compounding WORLD

February 2011

RECYCLING TECHNOLOGY TAKES OFF

MAKING THE MOST OF MINERAL FILLERS

NUCLEATORS DELIVER CLEAR BENEFITS

RETHINKING HOW KNEADERS WORK

Dr Chris DeArmitt was chairman for AMI's recent Minerals in Compounding conference in Atlanta, Georgia, USA. Here he reports on the wide range of presentations covering the latest developments in materials and processing technologies

Making the most of minerals

Interest in fillers is as strong as ever, as illustrated by the healthy attendance and the diversity of technologies presented at the recent AMI Minerals in Compounding conference in Atlanta, Georgia, USA. Topics spanned the range from traditional fillers to new entrants and from additives like dispersants and coupling agents to processing equipment to optimise production throughput and material properties.

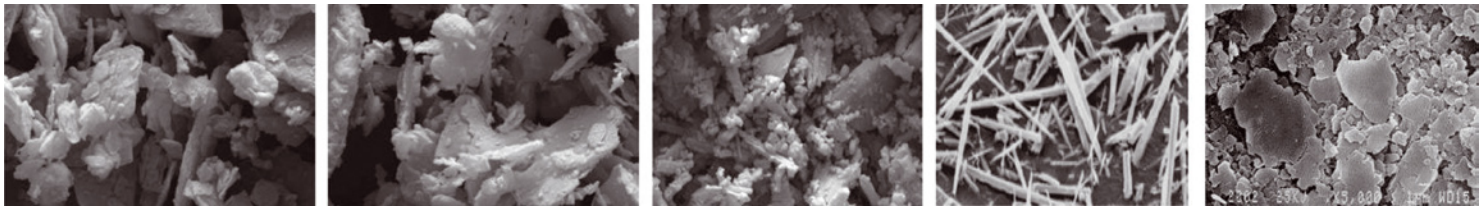
The conference was kicked off by Dr Chris DeArmitt of **Phantom Plastics** who gave an introduction to filled plastics including how different types of filler alter the mechanical and other properties of plastic materials. Each type of filler has its own niche according to the properties of the filler and the size and shape of the filler particles. He also emphasized the importance of dispersants and coupling agents in optimizing composite processing and properties.

He then dispelled some myths about filled plastics. For example, properties are usually plotted versus the weight % of filler, often resulting in curves which are hard to understand and complex equations are needed to fit the data. In fact it turns out that properties depend upon the volume percentage of the filler and polymer phases, not the weight percentage. Plotting data that way often results in straight lines. Another myth is that fillers have lower specific heat capacities than polymers, thus helping reduce heating and cooling times. Although fillers do indeed speed production through their high thermal conductivity, it was shown that the specific heat capacities of fillers and polymers are precisely the same on a per unit volume basis.

Charles-Etienne Houssa of **Omya** continued with a look at calcium carbonate which is one of the most popular fillers because it is inexpensive and improves several properties of polymers such as modulus and cooling times. In some cases, it can also increase impact performance and environmental stress cracking resistance.

The price of calcium carbonate is more stable than polymer prices and has historically increased more

Quarzwerke compared a selection of filler types in different engineering plastics



(Left to Right): Muskovite Mica, Phlogopite Mica, Low-aspect-ratio Wollastonite, High-aspect-ratio Wollastonite, Platy Kaolin

Mondo produces very high purity talc using a super-conducting magnet and a flotation process

slowly than that of polymers. For example HDPE prices increased 125% from 2000 to 2010. In contrast $CaCO_3$ increased just 50% over the same period. This gives the expectation that more and more filler will be used in future years.

Natural born fillers

Calcium carbonate filler is formed through a process known as diagenesis whereby sea organisms are deposited on the sea bed and then converted to calcium carbonate sedimentary rock. It turns out that 300 million metric tonnes are deposited in the oceans per year but only 75 million tonnes are quarried, making calcium carbonate a sustainable filler.

Omya showed some new particle morphologies, namely microplatelets agglomerated to make spheres. Potential applications were not mentioned but one can imagine that such high surface area particles would be effective for nucleating foam cell growth and for catalyst supports.

The next presentation by Frans Venema of **Mondo Minerals** focused on talc which has a higher aspect ratio than calcium carbonate, leading to improved stiffness, HDT and barrier properties. Talc also increases polymer strength and reduces creep (slow flow) of polymers. One caveat is that impurities are common, so Mondo performs a flotation process to remove other minerals. This process is combined with a special superconducting magnet to remove magnetic impurities like iron.

As with other mineral fillers, talc increases thermal conductivity substantially, leading to faster heating and cooling and therefore higher production output. In PP and PA, talc also helps nucleated crystallization leading to a further increase in production output.

Dr Jörg Zilles of **HPF The Mineral Engineers**, which is a division of **Quarzwerke**, presented studies on mica (Phlogopite and Muscovite variants), Wollastonite (low-aspect-ratio and high-aspect-ratio) and platy Kaolin all at 20 weight % in PA6, PBT, ABS, PPS and PSU. Mechanical properties were measured comprehensively as well as the difference in shrinkage parallel and perpendicular to the injection direction. The latter measurement gives an indication of the tendency to warp.

Overall, the fillers tended to increase modulus, strength and HDT while reducing warpage. The only downside was some loss in impact resistance commonly found when adding fillers to polymers. For each plastic there was a filler which provided the best property balance. Phlogopite was found to be the preferable filler for PA 6, while high-aspect Wollastonite showed the best balance of properties in ABS if anisotropy can be tolerated. Low-aspect Wollastonite gave remarkable increases in modulus coupled with excellent impact strength in PBT, PPS and PPU. Kaolin and Muscovite mica gave increases in modulus, tensile strength and heat deflection temperature, while shrinkage of the polymer is decreased in an isotropic way.

Added strength

Milliken is well known as the market leader for clarifying agents for PP and nucleating agents for PE and PP. However, Normand Niron's talk focused on its new product Hyperform HPR-803 which is marketed as a filler to replace talc in applications where density and surface finish are paramount.

The push for hybrid cars has added complexity and, ironically weight to the vehicles. Similarly, the continual addition of new features and devices also pushes up the weight of vehicles. The manufacturers therefore seek new ways to reinforce automotive plastics to bring the

Imerys presented a new reliable way to measure the aspect ratio of different fillers to help develop optimised grades

weight back down to retain fuel efficiency.

Compared to talc, Hyperform HPR-803 offers the same performance at lower loading levels, leading to reduced density as well as good scratch performance. The lower filler loading also improves colourability, meaning that a given colour can be achieved with less pigment or alternatively, more intense colours can be obtained.

Compared to glass fibre, Hyperform can deliver the same modulus but with Class A surface finish. The small particles lead to good weld line strength and good retention of properties after multiple extruder passes to simulate recycling.

Ensinger was represented by Larry DiSano who presented carbon nanotubes and a titanate/ceramic filler used in high-temperature thermoplastics like PEEK.

Carbon nanotubes are used in applications such as explosion-proof plants, trays for integrated circuits, heat exchangers, chemical purifier systems, pump housings and robotics. They provide electrostatic discharge while retaining good mechanicals, flow, surface finish and low density. One essential property is that they do not slough off which is critical in dust-free production environments.

The titanate/ceramic filler – $CHF_2[TiO]_n$ – has a density of 4.7 gcm^{-3}, a 3,200°C melting point, thermal conductivity of 17 W/m.K, a high modulus and a Vickers Hardness of 3400. These properties lead to:

- increased hardness
- abrasion resistance and wear resistance
- lower coefficient of friction
- enhanced dimensional stability
- excellent compatibility and bonding to the polymer matrix (through chemical reaction)

The filler dramatically increases abrasion resistance in unfilled and filled PEEK, UHMWPE and other polymers like PPS, PAI, PI, PAI, PPA, PES, PPSU, PSU, PEI and PTFE.

Milliken says that the move towards sophisticated hybrid cars, as signalled by VW's Formula XL1 prototype, will cause car makers to look for new ways to reinforce plastics to save weight

Size does matter

DuPont discussed the importance of particle size and refractive index on light scattering in polymers. To create the best whitening effect, one needs a particle or void with a refractive index as different as possible from that of the polymer matrix. For maximum scattering of visible light, the optimal particle or void size turns out to be 200 nm (0.2 microns) which is why commercial titanium dioxide white pigments are just that diameter. The intricacies of the measurement methods were discussed and then the tinting strength of Rutile type TiO_2 was compared to fillers and pigments such as calcium carbonate, zinc sulphide, calcium sulphate and barium sulphate. As expected, the relative tinting strengths depended upon the refractive index differential between polymer and filler.

A paper co-authored by Chris Paynter and David Taylor of **Imerys** also dealt with the importance of shape measurement and control. It was shown that although properties depend strongly on aspect ratio, it is not always easy or convenient to properly characterise the aspect ratio. Techniques such as Sedigraph and

Albemarle and Minelco presented alternative mineral filler choices for flame retardant compounds. Photo of cone calorimetry courtesy of ITRI Innovation's Fireproof division

laser light scattering can give very different and even erroneous results. Imerys therefore presented the use of Stopped Flow Conductivity as a reliable way to get aspect ratio and particle size information that compares well to direct, laborious techniques such as TEM analysis. This paves the way for the development and optimization of new filler grades.

Flame retardant fillers

Vijay Kotian of **Albemarle** opened discussions on fillers as flame retardants with a presentation on aluminium hydroxide (ATH), a popular inorganic flame retardant which has seen growth in recent years. This has been accelerated by the concerns and legislation against brominated flame retardants. Mineral flame retardants need to be used at high loadings, often in excess of 60 weight % to achieve the desired level of flame retardance. Such high filler loadings bring issues with filler feeding, extruder throughput and challenges to retain sufficient mechanical properties in the final compound.

By controlling the precipitation process used to manufacture ATH, it is possible to boost the properties in several important ways. Careful control of particle size distribution in Albemarle's new 104 LEO and 107 LEO grades has lead to the following advantages, while retaining identical flame retardance as shown by cone calorimeter:

- higher bulk density
- better powder flow
- reduced extruder torque and torque fluctuation
- increased thermal stability (by 5-15°C), reducing problems with foaming in the extruder
- reduced water pick-up and therefore better electrical resistivity (presumably though optimized surface treatment)
- lower viscosity

Minelco used the Minerals in Compounding conference to present Huntite, an inorganic flame retardant with the chemical structure $Mg_3Ca(CO_3)_4$ that gives similar performance to ATH while improving extruder output. Huntite is white in colour, has a particle size of 1-2 microns, a 1:20 aspect ratio and often occurs together with Hydromagnesite. Minelco sells the mixture under the tradename Ultracarb and has now commercialized pure Huntite under the Hypercarb name.

Stefan Viering described tests in EVA that showed that Ultracarb is more Newtonian than either ATH or magnesium hydroxide (MDH). This means that the melt viscosity is less dependent on shear rate, giving several advantages. However, because Huntite behaves very differently to ATH or MDH, Minelco warns not to use the same additives to modify flow. Overall, Viering summarised the advantages as:

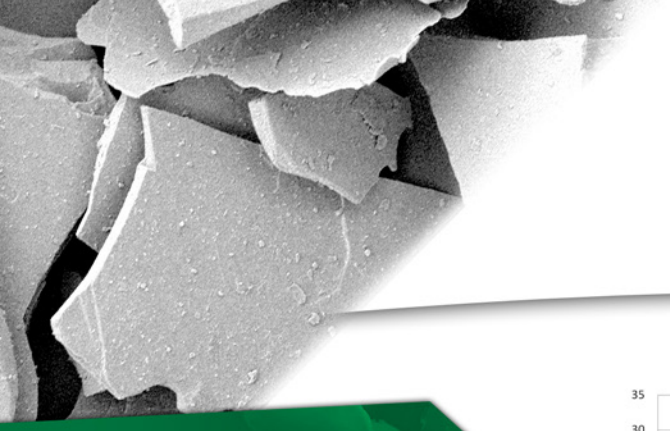
- 10-15% higher extrusion speed
- less polymer consumption
- lower expensive additive demand
- less energy consumption
- more fire retardant potential

Processing improvements

Michael Klinar of **Kärntner Montanindustrie** gave a paper on Miox, a micaceous iron oxide which has long been used in corrosion resistance paints and coatings and which, in recent years, has attracted attention as a filler for plastics. The platy filler has an aspect ratio of up to 50, a density of 4.8 gcm^{-3} and a Mohs Hardness of 6.0–6.5. Its high density improves sound damping and adds heft.

The materials is grey and metallic looking, but becomes red in appearance when ground below approximately 10 microns d50. The platy structure allows a 40% jump in thermal conductivity when dosed at just 1 weight % in PP homopolymer. This leads to faster injection moulding cycles. Other benefits expected from a platy filler are also realised using Miox. Examples include increased modulus, strength, HDT and reduced shrinkage. In PP homopolymer, the room-temperature notched Charpy was retained but at -20°C the notched Charpy actually increased, which is very unusual. In PA 6, both the room-temperature notched Charpy and low-temperature values were increased.

Successful commercial products include injection moulded crates, chairs and housings as well as



KÄRNTNER MONTANINDUSTRIE
INDUSTRIAL MINERALS

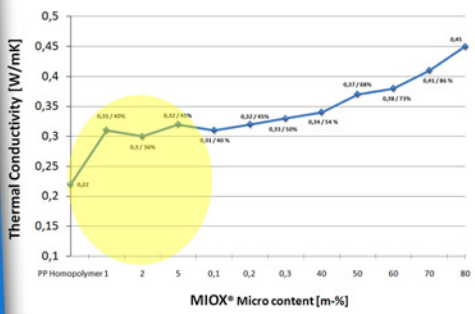
The quality of functional fillers makes the difference

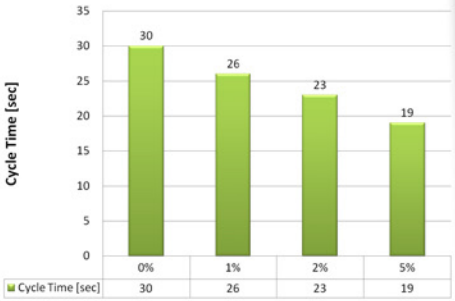
Kärntner Montanindustrie (KMI), located in Austria, is the market leader in Micaceous Iron Oxide (MIOX®).
KMI, as a specialist in micronization of high aspect ratio (HAR) minerals, extended their product portfolio to mica (muscovite, phlogopite) and wollastonite.

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

MIOX® for Process Optimization – Cycle Time Reduction

MIOX® Micro shows unique properties in Polypropylene.
A significant increase of thermal conductivity is reached already at low loading levels between 1 and 5 %-wt.





As a consequence, the cycle time could be decreased within the injection molding process, and consequently the process speed and the throughput could be increased while mechanical properties are maintained.

Industrial Applications

Injection Molding (e.g. Crates)

4 % MIOX® Micro filled PP/PE Copolymer shows a cycle time reduction from 20 sec to 12 sec with additional improvement of impact performance in the handle area!

Extrusion (e.g. Industrial Pipes)

Pipes with wall thickness of 18 mm; 20 % improvement of productivity (increased material throughput) with 3 % MIOX® Micro.

www.kmi.at

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

KMI´s Product range includes

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Booth 308, hall 08

Machinery matters

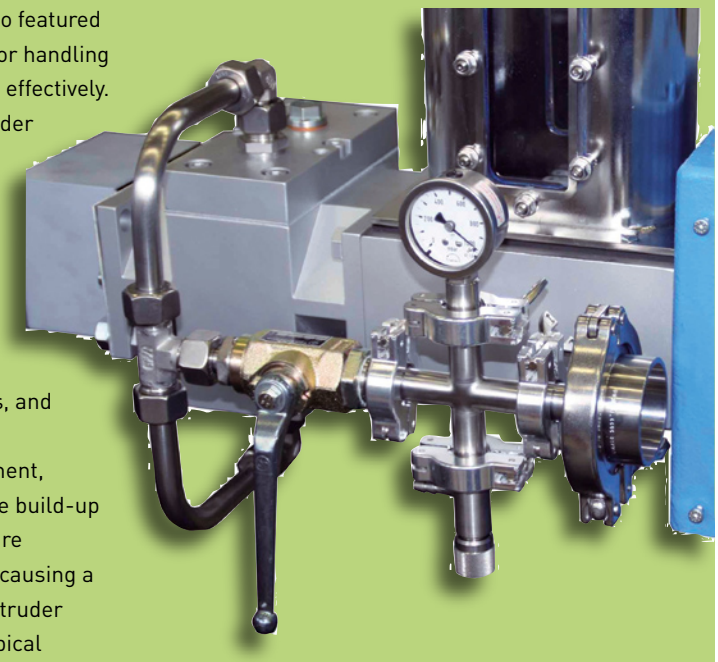
The Minerals in Compounding conference also featured presentations on machinery and equipment for handling and processing filler materials efficiently and effectively.

Coperion showed the importance of extruder set up and optimisation for maximising filler dispersion and throughput. Eberhard Dieterich explained that its ZSK Megavolume Plus system offers 40% more free volume giving advantages such as improved feed intake, reduced shear input, lower stock temperatures, lower product stress, improved quality for shear sensitive products, and safer venting.

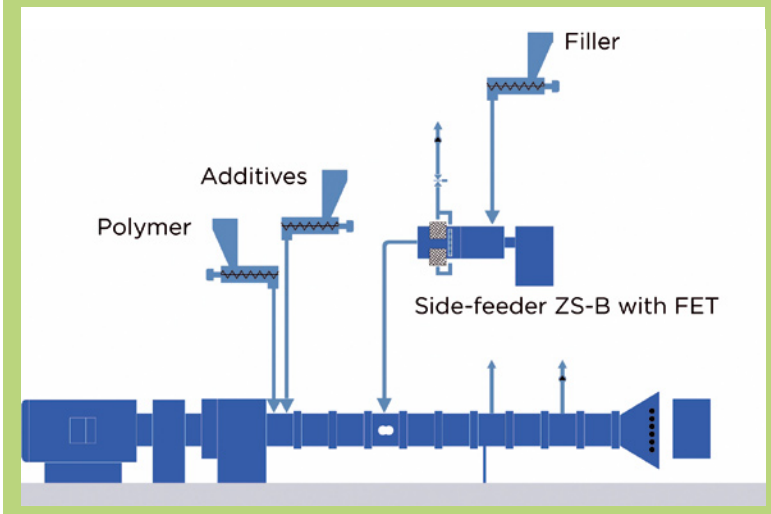
Using nano-particulate carbon black pigment, dispersion was tested by monitoring pressure build-up on the pressure filter pack. Increased pressure indicates agglomerates trapped on the filter causing a partial blockage. In LDPE, LLDPE and PP, extruder throughput improvements were seen with typical increases of 80-100%.

To allow for improved feeding of solids, Coperion showcased its FET system that applies a vacuum to increase the bulk density of powders. For three different talc grades in PP, extruder throughput was increased in the range of 140-200%.

Single-screw extruders are attractive due to their simplicity, reliability and relatively low cost compared to twin-screw variants. However, it is conventional wisdom that single-screw designs cannot achieve sufficient mixing for fillers, pigments and polymer blends, nor can they handle high filler loadings. Keith Luker of **Randcastle Extrusion Systems** is trying to change that perception with a new mixing element called the Elongator.



Coperion's FET system (above right and below) boosts filler throughputs by applying a vacuum to increase the bulk density of powders



He says that the new mixing technology stems from a fundamental understanding of mixing, arguing that proper mixing is achieved using elongational flow (as opposed to shear). So the new element incorporates that in the design. Also of importance is proper venting and because the element elongates the polymer melt into a thin film, a vacuum applied at the correct location is able to effectively remove any volatiles such as residual monomer or water vapour.

Dr Jaime Gómez of **K-Tron** explained the importance of setting up feeding and handling equipment to ensure maximum throughput and reliability. Each filler type behaves differently because each has a unique combination of particle size distribution, hardness, anisotropy, electrostatic build-up and tendency to bridge or compact. Even for two different grades of calcium carbonate it was shown that virtually every piece of equipment used would need to be changed (feeder model, filter receiver, hopper size, agitation, feeding device and weigh bridge).

Thus it may be that the least expensive filler on a materials cost basis is no longer the least expensive when the requisite investment cost is considered. This means that when preparing for scale-up it is best to contact experts to ensure the right choices are made and avoid costly mistakes.

- **www.coperion.com**
- **www.randcastle.com**
- **www.ktron.com**

extruded pipe applications and table components.

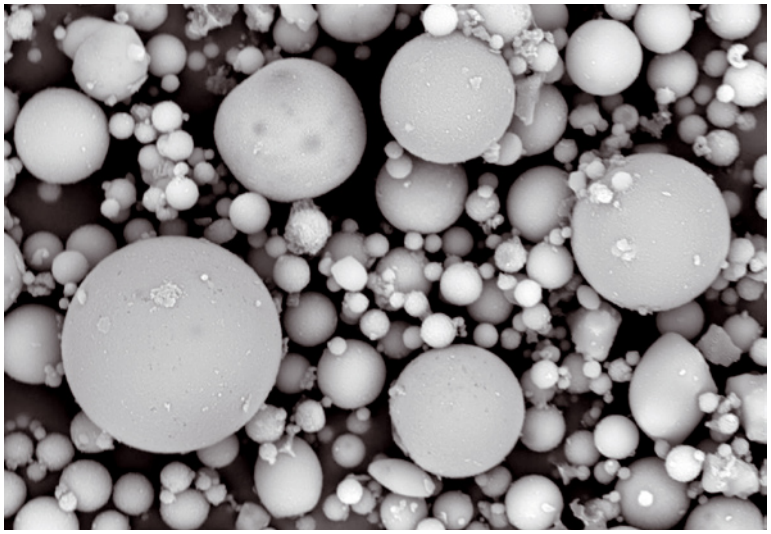
Richard Oder of **Energy Strategy Associates** presented Nan-O-Sil ASD, a high-purity silica product with a particle size range of 20-550 nm. Injection moulding cycle time reductions of 20-30% were reported in PP, HDPE and ABS, as well as in 33% glass fibre reinforced PA 6,6 and PBT. Normally, process aids work by one or more documented mechanisms such as improved flow, nucleation or improved thermal conductivity, but none of these modes fit the experimental data gathered so far for Nano-O-Sil. Nevertheless, used at a level of just 0.8 weight % it is employed commercially to good effect where it reduces warpage, improves colour and mitigates weld lines, so the science will have to catch up and give us the explanation. Investigations are underway.

Recycled fillers

Joe Keating of **Vitro Minerals** showed glass powders made from post-consumer and post-industrial waste that present an effective way to add recycled content to products. He explained that the post-consumer waste comes from bottles and is a mixture of colourless, green and brown glass. The post-industrial glass comes from fibre glass manufacture and is used to make Vitro's low-alkali glass which is colourless. Because the glass is amorphous, there are none of the health concerns associated with crystalline silica.

Vitro produces recycled glass fillers from post-industrial fibre waste (pictured) as well as post-consumer bottles

Godfrey Short of **RockTron Advanced Products** discussed how his company is producing fillers from fly ash, a waste product from coal-fired power stations that is both inexpensive and abundant. Although it has been



RockTron's MinTron fillers are made from recycled fly ash

targeted for use as a filler for decades, until now its potential has not been realized. This is because raw fly ash is a mixture of several different components which bring problems such as abrasion and concerns over heavy metal content. In order to overcome these issues, RockTron has introduced a dedicated benification plant. This allows them to separate the fly ash into its constituent components such as magnetite, which is marketed as MagTron, and solid alumino-silicate glass spheres which are sold as MinTron.

MagTron is utilized primarily for its high density and magnetic properties, whereas MinTron competes with traditional fillers and glass beads. Because MinTron has been purified and the metals leached away, it can be used without the concerns that have traditionally hampered the use of fly ash.

Data was shown for 10, 20, 30 and 40 weight % MinTron in PBT compared to 30 weight % glass beads. MinTron showed markedly lower melt viscosity with mechanicals matching or in some cases exceeding those of the glass spheres.

Tests show that PP filled with 15% RockTron MinTron (left) is more scratch resistant than PP with 15% talc (right)

During his presentation, Short also announced that RockTron is working with the **Ford Motor Company** and materials manufacturers to develop compounds for interior, exterior and under-the-bonnet applications. The work is looking at incorporating RockTron's 100% recycled fillers as replacements or partial substitutes for other fillers. According to Short, the spherical shape of MinTron offers advantages in dispersion compared to irregularly-shaped fillers. In addition, the hardness of the glass spheres (5-6 on the Mohs scale) gives high scratch resistance.

Examples were shown of scratch test plaques where a PP co-polymer containing 15% talc was compared to an identical co-polymer with 15% MinTron replacing the talc. In addition to the significantly improved scratch resistance of the MinTron-filled plaque, a 50% reduction in emissions was measured. The meeting of automotive OEM emissions specifications and the control of interior emissions are important factors in the reduction of interior fogging and odour.

Another potential advantage to automotive OEMs of using MinTron compared with talc is its 20% lower density. If MinTron is substituted on an equal volume basis, then lower weight components can be produced, helping automotive OEMs to reduce vehicle weights and meet emission requirements.

In addition to the automotive applications, other non-automotive products were shown, including a PA 6 product containing MinTron and a recently patented PP roof tile developed by **The Green Tile Company**. It is using 25% MinTron in the tiles to help meet its targets for using recycled, sustainable materials with weight reduction potential. Following successful prototype testing, production tooling is being manufactured with an expected product launch date of late March 2011.

The perfect couple

Jeremy Austin of **Cray Valley** presented the company's diverse range of tailor-made additives which find use in thermoplastics, thermosets, elastomers, inks, coatings and adhesives. The Cray Valley products are based around two distinct chemical families: the styrene-maleic anhydride copolymers (SMA) and derivatized polybutadienes (Ricon). Because Cray Valley has control over the monomer ratios, derivatization level and molecular weight of its additives, it is able to tune the products to suit the needs of different fillers and polymers.

It has been shown that the chemistry of the dispersant or coupling agent must be correct in order that it bonds to the filler surface and yet most companies offer only organosilane or carboxylate anchor groups. In contrast, Cray Valley has a very diverse array of

HIGH PERFORMANCE FILLERS FOR MODERN THERMOPLASTICS

Polymers alone are not able to meet the many different requirements in modern plastics. For this reason various high quality, functional mineral fillers are used. To achieve an optimum bond between the polymer and the functional filler, a surface treatment specially adapted to the polymer system can be applied.

High Performance Fillers effect in thermoplastic compounds

- enhanced tensile strength
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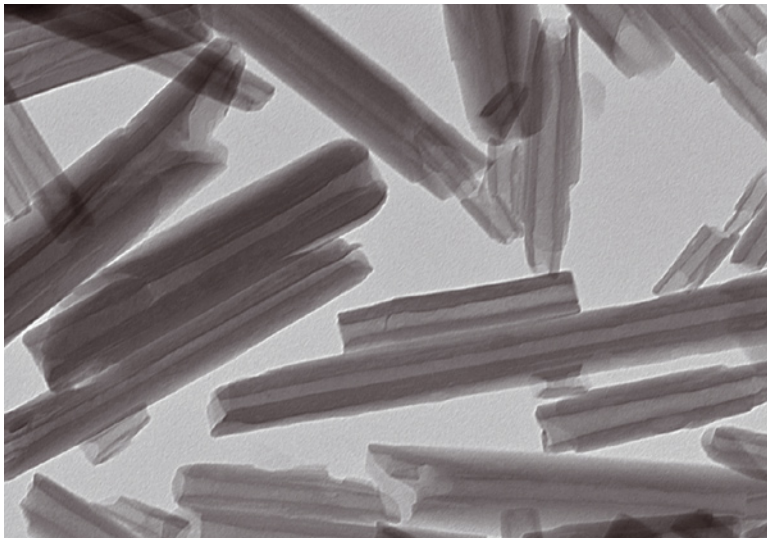

Cray Valley has begun work to find the optimal surface treatment for Halloysite. Photo: Applied Minerals Inc.

chemistries including maleic anhydride (known to be a very effective anchor group for several filler types), carboxylic acid, epoxy, imide, sulphonate, acrylate, amine, bromine and even siloxy groups.

As an example of commercial applicability, Cray Valley screened various chemistries in order to hit customer performance targets for elongation to break and tensile strength for an EVA/ATH flame retardant formulation. While low anhydride, amine or epoxy polybutadienes all showed promise, the low anhydride polybutadiene was the one that exceeded customer targets.

Recently, the mineral Halloysite has attracted considerable commercial interest as it boosts mechanical properties dramatically at loadings as low as 1 weight % and being a hollow nanotubular material, it can be used to deliver additives in a controlled time-release manner.

Cray Valley has begun work to find the optimal surface treatment for Halloysite. In PP it showed improved elongation and impact resistance and interestingly a decrease in crystallinity when using a combination of Halloysite and surface treatment. This latter effect is under further investigation.

Safer silanes

Gelest is a leader in organosilanes and related specialty chemicals. Organosilanes have long been used as dispersants and coupling agents for fillers and pigments. Normally these additives have three disadvantages. They liberate methanol or ethanol upon reaction, thus creating unwanted VOCs, plus the organosilanes simultaneously self-condense as a competing reaction to deposition on the filler surface. In addition, the trialkoxysilane types are not as reactive as the trichlorosilanes (the latter are not widely used as they are hazardous).

However, Yun Mi Kim of Gelest explained how the new cyclic azasilanes react with silanol groups present on the surface of fillers without the liberation of volatile by-products. This is advantageous from safety and environmental viewpoints. Also of note, the new silanes are more reactive than the conventional types, so they provide better coverage for standard fillers and can also react with some fillers that are not normally receptive to trialkoxy silanes.

Conclusions

Filled plastics represent a multi-billion dollar market because fillers tune the properties of plastics to meet the needs of diverse applications. Each type of filler imparts a different property set and has its own niche. In addition to continual improvement of existing fillers, new fillers are still being introduced as are new additives and improved processing methods. These factors combined with renewable fillers, attractive environmental profile and low cost, ensure continued growth in coming decades.

The next conference

The next **Minerals in Compounding** conference will take place on 30 November to 1 December 2011 in Atlanta, Georgia, USA – **click here for details**. If you are interested in giving a presentation, attending as a delegate, or promoting your company as an exhibitor or sponsor, then please contact Jessie Martin at AMI's American office for more information: jm@amiplastics-na.com Tel: +1 610 478 0800. She is also the contact if you are interested in purchasing a set of papers from the 2010 event.

www.amiplastics-na.com

Click on the links for more information:

- **www.phantomplastics.com**
- **www.omya.com**
- **www.mondominerals.com**
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