives and in particular, from the addition of fillers which can enhance the intrinsic properties of plastics, compensate for deficiencies, or introduce completely new properties not attainable in pure plastic materials. This article looks at the latest news with an emphasis on specialty fillers.

Any particulate material can potentially be used as a filler for plastics and elastomers. Minerals are often used, and as there are tens of thousands of different minerals, the possibilities are almost endless. However, not all candidates are ideally suited to use as fillers. The best materials tend to be those with the following properties:

- Readily available worldwide
- Chemically inert and insoluble
- Low hardness to avoid undue wear
- Safe, meaning non-toxic and non-flammable
- Free from transition metal impurities that can degrade plastics

Thus, of the countless potential options, a narrower list emerges, including such materials as calcium carbonate, dolomite, silica (as beads or fibres), carbon black, mica, wollastonite and kaolin. That small group represents by far the majority of fillers by volume usage or by total value (estimated to be over €5 billion per year). They are used primarily to tune mechanical properties of polymers whereas other, more esoteric fillers, are used to achieve other performance goals.

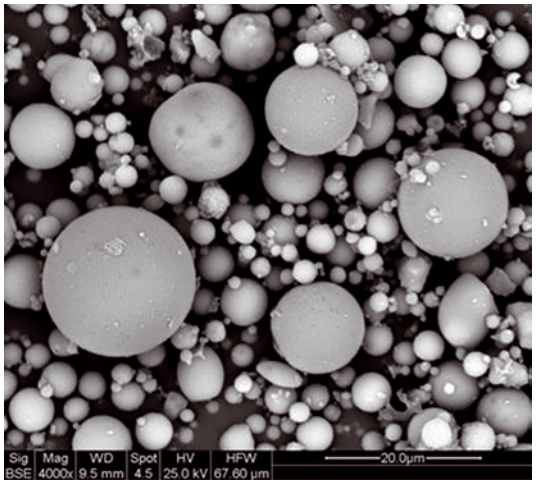
Three of the main weaknesses of plastics are:

- Specific modulus / stiffness (stiffness per unit weight)
- HDT / Vicat softening temperature (maximum temperature for load bearing parts)
- Creep (slow flow of the plastic under load)

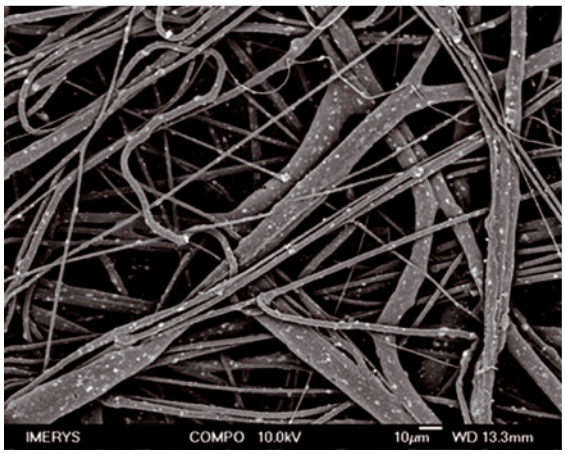
It turns out that fillers help overcome all three of these three drawbacks, so it is easy to understand why filled plastics have been so successful.

Conventional fillers

The effect of conventional fillers on the mechanical properties of thermoplastics is summarised in Table One. Isotropic (round or cubic) fillers include calcium carbonate, dolomite, glass beads, fly ash and silicas. Common platy fillers are kaolin and mica. Short fibre fillers include mineral fibres and wollastonite. The most dramatic property enhancements come from the high



Rocktron's MinTron solid glass micro-spheres are produced using fly ash from a coal-fired power station



aspect ratio fibres such as glass, carbon, graphite or Kevlar fibres.

Dispersants help processing by lowering viscosity and they raise impact resistance by breaking up agglomerates that can act as stress concentration sites where cracks form. Coupling agents are used to improve filler-resin adhesion which improves the strength of the composite particularly in hot, humid conditions.

We will now look at some individual fillers to see the property improvements that each type brings.

Calcium carbonate

Although fillers like calcium carbonate, kaolin, mica, wollastonite and silica have been around for decades, new advances are still occurring regularly, either to improve performance in existing applications or to enable their use in completely new areas. **Imerys** is one company that is active in the field of engineered fillers where careful control of particle size distribution and surface treatment lifts the filler to new heights. The company's FilmLink products are well-established in the breathable films market, and it has now developed a new FiberLink range of engineered, surface-treated calcium carbonates for use in fibre and non-woven products. The presence of even traces of large particles can cause serious production problems during fibre spinning. Imerys market manager Renita Anderson explains that the FiberLink products eliminate that problem by controlled top-cut and through optimised surface treatment that enables excellent dispersion.

There are many advantages such as increased production rate due to the high thermal conductivity of the filler, reduced carbon footprint compared to an unfilled PP and also a welcome reduction in raw materials costs.

Imerys has developed its FiberLink calcium carbonate filler for use in fibre and non-woven products

Renewable fillers - fly ash

RockTron introduced an interesting alternative to established fillers last year with the launch of its MinTron ecominerals which are produced from fly ash recovered from coal-burning power stations (**click here** to see our full report on the technology).

The company has now announced further results from tests using MinTron as a replacement for fillers

Table One: The effect of conventional fillers on the mechanical properties of thermoplastics

Property	Isotropic	Platy	Fibres
Modulus	↑	↑↑	↑↑↑
Yield Strength	–	↑	↑↑
HDT amorphous polymer	–	–	–
HDT semi crystalline polymer	↑	↑↑	↑↑↑
Impact resistance	↑ or ↓	↓	↑ or ↓
Elongation to break	↓	↓↓	↓↓↓
Permeability	↓	↓↓	↓

Table two: Properties of Halloysite nanofillers

Particle shape	Halloysite
Dimensions	Length 0.5-3 microns, Diameter 50-70 nm
Material	Silicate
Density	2.52 g/cm^3

such as talc and carbon black. Significant improvements in both scratch resistance and emissions have been observed when working with PP producers, replacing talc in a PP co-polymer. The objective was to meet the specification of an automotive OEM and the substitution of MinTron solid glass microspheres for talc resulted in the requirements of the specification being exceeded. In addition, the Heat Deflection Temperature (HDT) was increased.

These successes create the possibility of producing interior, under bonnet and exterior components using MinTron. The filler's low density (2.1-2.3 g/cm^3) offers weight reduction possibilities by replacing talc (density 2.7 g/cm^3). As it is 100% recycled and has a low carbon footprint (0.08 kg CO_2 / kg product), MinTron can also help automotive OEMs realise their desire to use more environmentally friendly materials in their vehicles.

Another recent development is the partial substitution of carbon black with MinTron by an OEM tyre manufacturer, which resulted in improved physical properties for certain parts of the tyre compound. This is leading to further development and testing.

Nanofillers

Nanofillers can give remarkable properties at low filler levels. However, such small particles can be difficult or impossible to disperse, leading to problems with impact resistance and elongation to break. Recent advances have helped with the dispersion issue. Whereas platy type nanoclays are hard to exfoliate, these issues can be avoided using tubular nanoclays instead. Halloysite tubular nanoclay is easier to disperse and does not require exfoliation to achieve good properties. **Applied Minerals** has shown that 35-40 weight % of Halloysite can be incorporated without the need for surface treatment. Modulus and strength are both improved but without sacrifices in impact resistance or weld-line strength.

Halloysite can also be used as a flame retardant synergist, increasing decomposition temperature, reducing peak heat release rate, and improving char density. Other enhancements include nucleation of crystallisation for reduced cycle times and the possibility to encapsulate additives within the hollow core of the tubules. In particular, there is a lot of interest in slow release of active ingredients which can be anything from fragrances to insecticides.

Boosting dispersion

Sasol has been developing and marketing nanoparticulate materials for many years. Its Boehmite aluminas are well known as they are easy to disperse and are very pure thanks to the synthetic route used to produce them. More recently, the company's hydrotalcite products have gained increasing attention. In contrast to the well-known montmorillonite nanoclays composed of anionic sheets, the hydrotalcites are just the opposite. The sheets are cationic in nature and can be readily dispersed in polymers. Surface treatments are available whereby anionic organic molecules bond to the surface and prevent agglomeration.

Sasol product manager Olaf Torno points to a recent publication entitled "The influence of the compatibiliser

Finding the perfect couple

Coupling agents improve the properties of composites in multiple ways. By bonding to both the filler surface and the polymer, they can enhance dispersion, wetting and the strength of the composite, especially in hot or humid conditions.

Organosilanes are probably the most well-known class of coupling agent but they are not able to bond to all types of fillers, so maleated PE and PP have grown in popularity because maleic anhydride can react with a wide range of fillers such as calcium carbonate, dolomite, ATH and magnesium hydroxide.

Jeremy Austin, market development engineer at Cray Valley USA explains how they have taken the use of maleated polymers a step further with their range of SMA brand maleated polystyrenes and Ricon maleated polybutadienes. Available with controlled molecular weight and tailored maleic anhydride derivatisation level, they are suitable for a wide range of fillers in polymers, elastomers, coatings and adhesives.

Dosing and application of the products is simplified because they are available as liquids, solids and even in a water-dispersible form. The options extend beyond maleated products including amines, epoxies, carboxylic acids, hydroxyls and even imides. The diversity of chemistries available means that Cray Valley can help you find the right additive to maximize the performance of your filler-polymer combination.

www.crayvalley.com

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The quality of functional fillers makes the difference

Besides the large volume commodity minerals, such as carbonates, quartz, and clay, specialty minerals such as talc, mica and wollastonite could be found at much smaller volumes.

These minerals have a higher aspect ratio (HAR), either platy or acicular, and heavily influence the crucial properties of thermoplastic polymers, such as stiffness, impact resistance, and surface scratch resistance.

The variable mineral properties are purity, color, fineness, and, very critical, the preservation of the aspect ratio during the micronization process.

A widely unknown mineral in plastics is micaceous iron oxide (MIO), also a low volume mineral.

MIO – an outstanding material

Kärntner Montanindustrie (KMI), located in Austria, is the market leader in MIO. This is a very rare industrial mineral worldwide, as only a few mines show a good lamellar shape and purity, and a consistent ore body.

The traditional application fields for MIO are the anticorrosive, marine, and decorative coatings markets, as well as powder coatings.
KMI has unique know how in processing and especially in micronization of such lamellar products to a median particle size of around 1 µm.

KMI is expert in micronization of high aspect ratio minerals

The usage of MIO in plastics applications is relatively new. Besides lamellarity, with all its well balanced effects on the mechanical properties in plastic materials, the UV- and heat resistance, the chemical inertness, as well as the thermal conductivity are the most valuable characteristics.

KMI, as a specialist in micronization of HAR minerals, extended their product portfolio with mica (muscovite, phlogopite) and wollastonite.

Premium raw material resources are secured for KMI to become a reliable and established supplier to the plastics industry.

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Kärntner Montanindustrie (KMI) is a world leading mining and processing company in micaceous iron oxide (MIOX®)

KMI uses unique processing technologies for micronization of high aspect ratio minerals

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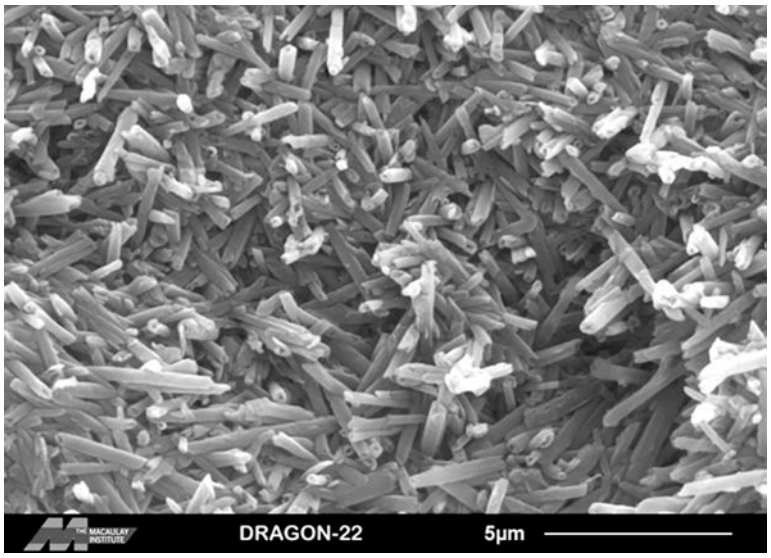


Halloysite tubular nanoclays are easier to disperse than platy materials

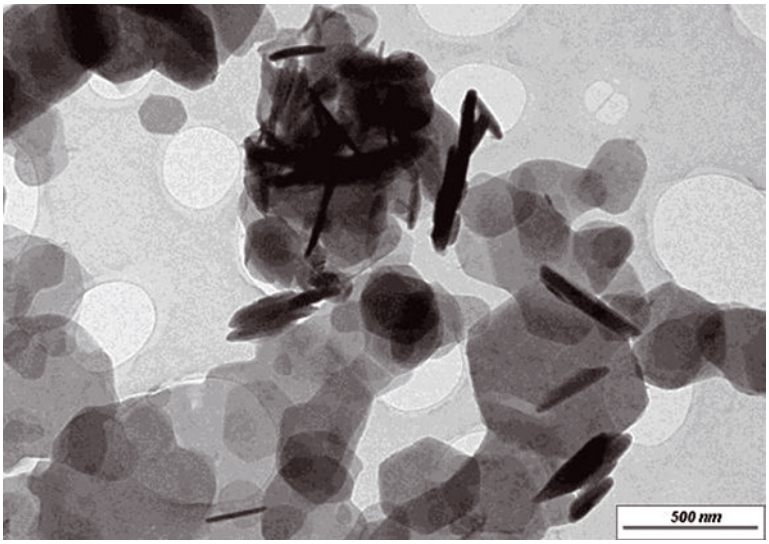
on the morphology and thermal properties of polypropylene-layered double hydroxide composites" (*Polymer Composites*, Volume 31, Issue 4). Untreated nano hydrotalcite was successfully dispersed in PP with a corresponding boost in mechanical and barrier properties, comparable to that obtained using nanoclays. Dodecylbenzene sulfonic acid acted as a dispersant whereas maleated PP acted as a coupling agent by bonding to both the filler and the PP matrix. These results were achieved using a Brabender mixer and could be expected to be even more impressive with more thorough dispersion, for example using a twin-screw extruder.

Specialty fillers

Specialty fillers are often dual- or multi-functional and blur the line between fillers and other types of additive. A prime example is MIOX micaceous iron oxide, a filler that has enjoyed commercial success in coatings for decades and is now making inroads into the plastics market. Due to its platy shape, MIOX enhances modulus, yield strength and barrier properties. Because finer grades of MIOX have a characteristic red colour they are also used for the pigmentation they provide. Courser grades are black in colour, again useful as a pigment and for UV protection. Christian Rupp of **Kärntner Montanindustrie** says that the versatility of MIOX does not end there. Two newly developed grades have proven to be extremely effective process aids for thermoplas-

tics like PE, PP and PA. Dramatic reductions in cycle time, thermal conductivity and shrinkage have been reported in a recent study. MIOX is a very inert material and can be used even in very high temperature plastics like PSU and PEEK. Its high density (~5 g/cm^3) and platy shape make MIOX ideal for sound deadening applications, for example in the automotive industry.

Nan-O-Sil from **Energy Strategy Associates** is another specialty filler that has the ability to act as a process aid for thermoplastics including polyolefins, nylons and polyesters. Richard Oder, president of Energy Strategy Associates, explains that even at loadings of just 0.4-0.8 weight percent, Nan-O-Sil can greatly lower cycle times as shown in independent studies. Not surprisingly, the product has enjoyed commercial success for several years at major compounders and continues to penetrate new markets. Because Nan-O-Sil is an engineered silica, it does not give any colour of its own, a big advantage in some applications. In fact, addition of Nan-O-Sil can actually improve colour. When used in pigment masterbatches, Nan-O-Sil boosts pigment strength allowing more intense colours or a reduction in the amount of pigment needed to achieve a set colour.



NX Ultra is a new product from **Stabilization Technologies** that goes beyond the role of a typical filler as it also acts as an acid scavenger. Although several fillers are acid scavengers, NX Ultra is unique in its performance in fluoropolymers and fluoroelastomers.

Sasol says that its nano hydrotalcite fillers are easy to disperse in polymers

Curv, which can be thought of as PP filled with PP fibres, is providing high levels of strength for Samsonite's Cosmolite suitcases

Joe Webster, president of Stabilization Technologies, explains that most acid scavengers like calcium carbonate or hydrotalcite are basic in character and actually promote degradation of fluoropolymers at high temperatures. NX Ultra is not itself basic so it does not induce thermal degradation and yet, due to its special molecular structure, it can trap acids liberated as the polymer begins to degrade and prevent them from catalyzing further degradation. The result is fluoropolymers that are stable at higher temperatures for longer periods. Other interesting technologies from Stabilization Technologies include a range of zeolites that can stabilize dyes and additives for plastic film that help prolong the shelf-life of flowers and foods.

Curv is a revolutionary material from **Propex Fabrics** and provides a novel twist on the concept of a filler. Curv is supplied as a sheet and is made up of 100% PP where a woven PP fabric has been pressed and heated to melt the fibre skin and fuse them together. The resultant material can be thought of as PP filled with PP fibres and the properties are truly remarkable. The material has been commercially available for some time and is now enjoying commercial success.

With a modulus and strength far higher than PP, one can already begin to see the advantages. However, it doesn't end there, as Kirk Smith of Propex explains. Curv has spectacular impact resistance. Whereas PP becomes brittle around 0°C, Curv retains and even gains impact resistance as the temperature is lowered down into the cryogenic domain. An impressive demonstration of "Curv appeal" is the new range of Samsonite Cosmolite suitcases marketed as "the strongest and lightest Samsonite ever". Naturally, the light weight is appreciated by customers and the superb impact resistance means that there has never been a single instance of failure. Other applications for Curv include speaker cones, soccer shin-pads and personal armour.

Table three: Properties of a 1 mm thick sheet of Curv

Property	Value	
Tensile Modulus (MPa)	3500	
Tensile Strength (MPa)		150
Elongation to break (%)	17.0	
Puncture Impact (J)		26
Density (g/cm^3)	0.92	

More information

As you can see, the fillers arena is full of innovation in all areas from the established fillers to new entrants. If this article has whetted your appetite to know more about the latest developments in filled plastics then you might want to attend the upcoming **Minerals in Compounding conference** to be held in Atlanta USA on 1-2 December (**click here** for details). You will get a chance to see the new developments and also to meet many of the companies mentioned in this article so you can discuss their innovations face-to-face. As conference chairman, I am looking forward to seeing you there!

Click on the links for more information:

- **www.imerys.com**
- **www.rktron.com**
- **www.appliedminerals.com**
- **www.sasolalumina.com**
- **www.kmi.at**
- **www.nanosilasd.com**
- **www.stabilization-technologies.com**
- **www.curvonline.com**

About the author

Dr Chris DeArmitt is a leading name in plastics, additives and problem solving. Based on his experience at companies like Electrolux and BASF, he has now founded his own company Phantom Plastics. With over 40 publications including numerous patents, he puts his expertise to good use helping clients around the world. Chris's track record of innovation includes three Innocentive open innovation cash prizes and the development of many revolutionary new products including plastics, smart materials and more. E-mail: chris@phantomplastics.com. Tel: +1 601 466 8342.

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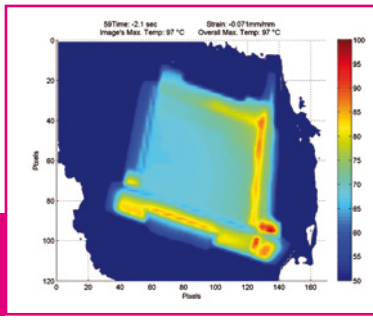
* *recommended loading just 0.8% weight*



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