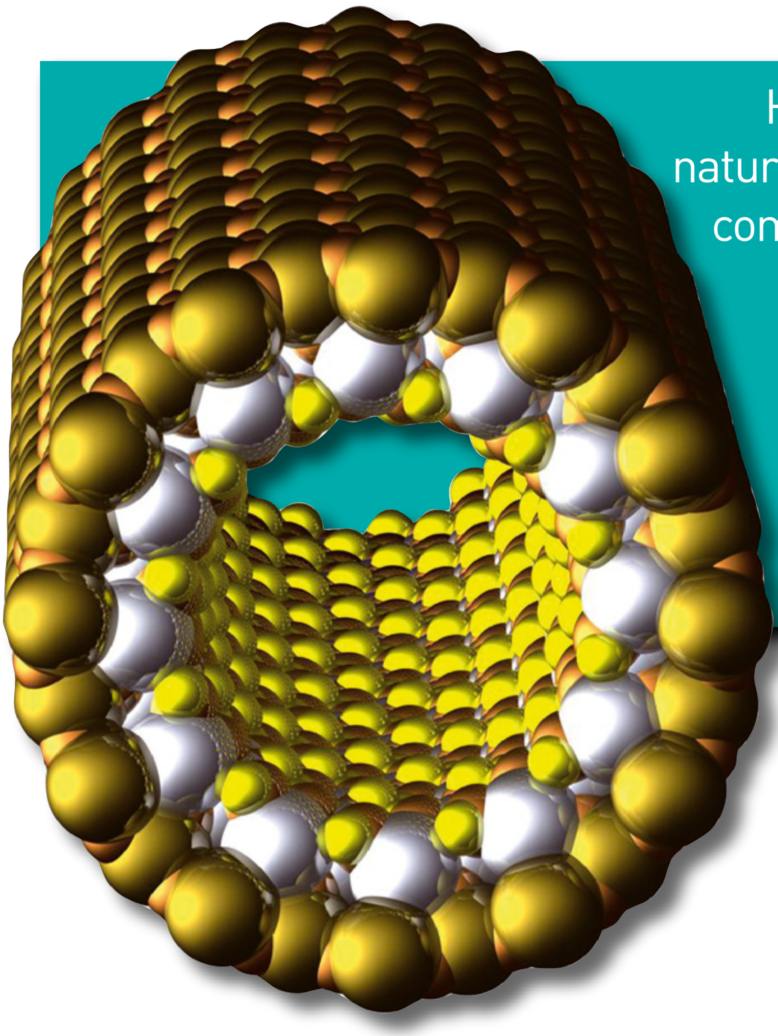


Halloysite clays are described as natural nanotubes and are now being commercialised for nanocomposite applications. **Lilli Sherman** examines the potential benefits for mechanical and processing performance, flame retardance and the controlled release of active ingredients

The natural option for nanotubes

Recent years have witnessed increasing interest in nanocomposites based on a growing variety of additives, including carbon nanotubes and naturally occurring nanoclays.

Halloysite clays are one of the latest nano-scale additive options to reach the commercial market. They are naturally occurring materials, but they have a hollow tubular morphology rather than the platey structure found in the montmorillonite clays typically used in nanocomposites.

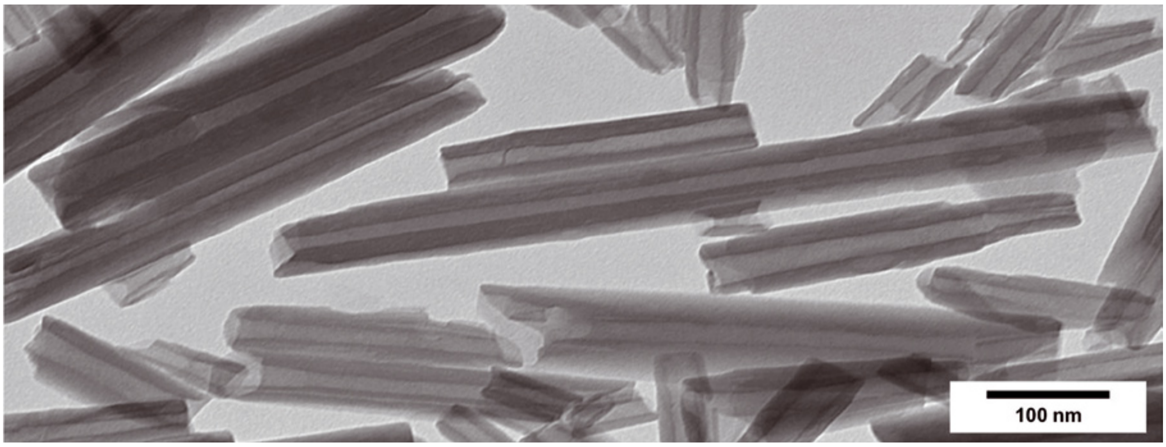
Part of the kaolin family, halloysite nanotubes usually have diameters smaller than 100 nanometres and lengths that range from 200 nanometres to 2 microns. The aluminosilicate clay has traditionally been used in fine china, or as a food extender, catalyst, molecular sieve or as a filler in paint and paper.

Now the material is being targeted at plastics applications. US-based Applied Minerals (formerly Atlas Mining) is commercialising halloysite nanotubes as a polymer additive under the Dragonite trade name. Dragonite XR grades are designed to be used as a functional filler while HP grades are functional additives.

Applied Minerals owns and operates the Dragon Mine halloysite clay deposit in the US state of Utah, which it claims has the purest measured resource of halloysite clay in the world. Its chief technology officer Dr. Chris DeArmitt says that a recent geologic evaluation of the mine showed it to be a proven resource with a life of more than 30 years.

The company can supply halloysite as a raw powder, as a low-dust wax concentrate, or in masterbatch form. The latter typically has an LDPE carrier, although other resins are offered. Because of the inherent exfoliated morphology of halloysite nanotubes, there is no need to chemically separate particles and they provide easy dispersion compared to platey nanoclays which need to be exfoliated. Applied Minerals says that the good dispersion properties of the nanoclay means that it can be compounded into masterbatches with loadings of 40% or even 60% by weight, using a wide range of

The hollow tubular morphology of halloysite nanotubes means that they can be filled with active ingredients



Typical Halloysite nanotubes have diameters smaller than 100 nanometres and lengths that range up to 2 microns

carrier materials including polyolefins and nylons.

According to Applied Minerals, Dragonite delivers a significant improvement in the mechanical properties of a range of polymers. Because of the clay's high stiffness and high aspect ratio of about 20, the material can be used as a reinforcing filler.

In addition, Dragonite HP can be used as a nucleator in PE, PP and nylon 12, reducing cycle times by as much as 35%, according to the company. It has also been used in the production of clear PE, PP, EVA and PVC films with as much as 20-25% loadings.

Dragonite XR has been shown, to date, to provide flame retardance in PE, PP, EVA, EPDM and nylons 6 and 12. Halloysite is a 'natural' flame retardant which releases water above a certain temperature.

Perhaps one of the key factors to consider with this newer option is the cost. Depending on the grade, Dragonite nanotubes are priced at \$1/lb to \$3/lb (€1.5/kg to €4.5/kg).

Signature is using Dragonite HP in its MegaDeck access mats for supporting heavy vehicles on difficult terrains

Reinforcing polyolefins

Signature Fencing & Flooring, the world's largest manufacturer of modular flooring systems, is using Dragonite HP masterbatch in its MegaDeck extra-large access mats for supporting heavy vehicles on difficult terrains. It has found that as little as 1% loading of masterbatch is an ideal drop-in replacement for other reinforcing minerals that are typically used at much higher loadings.

Used at 1-2% loadings, the additive is claimed to give a 20-30% increase in stiffness, 15% improvements in flex and tensile strengths, retention of notched izod impact properties, plus improvements in surface finish, pigment dispersion and dimensional stability. Cycle times are said to be reduced by 15-30%.

Arnon Rosan, president and CEO of Signature, commented: "We have tried various fillers and additive systems to resolve issues with shrinkage and heat dissipation for a part as large as MegaDeck and found that incorporating Dragonite-HP into our formulation yielded these processing benefits in addition to the increase in strength."

In a separate ongoing field study at a producer of an injection-moulded HDPE part, it has been shown that the use of Dragonite HP at 1% loading results in a 25% cycle-time reduction compared to using an unreinforced material. Also reported is a 20% increase in stiffness without affecting impact performance, and a significant reduction in the visibility of sink marks.

Further testing now in progress is aimed at achieving additional savings through reducing wall thicknesses by taking advantage of the improvement in physical properties. So far, results show the potential for a 5-10% reduction in wall thickness, and a 10% further cycle-time reduction. Similar results have been achieved in PP homopolymer and copolymers.

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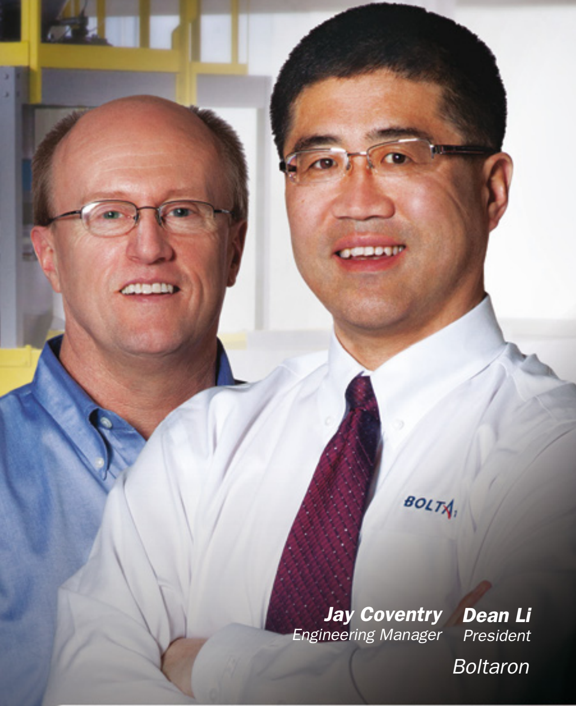

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Above left: Applied Minerals says that its Dragon Mine mine has the purest measured resource of halloysite clay in the world

Above right: Halloysite can be supplied as a raw powder, as a low-dust wax concentrate, or in masterbatch form

Overall, the improvement in mechanical properties is significant. In HDPE this is claimed to include a 9% increase in tensile strength, a 22% improvement in flexural modulus, 18% better flexural strength, a 6% improvement in elongation at break, as well as retention of both notched and unnotched Izod impact strength. The last two are particularly significant as with other reinforcing fillers, there is typically a decrease in both elongation at break and impact strength. Other studies have shown similar improvements in engineering resins such as PA 6, PA 66 and PEEK.

Interesting results have also been shown by studies of Dragonite XR in PP homopolymer. In one study, PP cable formulations were made using straight Dragonite XR (rather than masterbatch) at loadings ranging from 3% to 27%. The materials were compounded on a twin-screw extruder, with no silane, impact modifier or coupling agent. Results showed significant increases in both flexural modulus and flexural strength while retaining impact strength.

Improving fire resistance

The flame retardancy properties of halloysite nanotubes in PP have also been explored. For example, Dragonite XR has been used commercially as a synergist to magnesium hydroxide in PP formulations, where it provides excellent char formation and low smoke generation.

Further Applied Minerals studies have examined the performance of halloysite at various levels with and without magnesium hydroxide in PP homopolymer. In addition to the improvement of mechanical properties, they have shown that using Dragonite XR can achieve UL 94 V1 with very low smoke generation even without any magnesium hydroxide. According to DeArmitt, the company expects these kind of results can be achieved in high-temperature engineering thermoplastics such as PES and PEEK. Halloysite nanotubes can be processed at temperatures above 400°C, compared to 300°C for magnesium hydroxide and 182°C for ATH.

In other recent studies, Applied Minerals has shown the synergistic effect of halloysite nanotubes with glass fibre in forming char strength. In a glass-filled PET, the addition of Dragonite improved mechanical properties and boosted the char strength formation.

Results showed that char formation with just glass fibre or just halloysite was poor. The two were then tested together at halloysite/glass fibre levels of 30/5%, 30/10% and 30/15%. Char formation was shown with all three combinations, but the latter formulation resulted in a very homogeneous, high-integrity char which is crucial for optimal flame retardancy. The company expects similar results can be achieved with other glass-fibre filled thermoplastics including high-temperature nylons, PES and PEEK.

Controlled release

The hollow tubular morphology of halloysite nanotubes means that they can be filled with active ingredients that are then released into the host material. For example, Dragonite HP was used in the production of an LDPE bag that protects bananas from insects during the fruit's growing season.

The aim was to have controlled release of an all-natural blend of essential oils, such as cedar, from the clear polymer film. This was a replacement for Dursban insecticide which is being restricted due to safety concerns. The LDPE film was loaded with 5% Dragonite HP impregnated with the natural oil insecticide. Dragonite HP was shown to efficiently control the release of oils from the banana bag for four weeks during heavy infestation.

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