

HALLOYSITE

HANDBOOK



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Preface

Halloysite is a special type of natural aluminosilicate clay with a tubular morphology. It has attracted tremendous interest for decades because of its shape and other properties. Now, with the extreme interest in tubular materials, there is more attention than ever on halloysite, which is Nature's answer to high-tech materials. In fact, in some respects, Mother Nature has outdone our scientists as attempts to mass-produce tubular materials have proven inefficient and expensive. Furthermore, these synthetic materials have no history leading to safety concerns. In contrast, halloysite has been used commercially for several decades with excellent safety.

High purity halloysite has attracted commercial interest from hundreds of companies the world over. It is my goal to support these companies in developing new applications. To that end, I have collected a huge amount of information about the material. This document condenses some of that information and references to the original articles are given so you can do further reading on topics of interest.

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Introduction

There is a constant drive to develop new materials that provide better performance levels. This, in turn, leads to new and better products with increased sales and a competitive edge for the companies that pioneer the use of such materials. Nanotubes have garnered tremendous interest globally because of their potential in areas such as reinforcement, catalysis, remediation and healthcare to name just a few. Although such materials have proven effective and interest has remained intense, the progression to commercial products has been severely hampered. Scale-up of production has presented serious issues. Some products do not scale at all and even those that can be produced in commercially relevant quantities require huge investment. An example is carbon nanotubes where production capacity is growing but the resultant product is too expensive for all but very niche applications.

Ironically, it turns out that Nature has provided an abundant supply of high quality nanotubes in the form of halloysite, a mineral in the Kaolin Group. Halloysite is an aluminosilicate mineral with the same chemistry as kaolinite but instead of the flat sheets typical of kaolinite, the sheets have been rolled up into tubes by a natural hydrothermal process. First described in 1826, halloysite is far from being a new material. In fact it has been commercially mined and sold for numerous applications for well over half a century. Halloysite is used to produce the highest quality bone china and porcelain where it adds whiteness, transparency and exceptional strength to the fired product. Another well-established application is in petroleum cracking catalysts¹. Over a million tons of halloysite was produced from the Dragon Mine in Utah for that application alone (Filtrol 1949-1976). High purity and in particular, low iron was needed so the Dragon Mine deposit was the ideal choice.

With the intense interest in tubular materials, one can understand why workers the world over are turning their attention to halloysite. Thousands of published articles already exist showing outstanding performance in multitudinous applications including reinforcement of elastomers, plastics and coatings. Fire retardance, catalysis and controlled-release effects have also been demonstrated and the list does not end there. The commercial significance of these findings has been widely recognized with companies designing new materials based around halloysite as the key ingredient. This has been underlined by the increase in patent activity and also by the rapid commercialization of halloysite in new plastics, coatings and multiple other applications.

This handbook will describe the unique attributes of halloysite and show how those intrinsic material properties lead to new, enhanced products. In particular, we will show how high purity halloysite opens up new possibilities for commercial products ranging from plastic parts to water and oil-spill remediation.

Halloysite the Material

In order to understand what halloysite can do, one must first understand the intrinsic properties of the material. Once those are identified, commercial applications become immediately apparent. An excellent overview of the nomenclature^{2,3} and characterization of halloysite has been given by Churchman and Carr⁴. Other excellent overview texts exist^{5,6}.

Morphology and Mechanical Properties

The tubular, high aspect ratio particles are ~1-2 microns long, ~50nm across and with a ~15 nm hole or “lumen” (Figure 1). The surface area of halloysite depends on processing and can be selected in the range ~ 50-150 m²g⁻¹. The measured modulus is ~150 GPa^{7,8}, compared to the calculated value of ~ 200-300 GPa⁹. The tubes can flex almost 90 degrees without breaking⁷ and have a dry crush strength¹⁰ of >1500 GNm⁻², >250 000 psi or >130 tons per square inch (beyond the limit of the machine used).

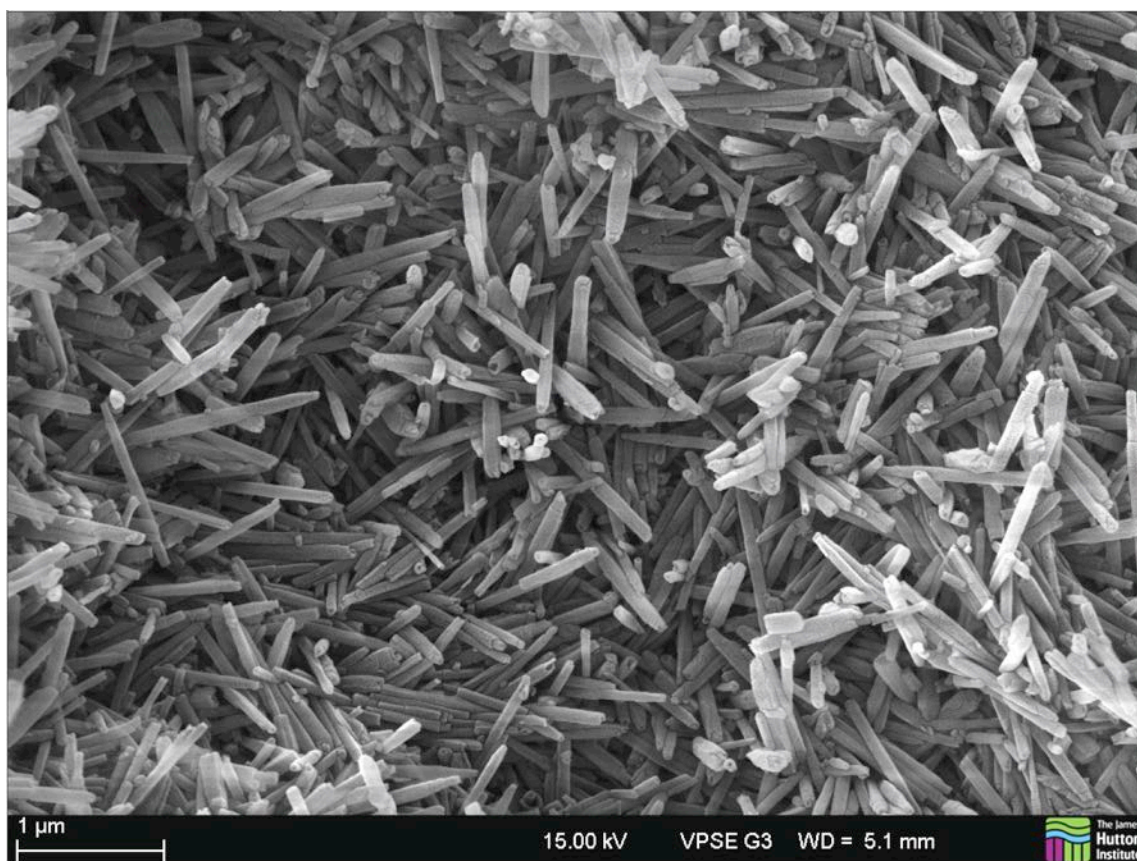


Figure 1 Scanning electron micrograph of pure, as-mined, Halloysite

The formation mechanism was the subject of intense debate for decades¹¹⁻¹⁶. Now it is generally accepted that halloysite can form from kaolinite¹⁷⁻¹⁹ feldspar^{14,20,21}, rhyolite²² or ferruginous chlorite²³ under the influence of hydrothermal action²⁴ or weathering in nature.

Chemistry and Surface Chemistry

In terms of chemistry, halloysite is the same as kaolinite except that the sheets are rolled into tubes. The asymmetrical sheets, when rolled up, give the outside of the tube a silica-like chemistry and the inside an alumina-like chemistry (Figure 2). This has been confirmed by spectroscopic means. For example RAMAN²⁵⁻²⁸ and FTIR^{26,29} spectroscopy indicate the presence of Al-OH groups inside the lumen but no silanol (Si-OH) groups have been detected, indicating a low concentration. Such spectroscopic studies have been useful in several ways. It can be shown that certain small, polar molecules intercalate between the sheets (discussed in detail in the remediation section). Dehydroxylation of halloysite upon heating can also be followed and surface treatment can be confirmed by spectroscopic means³⁰.

Aluminosilicate mineral: $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$

Molecular weight: 294.19

CAS: 1332-58-7

Surface energy³¹: 420-530 mJm⁻²

Halloysite forms in the presence of water and has the formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ where the water is located between the rolled sheets. The spacing between the sheets of as created halloysite is 10Å. Newly-mined material can be of the 10Å type³² but it is only stable if stored under water or at high humidity³³ so it is rarely observed.

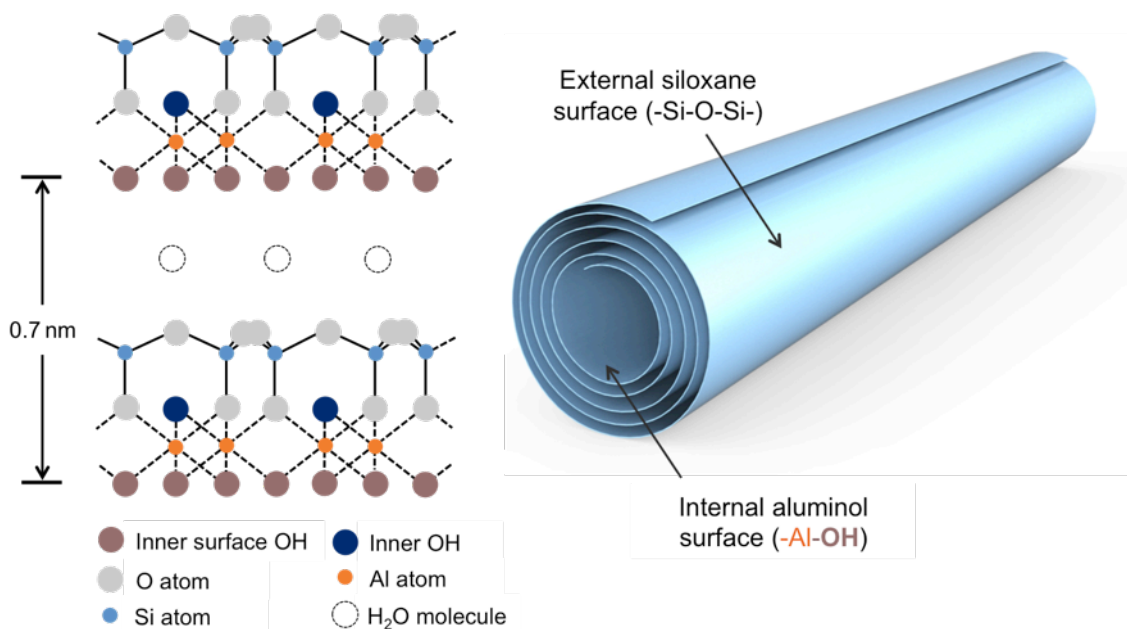


Figure 2 Structure and chemistry of Halloysite

One study used environmental TEM to keep the sample wet and to watch as the halloysite dehydrated to form the 7Å type. Interestingly and counter-intuitively, the diameter of the tubes was found to increase by approximately 10 percent as the water was lost in forming the 7Å material³³. Other workers reported a 60 percent expansion from 300 to 500nm tube diameter³⁴. This was attributed to an effect analogous to a scroll loosening as the water that held the layers tightly together is lost. Dehydration temperature was found to depend on humidity. At room temperature 10Å converts to 7Å at 30 percent humidity or below. At 40 percent humidity 40°C is required. At 100 percent humidity 65°C is needed and when submerged in water dehydration takes place at 95°C³³.

Once 7Å halloysite has formed, it cannot be rehydrated to form the 10Å variant³⁵⁻³⁸. No rehydration occurred even after exposure to 100 % humidity for 2 months³⁹. This is in contrast to other clays such as Montmorillonite, which will rehydrate and swell when exposed to high humidity or water³⁹. However, the 10Å spacing of halloysite can be retained if the interlayer water is first exchanged for ethylene glycol⁴⁰.

		[Interlayer H ₂ O] (Surface H ₂ O)
Halloysite 98% humidity	Si ₂ Al ₂ O ₅ (OH) ₄	[2.0] (0.6) H ₂ O ³⁵
Halloysite 55% humidity	Si ₂ Al ₂ O ₅ (OH) ₄	[2.0] (0.3) H ₂ O ³⁵
Halloysite dried at 250°C then held at 55% humidity	Si ₂ Al ₂ O ₅ (OH) ₄	[0] (0.3) H ₂ O ³⁵
pH in water ^{41,42}		6.4-7.2
CEC Halloysite 7Å ⁴³		11 meq/100g

Halloysite pH behavior related to mineral formation and stability has been studied^{44,45}. The effects of acid on halloysite were reported as early as 1925⁴⁶ and then again in 1943⁴⁷, the latter on both halloysite and calcined halloysite. More recently, White et al. showed that the tubular shape remains intact even after 84 days of exposure to 1M NaOH (pH 14) or 1M H₂SO₄ (pH 0) although slow etching does take place resulting in an enlarged lumen and correspondingly thinner walls⁴⁸. Acid etching can be accelerated using 3M H₂SO₄ and heating to 90°C which increases the pore volume and surface area to create a highly effective sorbent⁴⁹. Acids remove the aluminium containing layers whereas alkali etches away the silica layers. Abdullayev et al. etched out the alumina inside the tube using sulfuric acid which increased the lumen volume considerably⁵⁰. Extraction of alumina from halloysite is particularly favorable compared to other clays with recovery of up to 100%⁴⁷.

The cation exchange capacity of 7Å halloysite is generally reported to be ~11 meq/100g and this can be increased to almost 50 meq/100g simply by soaking in sea water⁴³. For comparison, kaolinite has a CEC of 5 and that increases to just 8 meq/100g upon soaking in sea water. It has also been stated that the CEC for 7Å lies between 5-10 meq/100g compared to 40-50 meq/100g for the 10Å material⁶.

Identification of Halloysite

All natural deposits contain different minerals. For example, kaolinite and halloysite occur together in many instances. It is vital to be able to distinguish between the two. For many years there was no reliable method to do so because the two minerals are so similar in chemistry and structure⁵¹. The James Hutton Institute in Scotland (formerly known as the Macaulay Land Use Research Institute) are the leading experts in mineral characterization and identification. In particular with Dr. Stephen Hillier who is Chairman of the Clay Minerals Group and winner of the prestigious Reynolds Cup for identification of complex mineral mixtures. He employs an x-ray diffraction method, which is the only technique to unambiguously identify pure halloysite and mixtures of halloysite and kaolinite^{52,53} (Figure 3). This is supplemented with further methods including mercury porosimetry⁵⁴, XRF, ICP-MS, TEM⁵⁵, SEM and several other techniques that ensure the material is thoroughly characterized.

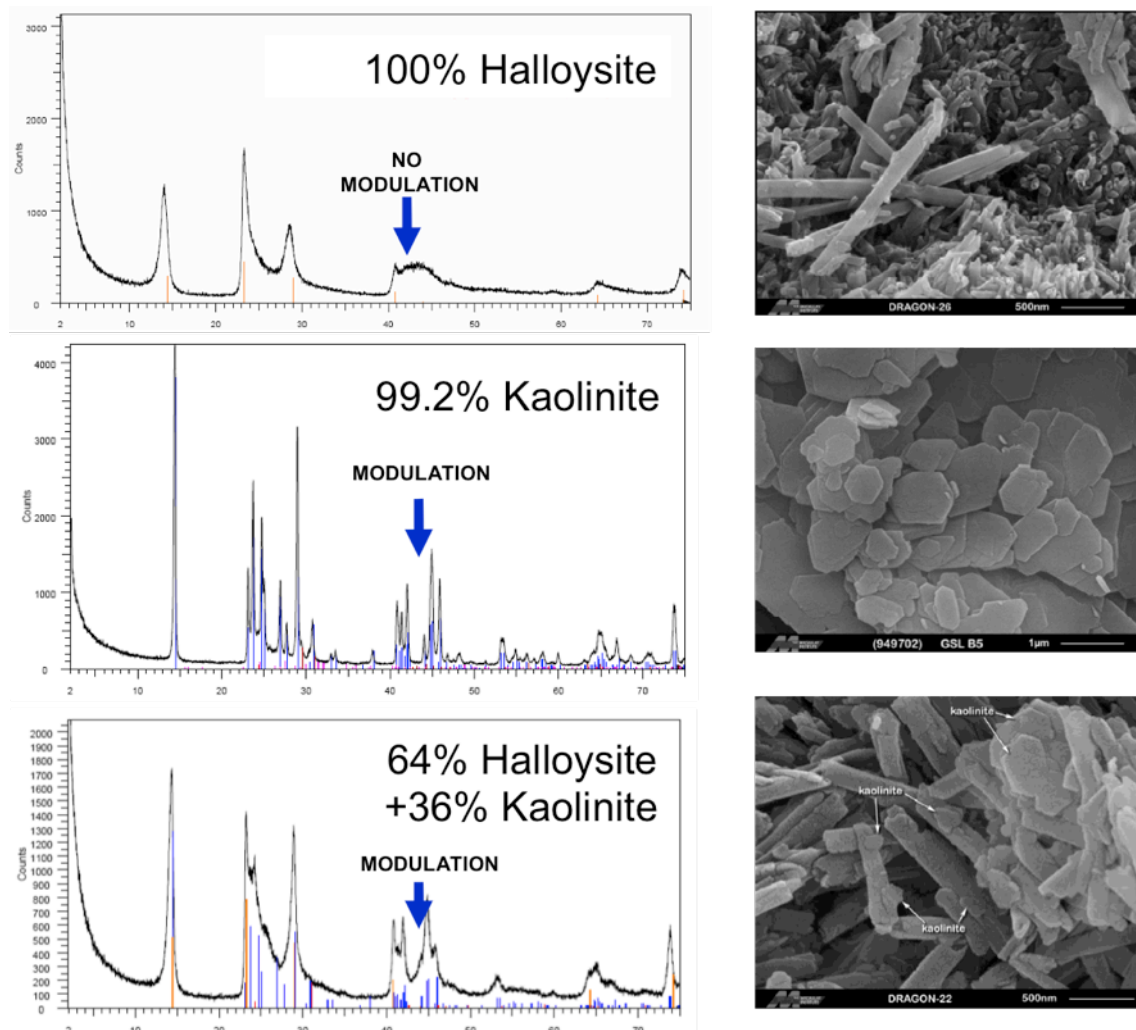


Figure 3 XRD to measure halloysite purity

Density

Halloysite can occur in several shapes including spherical, sheet and the elongated tubular form⁵, the latter is most prevalent and of most use due to its higher aspect ratio. The published density for halloysite varies over a range. One source⁵⁶ lists 2.55 – 2.65 gcm⁻³ consistent with a calculated density of 2.59 gcm⁻³.

Density: **2.54 ± 0.03 gcm⁻³**

The hollow shape means that halloysite has around 20 percent unfilled volume. This has an effect on the effective density of halloysite when it is encapsulated within a matrix. For example, if a composite is made in thermoplastic and the polymer fills the inside of the tube then the effective density of the halloysite is 2.54 gcm⁻³. However, if the inside of the tube is not filled by the polymer then the effective density of the halloysite is 20% less, i.e. ~ 2.00 gcm⁻³ because of the air trapped inside the lumen.

It is possible to determine whether the halloysite particles are unfilled, partially filled or completely filled by comparing the measured density of the prepared composite to the calculated theoretical density (Figure 4).

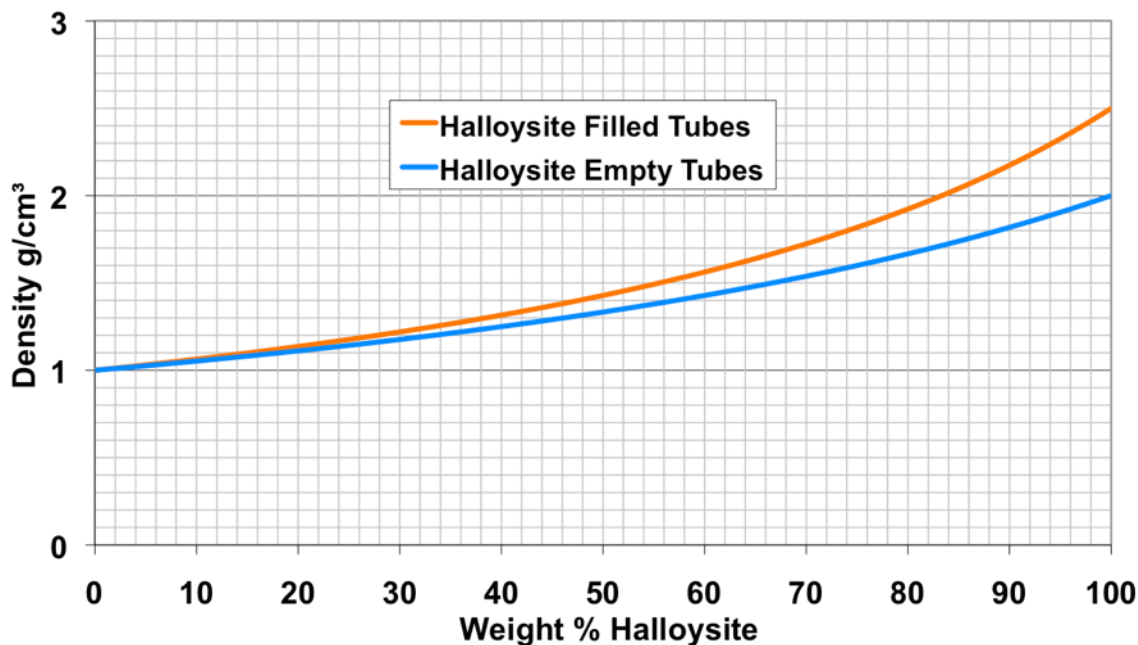


Figure 4 Calculated density of halloysite-filled polymer with either filled or empty tubes

There are potential advantages to leaving the tubes unfilled. For example, this gives thermal insulation, as found for hollow glass beads (see Thermal Properties section). Unlike glass beads though, halloysite also reinforces. Leaving the tubes unfilled also provides a reinforced composite of lower density, which is especially desirable for example in the automotive and aerospace industries.

Hardness

Mineral hardness is normally measured on the Mohs scale with values ranging from 1 (softest) to 10 (hardest). The Mohs scale is far from linear so in some instances it is more appropriate to use another scale such as Knoop, Brinell or Vickers Hardness. When it comes to the use of minerals as fillers in plastics, elastomers and coatings, the Mohs scale is particularly suitable because it relates to the ability of the mineral to scratch other materials. This means that it can give an indication as to whether the mineral can cause wear in processing equipment. Typical fillers have Mohs hardness between 1 (talc) and 3 (calcium carbonate). halloysite has Mohs hardness of 2.5 and there is therefore no concern over wear in extruders or other processing equipment.

Mohs Hardness: 2.5⁵⁶

Optical Properties

While spectroscopy can be used to characterize halloysite as mentioned above, the optical properties of the material itself indicate further commercial applications for the material. Halloysite in its pure form is a white solid which is ideal for incorporation into plastics, paints and coatings.



Figure 5 Exceptionally pure Halloysite ore and powder from the Dragon Mine Utah

The refractive index of halloysite⁵⁷ depends on the degree of hydration^{58,59}.

10Å form (fully hydrated) 1.522 ± 0.003

7Å form (partially dehydrated at room temperature) 1.534 ± 0.003

7Å form (dried at 100°C) 1.548 ± 0.003

Birefringence is reported as > 0.002 ⁵⁸

The birefringence (differing refractive index parallel and perpendicular to the long axis of the tube) is expected for particles of asymmetrical atomic structure. Non-linear optical properties have been reported as well^{60,61}.

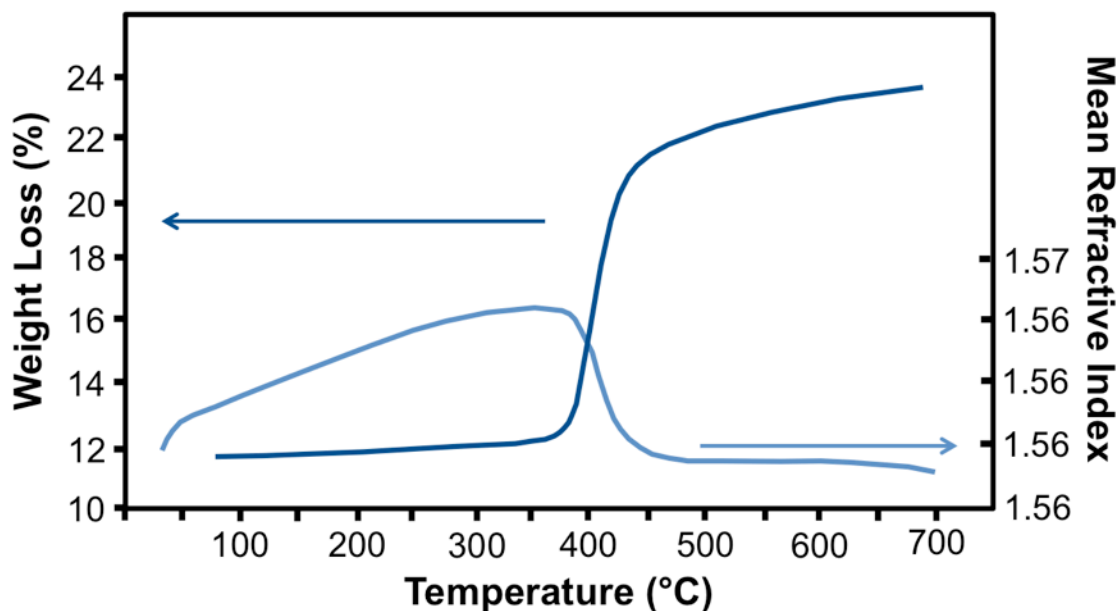


Figure 6 Dependence of refractive index on heat treatment⁶²

It has proven possible to make transparent, colorless films of halloysite in LDPE (25 weight % loading) PLA (30 % loading), PVA¹⁰⁸ (10% loading) and SBR¹⁷⁷ (65 % loading).

Ultraviolet Transparency

Unlike other minerals, halloysite is transparent to UV light⁶³. This was attributed in part to the very low iron content in pure halloysite compared to other minerals. In fact, one study used several clays as UV blockers for sunscreen and found that all clays tested were effective except for halloysite because it is UV transparent⁶⁴. As we shall see later, this UV transparency has already proven useful in commercial products.

Thermal Properties

Surprisingly little work has been done to measure the thermal properties of halloysite. However, one very detailed paper does exist⁶⁵. The specific heat, thermal diffusivity and thermal conductivity were investigated between room temperature and 280°C. It was found that thermal conductivity and diffusivity both decreased sharply upon heating to 100°C due to water loss and from then onward maintained steady values shown below.

Specific heat capacity:	0.92 kJkg ⁻¹ K ⁻¹ (0.22+0.008 cal g ⁻¹ deg ⁻¹)
Thermal conductivity:	0.092 WK ⁻¹ m ⁻¹ (2.2 x 10 ⁻⁴ cal cm ⁻¹ sec ⁻¹ deg ⁻¹)
Thermal diffusivity:	5.04 x 10 ⁻⁴ cm ² sec ⁻¹

The specific heat capacity is identical to kaolinite over the temperature range 50 to 300K⁶⁶. The volumetric specific heat capacity for halloysite is 2.3 kJL⁻¹K⁻¹, i.e. the same as for other minerals, polymers and other solids. Note that the volume specific heat capacity (not weight) is the correct unit to use for mineral fillers.

Heating studies have determined that the tubular structure remains intact to very high temperatures^{67,68} in the range 900°C⁶⁹ to 970°C⁷⁰.

Mineral or Metal	Thermal Conductivity (WK ⁻¹ m ⁻¹)	Mass Specific Heat (kJ/kg.K)	Volume Specific Heat (kJ/litre.K)
BN (hexagonal)	6 (), 0.3 (⊥)	0.794	1.8
Quartz / Fused Silica	1.3	0.8	2.1
TiO ₂	0.065		
Talc	0.02	0.82	2.3
Hollow Glass Beads	0.06-0.16		
Beryllium Oxide	330	1.03	2.9
Glass Fibers	1.0	0.83	2.2
Halloysite	0.092	0.92	2.3
Average	---	---	2.2

Table 1 Thermal properties of halloysite compared to other fillers

The thermal conductivity and diffusivities are very low, in the same range as for hollow glass beads used as an additive to improve thermal insulation. Halloysite could therefore be used in similar applications but with the added advantage of mechanical reinforcement, which is not the case when using hollow glass beads.

The initial weight loss is due to removal of surface moisture. Thereafter halloysite is thermally stable up to over 400°C, which means that it can and has been compounded into all types of polymer from up PE to PEEK (Figure 7).

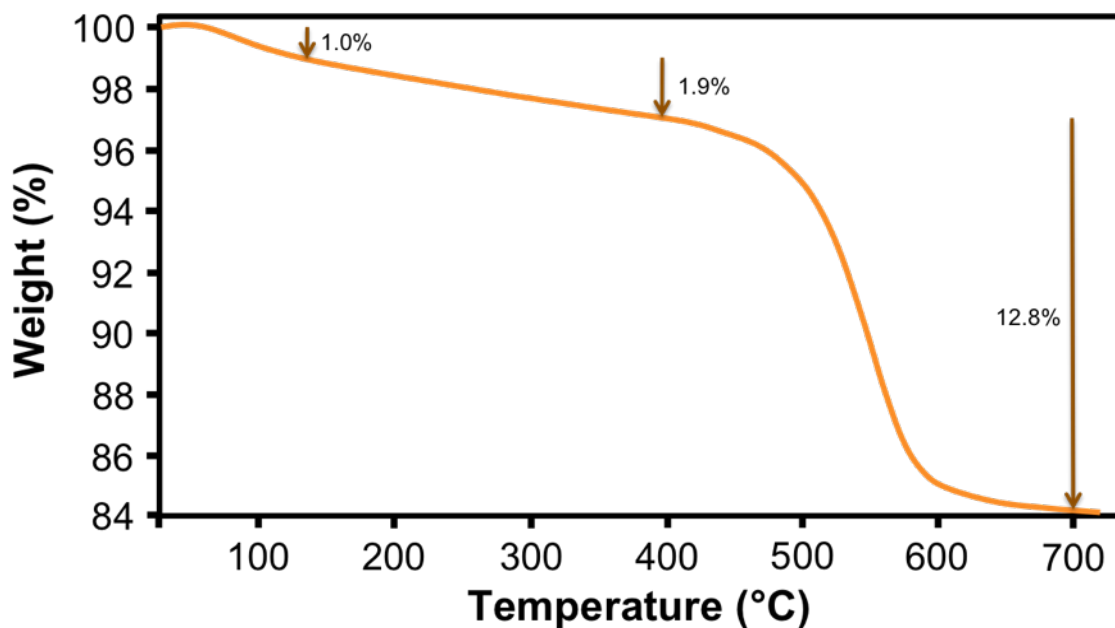


Figure 7 TGA of halloysite showing loss of water at 100°C and above

The loss of water above 400°C makes halloysite a good reinforcing and halogen free flame retardant as the water released quenches the fire. More information on halloysite as a flame retardant in plastics and elastomers is given later.

It is often desirable to lower the coefficient of thermal expansion for ceramics, plastics, adhesives or coatings by incorporating a particulate reinforcement that has a low CTE. The CTE of halloysite has been measured for the temperature range 25-350°C and found to be low compared to several other common minerals⁷¹.

CTE	$10.0 \times 10^{-6} \pm 1.5$	perpendicular to the layer
	$6.0 \times 10^{-6} \pm 2.0$	parallel to the layer

The low CTE and high aspect ratio of halloysite make it an effective additive to reduce the CTE of plastics. This has been demonstrated in epoxy resin⁷² (Table 9).

The reduction in CTE and warpage is also applicable to other polymers. For example, this effect has been commercialized in HDPE⁷³ where it gave significant advantages compared to other fillers tested.

Electrical Properties

Kaolinite is used as a filler in electrical applications due to its insulating properties. As halloysite is chemically analogous to kaolinite, it would be expected to be a good electrical insulator as well. Modeling predicts a high band gap indicative of a good electrical insulator. Measurement shows a low conductivity⁷⁴ of just $3.5 \times 10^{-5} \text{ Scm}^{-1}$.

Although chemically speaking halloysite and kaolinite are identical, halloysite possesses additional water bound between the layers. These water molecules can move in an applied field, thus the dielectric constant is increased somewhat compared to kaolinite, which does not contain such bound water (Figure 8).

Heating halloysite leads to lower dielectric constant due to irreversible loss of water. Even heating to just 220°C gives a marked improvement (Figure 8). It can be expected that heating to 400-600°C, which drives off all bound water and dehydroxylates the mineral, will lead to very low dielectric constant values across the frequency spectrum.

Kaolinite						Halloysite					
75°C		140°C		220°C		75°C		140°C		220°C	
kHz	ϵ	kHz	ϵ	kHz	ϵ	kHz	ϵ	kHz	ϵ	kHz	ϵ
45.58	6.45	42.22	5.30	50.17	4.11	35.01	13.91	38.94	9.91	43.04	6.63
84.17	6.15	86.61	5.18	88.24	4.10	64.68	13.51	71.88	9.51	79.40	6.65
165.80	5.88	171.21	5.14	173.10	4.06	128.66	12.64	141.96	9.25	156.35	6.21
324.50	5.64	331.09	5.02	335.40	4.06	255.00	11.73	278.50	8.62	305.80	5.99
653.0	5.41	663.90	4.90	671.80	4.04	519.20	10.88	566.40	8.02	617.40	5.71
1387.5	5.30	1394.7	4.79	1408.2	4.04	1110.9	10.09	1204.3	7.36	1301.4	5.52
2879.0	5.24	---	---	---	---	2361.5	9.42	2569.4	6.91	3040.3	5.40

Figure 8 Dielectric constant (ϵ) of halloysite compared to kaolinite⁷⁵

Although halloysite is intrinsically a good electrical insulator, it can be made conductive. This has been accomplished by electroless coating with metal⁷⁶⁻⁷⁸ or by polymerizing a coating of conductive polymer such as polyaniline⁷⁹⁻⁸² or polypyrrole⁸³ onto the tube surface. Such anisotropic, conductive particles are in demand for applications including EMI shielding and z-axis adhesives. See also the section on electrically conductive halloysite.

Dispersibility

Dispersibility is paramount in most, if not all, applications. For example, reinforcements in plastics, elastomers and coatings must be well dispersed because poor dispersion leads to inferior impact resistance, elongation to break and gloss. Likewise, good dispersion leads to lower viscosity enabling easier processing and higher filler loadings to be attained.

Halloysite is well known to be easily dispersible. This explains why it has proven effective in so many systems without the needs for surface treatment in the form of dispersants or coupling agents. Surprisingly, halloysite disperses well in all kinds of media from very low polarity polymers like FKM fluoroelastomer, through the low polarity PE and PP, high polarity nylon 6 and even in water, an extremely polar liquid (Figure 9). The reason halloysite can be easily dispersed can be traced to its surface chemistry. As the outside of the tube is silica-like any surface groups would be expected to take the form of silanols (Si-OH). As mentioned in the chemistry section, no silanols have been detected so their concentration must be low. This absence of surface functional groups explains why halloysite tubes do not agglomerate.

This can be confirmed by comparing halloysite to Imogolite. Imogolite has the same chemistry as halloysite but the sheets are rolled the other way around leaving an alumina-like outer surface covered with Al-OH groups and a silica-like tube interior. Imogolite is notoriously difficult to disperse. In fact, a recent review stated that surface treatment is needed and even then, the tubes remain as tight bundles⁸⁴. Other major obstacles prevent Imogolite from being commercially attractive including lack of a pure deposit of material and the need for major beneficiation to remove chemical impurities and color⁸⁴.

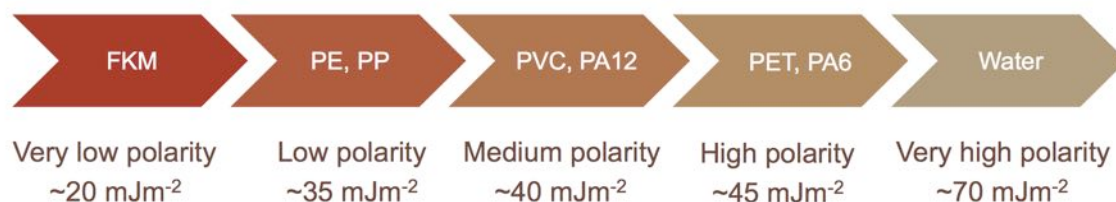


Figure 9 Halloysite disperses regardless of the polarity of the medium

As mentioned, it is possible to disperse halloysite without the use of dispersants or coupling agents but these additives may be used if so desired. Effective chemistries include organosilanes⁸⁵⁻⁸⁸, cationic surfactants⁸⁹, ionic liquids^{90,91}, cyanate esters⁹², bismaleimides⁹³, carboxylic acids^{94,95} and maleic anhydride derivatives⁹⁶. In one paper Complex of resorcinol and hexamethylenetetramine were used to disperse and improve adhesion⁹⁷. The authors showed hydrogen bonding between the resorcinol / hexamethylenetetramine resin and the halloysite surface.

Safety

Halloysite has been used since the 11th century to make porcelain⁹⁸ and more recently, over several decades, as a petroleum cracking catalyst¹. It is a component of natural soil⁹⁹ and, in some parts of the World, it is traditional to eat halloysite¹⁰⁰.

Halloysite is GRAS (generally recognized as safe)^{101,102,103}.

Furthermore, as a naturally occurring mineral, halloysite is REACH exempt¹⁰⁴.

Halloysite is considered safe to use in plastics food contact applications¹⁰³ even at very high loadings. This includes commercial surface treated versions.

Furthermore, halloysite received an extremely favorable rating of 3(DG)¹⁰⁵ as compared to other common plastics additives according to the EPA GreenScreenTM.

There has been specific testing on halloysite and it has proven non-toxic by inhalation¹⁰⁶ and cytocompatible¹⁰⁷⁻¹¹². Although fibrous in shape, halloysite is not asbestiform because the fibers are too short to be of concern¹¹³⁻¹¹⁵. Wagner, a leading authority, performed testing on 40 Fischer 344 rats and found zero mesotheliomas¹¹⁶.

Acute inhalation toxicity in rats was also tested (LC50 > 200 mg/liter) with zero fatalities. The conclusion was that:

“According to Federal Hazardous Substances Act Regulations (16 CFR 1500.3), and under the conditions of this test, the test article is not toxic to rats by inhalation.”

Because the safety is so well established, the focus has now moved to therapeutic uses of halloysite. Examples include drug delivery¹¹⁷⁻¹¹⁹, to heal gastric ulcers¹²⁰, for wound healing¹²¹, as an anti-inflammatory¹²² where “halloysite presented anti inflammatory properties comparable to Indomethacin” and also to combat cancer^{123,124}. It has also been shown beneficial in animal feed for laying hens^{125,126} and pigs¹²⁷ or as a preservative for animal feed where it inhibits growth of bacteria and fungi while decreasing mycotoxins¹²⁸. Halloysite is a proven antibacterial agent with broad applicability^{129,130}.

Analysis of trace elements in halloysite confirms very low concentrations (Table 2).

Element	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Mo	Ni	Pb	Se	Sr	Zn
Level (ppm)	3.6	<0.02	<0.05	0.85	<0.15	980	<0.3	5.5	<0.1	54	<0.01	0.72	20	25.0

Table 2 Trace elements by ICP-MS (average of multiple samples)

Quality

Various mines contains halloysite with very high purity, opening up a wide range of new applications.

Halloysite Typical purity: 90-100% (depending on source)

Availability

Commercial adoption of a material depends on demonstrable performance but also on availability. A sufficient supply of high quality material is essential. Various commercial mines around the world offer halloysite in commercial quantities.

To put this in perspective, the production capacity of halloysite tons exceeds the Global production capacity for carbon nanotubes, fullerenes, graphenes, carbon nanofibers and nanodiamonds combined¹³¹.

Property Overview and Corresponding Applications

Having now looked at the properties of halloysite, it is possible to see how the intrinsic properties indicate commercially relevant benefits.

High aspect ratio

Reinforcement of plastics, elastomers, coatings and more

High surface area

Catalysts, adsorbents, carrier for actives, elastomers, immobilization (e.g. proteins, enzymes), nucleation of crystal growth and foam cell nucleation, remediation of heavy metals

Hollow

Controlled release, thermal insulation, light-weighting, wicking, membranes, oil-spill remediation

Bound water

Fire retardance, temperature indicator, foaming agent

Many of these predicted effects have already been proven and published. A literature search (2011) reveals over 2000 articles and over 400 patents related to halloysite. This document will cover some of the most commercially significant applications.

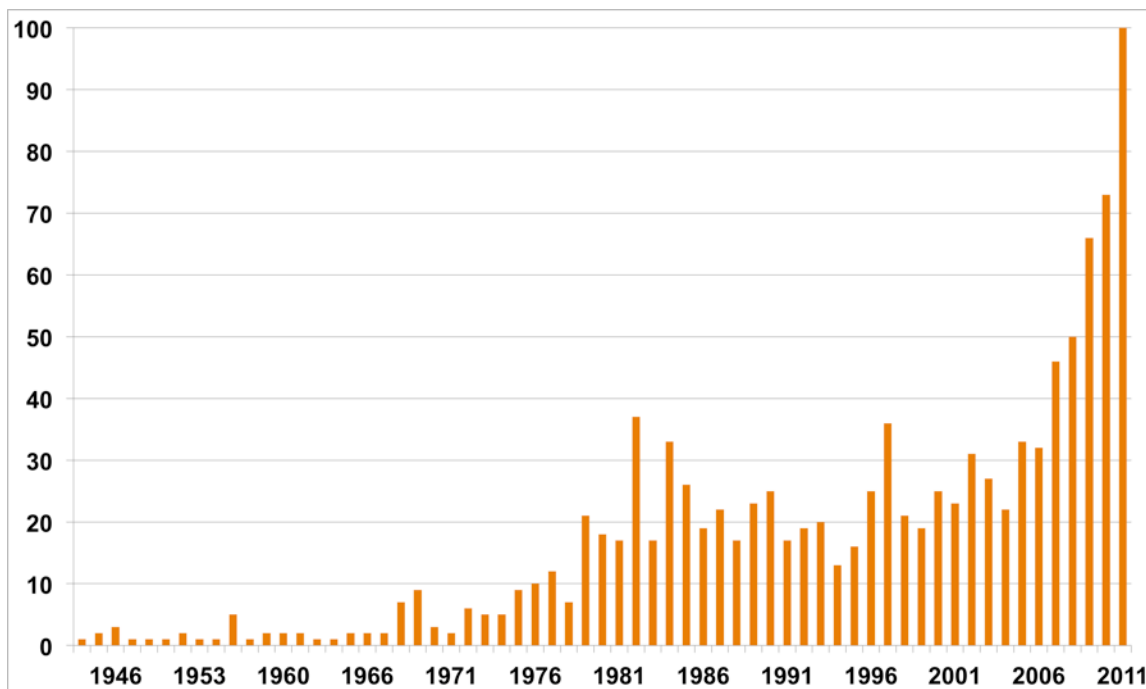


Figure 10 Publications on halloysite per year (source: Science Direct)

Halloysite as a Reinforcement

The use of minerals in polymeric materials is very widespread because they expand the range of properties attainable to meet end-use requirements. Each type of functional filler provides its own set of benefits and drawbacks¹³²⁻¹³⁵.

Isotropic fillers, being round or cubic in shape, have a low aspect ratio of approximately one. Such fillers include calcium carbonate, silica, glass beads, dolomite and barium sulfate. These fillers boost modulus moderately and are least detrimental to impact resistance but there is a penalty in terms of lost strength^{132,135}.

Anisotropic fillers such as mica, high aspect ratio talc and wollastonite are known to be effective reinforcements. That is, they improve both modulus and strength. The problem is that they also lead to a large loss in impact resistance (Figure 11). The reason being that the long dimension is too long. Upon impact, they act as stress concentrators, cracks form and grow leading to the poor impact resistance and low elongation to break.

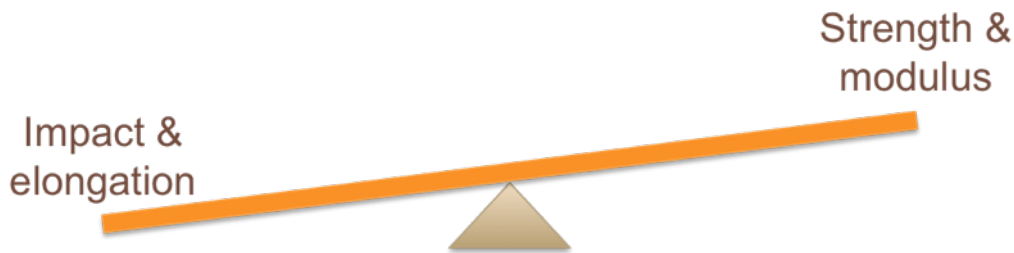


Figure 11 With other fillers there is a trade-off between reinforcement and ductility

From this, one can see that the ideal reinforcement would have a high aspect ratio but be easily dispersible and with the longest dimension too small to act as a stress concentrator. It was hoped that platy nanoclays would provide the answer but as the past 20 years of research have shown, they are notoriously hard to disperse and exfoliate requiring both chemical modification and high shear¹³⁶.

Halloysite gives just the right combination of aspect ratio, surface area and dispersibility. Because the longest dimension is in the 1-2 micron range, the particles are too small to act as stress concentrators. That means that impact resistance is retained or even improved. Elongation to break is also maintained at a high level or in some cases improved compared to the unfilled material. This has been shown multiple times in peer-reviewed articles and in thermoplastics, thermosets and elastomers. Recently, halloysite was even shown to reinforce metal. The microhardness of EN AW6061 aluminium increased by 27% and the yield stress increased by 67% when 15 weight percent halloysite was added¹³⁷.

Some specific property advantages are:

- Increased modulus
- Improved strength
- Retained or improved impact resistance
- Retention or increase in elongation to break
- Increased HDT
- Reduced CTE

Polyethylene

Halloysite has been compounded into LLDPE¹³⁸. As explained above, due to its shape and surface area effective reinforcement can be expected. Incorporation at loadings up to 60 weight percent was possible and significant improvements in strength and stiffness (Table 3). Impact resistance was not maintained in this case, indicating improper processing and poor dispersion. At higher loadings a halogen-free flame retardant effect was observed as well. Mechanical properties were further improved using a maleated LLDPE graft copolymer as compatibilizer. Much better impact resistance can be attained if proper measures are taken to disperse the halloysite as demonstrated in later examples with other polymers.

Property	LLDPE	10% Halloysite	20% Halloysite	30% Halloysite	40% Halloysite	60% Halloysite
Flexural Modulus (MPa)	180	327	453	570	635	1378
Flexural Strength (MPa)	8.2	12.7	14.9	16.8	19.1	23.0
Impact Resistance (KJm⁻²)	50	37.5	22.1	14.4	10.6	5.4
PHRR (KWm⁻²)	920	---	---	---	480	---

Table 3 Unmodified halloysite in LLDPE

Due to its excellent dispersibility, halloysite has been used to make blown film and PE monofilament fiber. Transparent, colorless films of 25 weight percent halloysite in LDPE were made by compounding without the need for dispersants. The high transparency is due to excellent dispersion combined with the refractive index match between halloysite and the polymer.



Figure 12 Transparent films of 25% (left) and 5 weight % (right) Halloysite in LDPE

The halloysite also provided a flame retardant effect as shown by the substantial reduction in the Peak Heat Release Rate (PHRR). Use of halloysite as a reinforcing, halogen free flame retardant has been reported in several other plastics and elastomers as shown later.

Work, particularly in HDPE demonstrated other advantages such as reduction in CTE, alleviation of sink marks and substantial reduction in cycle time for injection molded parts. This latter effect is related to nucleation of crystallization of HDPE and will be covered separately.

Polypropylene

Polypropylene is widely used because of its attractive performance to cost proposition which is further tuned and improved through the use of mineral fillers. Typical fillers include calcium carbonate, talc, wollastonite and mica. Each giving a different property set with pros and cons. Halloysite is unique in that it brings the advantages of the reinforcing fillers in terms of improved modulus and strength while allowing retention or even enhancement of impact properties. Traditionally, one has had to accept poor impact resistance when using reinforcing particulate fillers.

At low loadings one finds a significant boost in modulus and strength. Impact resistance is retained all the way to high loadings¹³⁹. Elongation to break is also retained at a high level. Strength was further improved by surface treatment of the halloysite with a methacrylate-functional alkoxysilane although with some sacrifice of impact resistance. Benzothiazole sulfide grafted PP was an effective coupling agent improving both dispersion and strength¹⁴⁰. Another paper reported mediocre results¹⁴¹ due to the very impure halloysite used. This emphasizes the importance of using good quality material.

Halloysite has also been shown to nucleated crystallization of polypropylene¹⁴²⁻¹⁴⁴. That gives rise to reduced cycle times in injection molding for example because the polymer solidifies at a higher temperature so it is possible to eject parts earlier. It is interesting to note that the use of talc in polypropylene became so widespread because that filler reinforces and nucleates PP. As halloysite has been shown to have those advantages and more, it could be anticipated that it will now emerge as the functional filler of choice.

As seen for LLDPE and other polymers, at higher loadings halloysite acts as an effective flame retardant¹⁴⁵. Peak heat release rate was dramatically lowered and time to ignition was extended as well. The workers concluded by remarking "It is proved that HNTs is a new kind inexpensive, easily processed and effective additive for improving the thermal stability and flame retardant of PP." They proposed that the lumen is able to trap volatile products created by combustion of the polymer.

	Control	1	2	3	4	5
Dragonite XR	0	0	20	30	40	60
Magnesium Hydroxide (ST)	0	60	40	30	20	0
PP 20 MFI	100	40	40	40	40	40
Flexural Modulus tangent (kpsi)	207	432	467	464	521	557
Flexural Modulus 1% (kpsi)	212	373	391	392	440	461
Flexural Strength (psi)	6517	5131	5350	5347	5666	6200
Tensile Modulus (kpsi)	150	277	275	285	300	294
Tensile Strength (psi)	5180	3242	3182	3189	3650	3818
Notched Izod Impact ft-lb/in	0.44	0.54	0.54	0.5	0.45	0.43
Smoke		low	low	very low	very low	low
UL 94 Rating		V2	V1	V1	V1	V1

Table 4 Halloysite as a reinforcing, halogen-free FR for PP

Following the good results reported in the literature, here is some work to compare halloysite to MDH, the established mineral fire-retardant for PP. Despite the fact that these were the very first experiments and no optimization was done, they show that compared to a commercial MDH, halloysite offers better mechanical results and FR performance either in combination with MDH or used alone.

Polyamides

The polyamides are a versatile family of materials used in structural parts, films and fibers. The properties can be tuned by addition of fillers, for example to alter mechanical properties or impart lubricity. Typical reinforcements include talc, kaolin, mica, wollastonite and glass

fiber used at loadings in the range 10-50% by weight. Not surprisingly, there has been interest in using halloysite as a reinforcement.

There are some publications pertaining to nylon 6^{88,146-148} nylon 11¹⁴⁹ and nylon 12¹⁵⁰. In nylon 6, it has been shown that halloysite is a very effective reinforcement. As with PE and PP, modulus, strength and HDT are raised considerably while retaining impact resistance (Table 5). In addition to mechanical properties, workers have noted the excellent processability, dispersibility as well as fire retardance. The fire retardancy aspects will be highlighted in a separate section. These properties were all achieved using standard compounding on a twin-screw extruder. It is reasonable to expect even better performance for the situation where halloysite is incorporated in the polymerization step because that is conducive to optimal dispersion, wetting and adhesion.

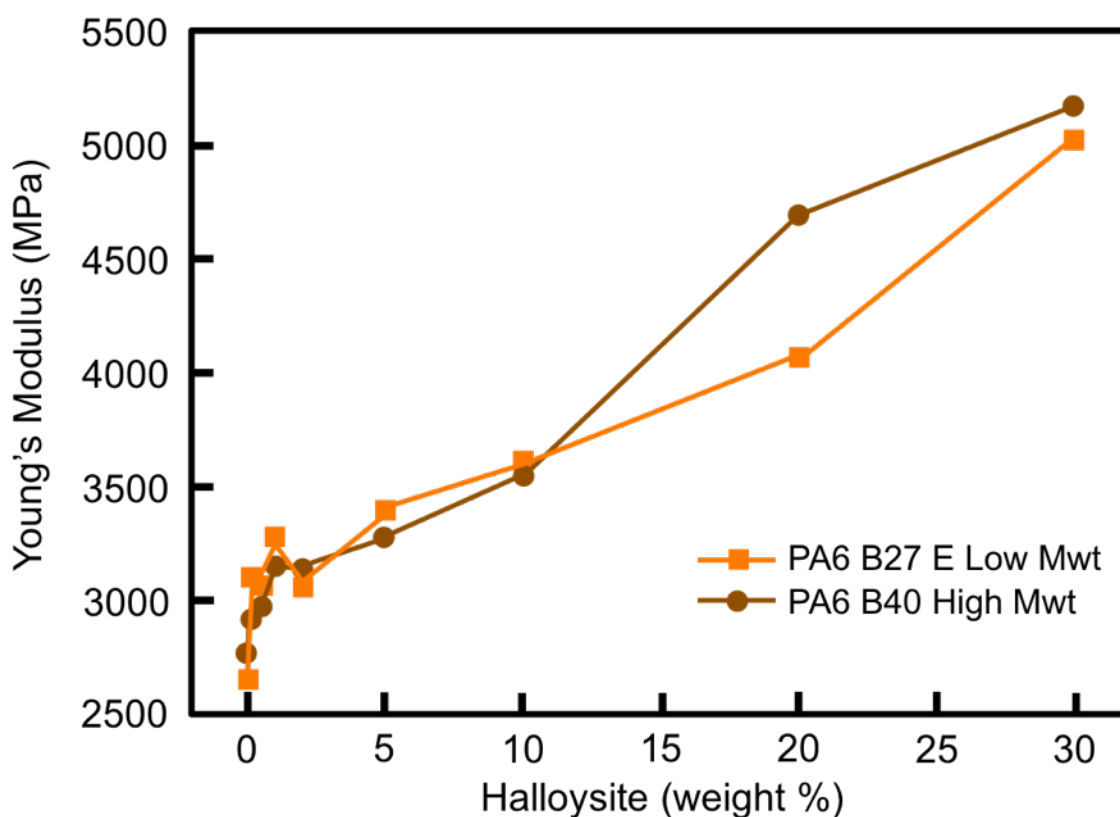


Figure 13 Halloysite gives remarkable stiffness at very low loading¹⁴⁷

The reinforcement at low loadings is very attractive because it means one can obtain a very high performance : weight ratio useful for automotive and other applications where density matters. Strength is also elevated by just 1 weight % halloysite so there is true reinforcement. An increase in the onset temperature of crystallization^{147,149,151} implies that injection molding cycle times can be reduced as well. This improved productivity translates directly to cost saving and greener production. Some of the mechanical enhancement may be related to the change of crystal habit brought about by halloysite. Specifically, halloysite induces the γ form over the more usual α type¹⁴⁷.

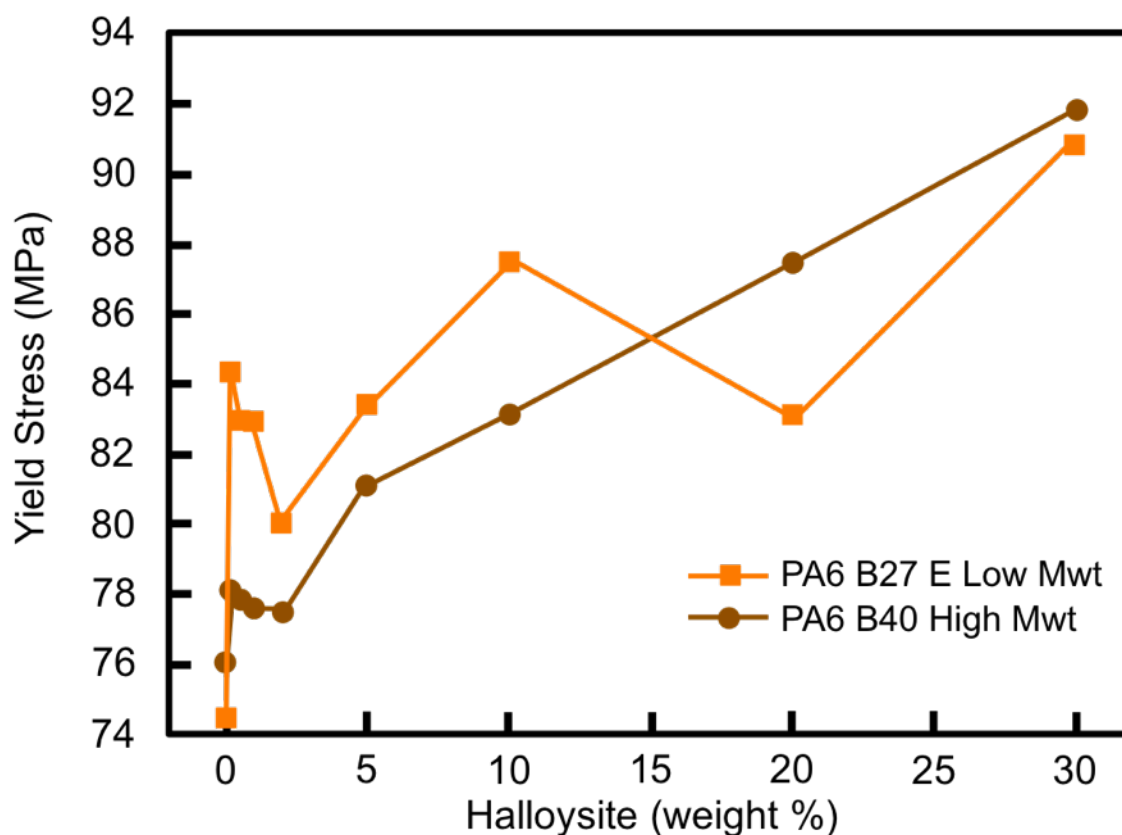


Figure 14 Tensile strength is dramatically improved at just 1 weight percent Halloysite¹⁴⁷

Some recent work showed halloysite increased modulus, strength and notched impact resistance of nylon 6 while retaining elongation to break. These workers also noted nucleation and an increase in the degree of crystallinity¹⁵¹.

“Interestingly, the tensile modulus, yield stress and notched impact strength of polyamide 6 also significantly increase without any loss of elongation at break.”¹⁵¹

Significant nucleation of crystal growth was also noted both for nylon 11 and nylon 12 as well as reinforcement and improved thermal stability (by TGA)^{149,150} as shown later.

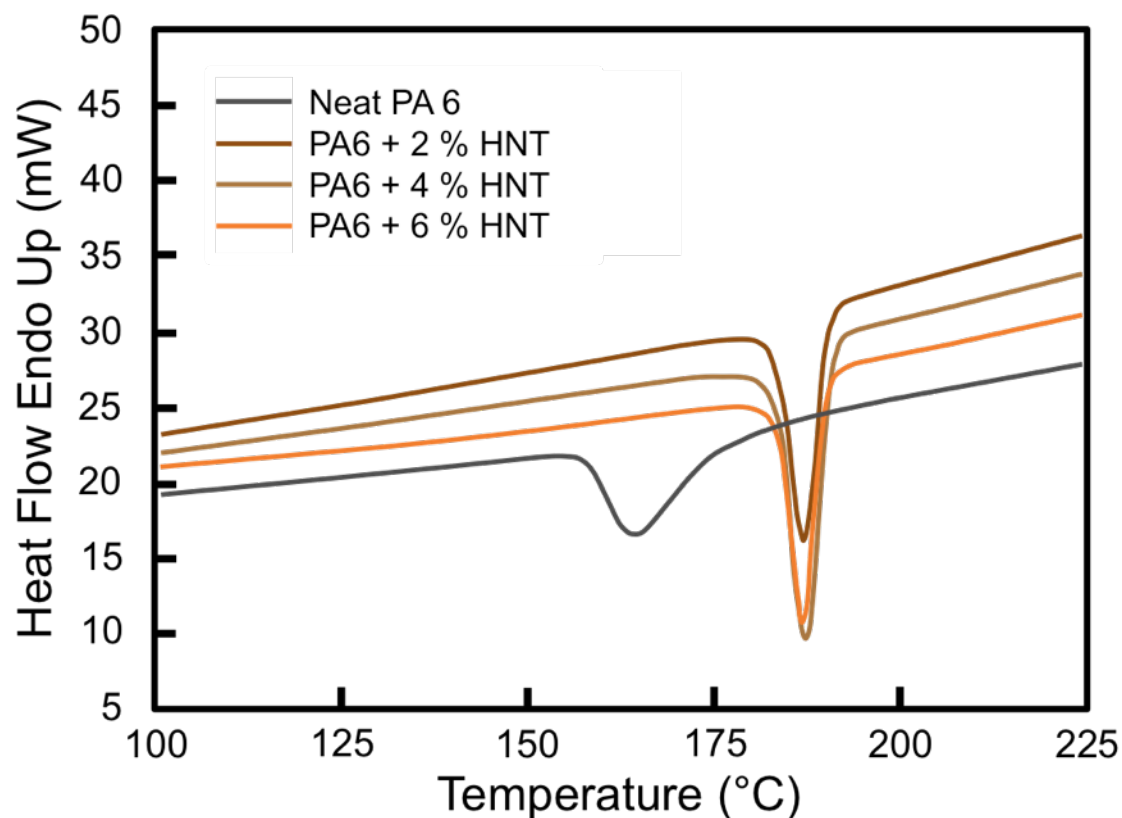


Figure 15 Halloysite increases crystallization onset temperature¹⁵¹

Further work has verified the reinforcement as well as excellent retention of impact resistance even at higher loadings (Table 5). This is another example of halloysite's unique ability to reinforce without the embrittlement suffered when using traditional reinforcing fillers.

Property	PA6	4% Dragonite	8% Dragonite	14% Dragonite	19% Dragonite	27% Dragonite
Flexural Modulus (Kpsi)	398	521	539	671	700	891
Flexural Strength (psi)	14785	18428	18351	20272	21041	21817
Notched Izod Impact (ft-lb/inch)	1.2	0.94	0.90	0.95	0.94	0.93
Density (gcm ⁻³)	1.13	1.16	1.186	1.226	1.262	1.317

Table 5 Halloysite reinforcement with excellent retention of impact resistance

The above was focused on PA6, one of the most commonly used nylon types. Excellent performance has been found in PA11¹⁴⁹ as well (Table 6).

Property	Neat PA11	PA11 +2% Halloysite	PA11 +4% Halloysite	PA11 +6% Halloysite
Modulus (MPa)	1220	1616	1781	1915
Yield Strength (MPa)	43.7	48.8	52.5	54.2
Elongation to break (%)	254	251	245	235

Table 6 Halloysite as a reinforcement in PA11 showing an excellent property balance

Once again we see that halloysite is able to do what other reinforcing fillers cannot. Modulus and strength are elevated as one would expect but uniquely, the elongation to break (ductility) is retained. This is possible because the particles are so small and well dispersed that they do not act as stress concentration sites (flaws).

The authors noted that all other significant properties were also boosted.

“Interestingly, good halloysite dispersion in PA-11 matrix increases the tensile strength and Young modulus of PA-11 without sacrificing the ductility. Highly dispersed nanotubes also bring favorable changes in the thermal stability, dielectric, and rheological characteristics of PA-11. Additionally, glass transition temperature, crystallization temperature, and degree of crystallinity of the nanocomposites tend to increase with increase in nanotubes loading.”¹⁴⁹

The property set was also shown to be superior to other specialty fillers including organoclay and MWCNT.

In PA12 the picture was very similar¹⁵⁰. Once proper dispersion was attained very good properties were noted. It was found that a batch mixer did not provide good dispersion whereas a twin screw separated the particles with correspondingly better mechanical performance plus higher thermal stability and crystal nucleation.

“Higher enhancements were observed for PA12/HNTs nanocomposites obtained by twin-screw mini-compounding. This finding was related to the better degree of dispersion and alignment of the silicate nanotubes throughout the matrix.”¹⁵⁰

PVC

Polyvinyl chloride is one of the highest volume plastics worldwide because it combines good mechanicals, good chemical resistance, weatherability and low cost. Typical uses include pipes, gutters, electrical insulation and siding. Halloysite improves not only strength and modulus but also elongation to break and unnotched impact resistance (Table 7). The latter two are a testament to the excellent dispersibility of the mineral because any agglomerates would have been very detrimental to those latter two properties. The same observations have been published by other workers^{152,153} who confirmed excellent dispersion in PVC by TEM.

Property	PVC	1% Dragonite	2% Dragonite	3% Dragonite
Modulus (kpsi)	459	490	488	521
Yield Strength (psi)	13084	13771	13834	14010
Elongation to break (%)	6	10	9	8
Notched Izod (ft-lb/in)	0.9	0.9	0.9	0.8
Unnotched Izod (ft-lb/in)	7.3	7.2	10.2	12.5

Table 7 Halloysite reinforcement of rigid PVC

“The notched impact, tensile and flexural strength, and flexural modulus of the nanocomposites were remarkably increased compared with those for the pure PVC.”¹⁵³

“The heat distortion temperature (HDT) and Vicat softening temperature (VST) of nanocomposites increased with increasing HNTs feed content.”¹⁵⁴

As well as excellent mechanical reinforcement, halloysite also improves the flame retardancy and smoke behavior of PVC as described in a later section¹⁵⁴.

Green Polymers

Halloysite has been incorporated into PLA¹⁵⁵⁻¹⁵⁹ giving large improvements in strength and modulus with retained impact resistance. A nucleation effect was shown leading to a substantial improvement in gas barrier performance¹⁵⁹. It is appealing to use a natural and safe additive like halloysite to tune the property profile of PLA and starch-based¹⁶⁰ materials.

"The mechanical parameters of PLA-based nanocomposites with the addition of kaolinite nanotubes were significantly better than those of pure PLA. For a nanocomposite with 1% wt. addition an increase of tensile strength from 29 MPa (pure PLA) to 43 MPa was noticed. The Young's modulus was three times higher and equal to 2.25 GPa." ¹⁵⁵

"Permeability tests were run on pure PLA and PLA reinforced with 1 and 3% -wt of HNTs. Addition of 1% HNTs on PLA matrix lead to a decrease both in oxygen and carbon dioxide permeability respectively up to 34 and 45% as a consequence of increased tortuosity induced by the presence of the clays." ¹⁵⁸

As well as simply compounding halloysite into PLA, the halloysite can be used as a polymerization catalyst to synthesize PLA¹⁶¹ and also reinforce the polymer. Colorless, transparent films of PLA can be made at halloysite loadings as high as 30 weight percent.

Another thermoplastic of interest is poly(ϵ -caprolactone). Halloysite has been found very effective in that polymer as well¹⁶².

"Tensile and dynamic mechanical tests showed great enhancement in strength and stiffness at low HNT content, while still maintaining the ductility of the PCL. The glass transition temperature (T_g) of the pristine PCL was substantially increased with increase in filler loading, which indicates good reinforcing effect imparted by the addition of HNT"

The authors also noted an increase in the onset temperature for crystallization plus an improvement in elongation to break. Once again, halloysite improves ductility whereas common reinforcements are deleterious in that regard.

Other Thermoplastics

By now it should be apparent that because of its aspect ratio and surface area, halloysite is effective in all thermoplastics spanning the polarity scale from polyolefins to nylons. This means that even for polymers as yet untested, one can expect equally promising results. For example, halloysite has shown promising results even in styrenic plastics¹⁶³⁻¹⁶⁵ which are renowned as being unsuitable in combination with fillers.

Epoxy Resins

Epoxy resins are a major class of thermosetting materials used as adhesives, in coatings and as the matrix for glass and carbon fiber composites. Such composites are used in sporting equipment, high performance automotive parts and increasingly in aerospace applications. Materials originally used only by the military now dominate civilian aircraft such as the Boeing 787 Dreamliner which is predominantly carbon fiber epoxy composite using ~35 short tons per aircraft.

In such materials the carbon fiber lends modulus and strength and the areas for improvement are impact resistance and fatigue resistance, both of which involve crack growth. Particulate rubber can be used to improve impact resistance but there is a sacrifice in both modulus and strength. Halloysite has emerged as an attractive solution because it increases the impact resistance of epoxies while reinforcing at the same time^{72,166,167}. The energy to form and grow a crack was also increased making the material more resistant to brittle failure (Table 8).

Property	Neat Epoxy	5% Dragonite	10% Dragonite
Flexural Modulus (GPa)	3.05	3.39 (+11%)	3.59 (+18%)
Flexural Strength (MPa)	111	116 (+5.5%)	120 (+8.1%)
K_{1C} (MPa.m ^{1/2})	0.90	1.26 (+40%)	1.35 (+50%)
G_{1C} (MPa.m ^{1/2})	228	456 (+100%)	517 (+127%)

K_{1C} – Critical stress intensity factor (energy needed to initiate a crack)

G_{1C} – Critical strain energy release rate (energy needed to grow a crack)

Table 8 Increased impact resistance combined with reinforcement

Even more impressive than those results are those of other workers who showed that addition of just 2.3 weight% halloysite increased the impact resistance by an astounding 400% while retaining other mechanical properties¹⁶⁶. The exceptional impact resistance was ascribed to micro-cracking ahead of the main crack accompanied by crack bridging by halloysite. The energy required to pull out and / or break the halloysite being responsible for the impact resistance increase. Interestingly, a different research team has shown that 2 weight % halloysite improved the wear resistance of epoxy by 80 percent¹⁶⁸. In other work it was found that just 3 weight percent halloysite improved the vibrational damping of glass fiber filled epoxy resin by over 20 percent⁸⁶. A study using surface modified halloysite revealed a 6 fold increase in impact resistance at just 3 weight percent loading and while simultaneously boosting but strength and modulus¹⁶⁹.

This combination of mechanical properties and wear resistance at just 2 weight percent halloysite is especially relevant to aerospace and automotive applications where weight is important. Adding 2 percent halloysite dramatically improves the material while leaving the density virtually unaffected.

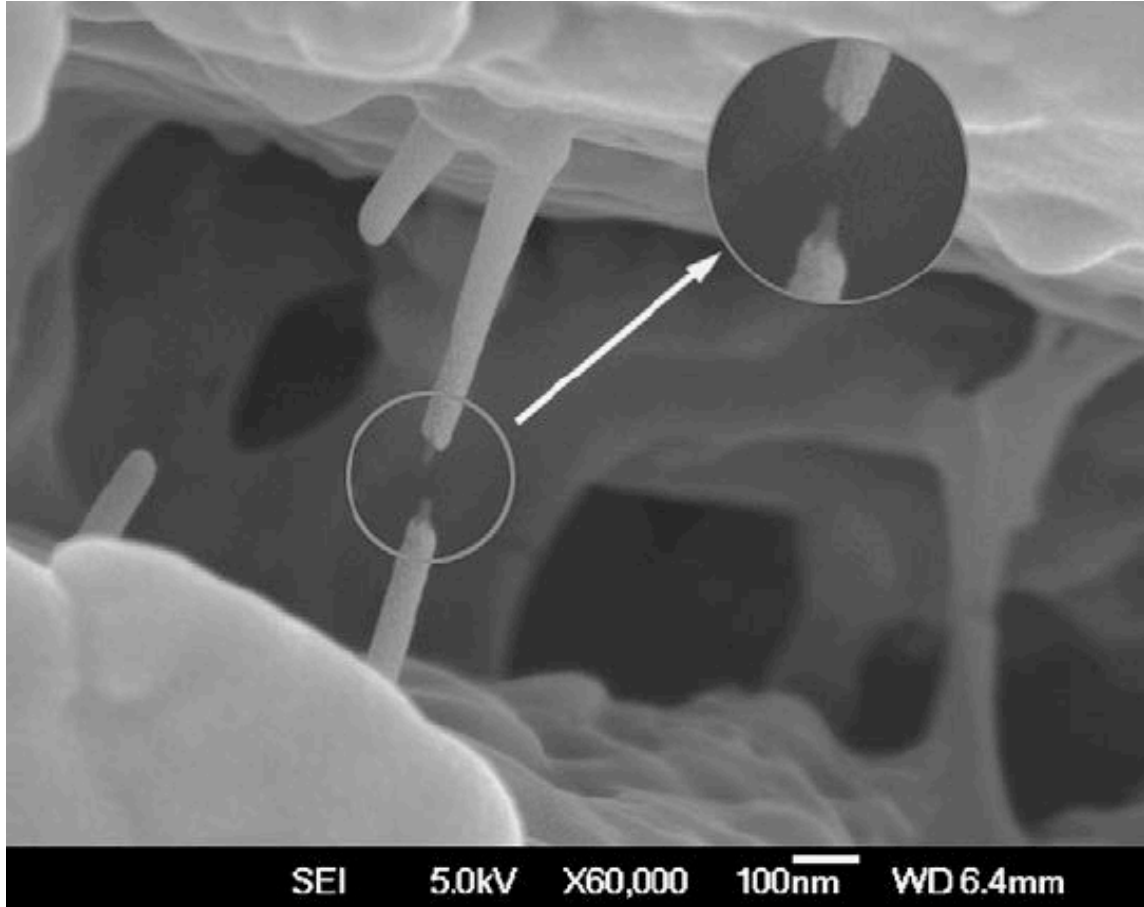


Figure 16 Fiber pull-out and cleavage showing excellent wetting matrix adhesion¹⁶⁶

Combinations of halloysite and carbon fiber in epoxy have proven synergistic. The weakness of carbon fiber reinforced epoxy is the interface between layers of prepreg because that region is deficient in carbon fiber and therefore not reinforced. By adding 1-5 percent halloysite increased interlaminar shear strength (ILSS) by up to 25 percent. This is similar to the performance of carbon nanotubes¹⁷⁰ but halloysite is less than one hundredth the price.

Although already effective at very low loadings, it should be noted that modulus, strength and CTE all continue to improve as the halloysite concentration is increased (Table 9).

Property	Neat Epoxy	4% Dragonite	8% Dragonite	12% Dragonite
Flexural Modulus (GPa)	3.26	3.65 (+12%)	3.85 (+18%)	3.98 (+22%)
Flexural Strength (MPa)	47	100 (+113%)	107 (+128%)	91 (+94%)
CTE (ppm/°C) 25-100°C	51.26	48.75 (-4.9%)	48.13 (-6.1%)	46.34 (-9.6%)
CTE (ppm/°C) 100-160°C	77.26	69.42 (-10.1%)	70.14 (-9.2%)	66.98 (-13%)

Table 9 Properties increase further at higher halloysite loadings⁷²

Similarly, in glass fiber reinforced epoxy major improvements in mechanical properties and wear performance have been reported.

“Addition of 2 wt% of HNT found 28% improvement of impact strength, 12% improvement in tensile strength, 4.2% improvement in hardness and 490% improvement in wear rate.”¹⁷¹

Workers looking to optimize the energy dissipation of carbon fiber epoxy composites studied several fillers and mixtures thereof. Their conclusion was that a mixture of halloysite and exfoliated graphite gave the best balance of properties.

Elastomers / rubbers

Fillers are used extensively in elastomeric systems where they enhance processability and reinforce the material. In fact, particulate additives are used in the vast majority of elastomer compounds creating a multi-billion dollar industry.

The requirements for an effective reinforcement for elastomers are very similar to the requirements in thermoplastics and thermosets. Specifically, high aspect ratio and surface area are preferred. Silica and carbon black are widely used due to their high surface area but they do not have high aspect ratio and are notoriously difficult to disperse. Halloysite then, having high surface area, large aspect ratio and being easy to disperse is expected to be a very attractive additive for elastomers.

Literature reports show that halloysite is indeed very effective in elastomers. To date work has been done in natural rubber¹⁷², EPDM^{96,173-175}, SBR^{90,91,94,95,97,176,177}, NBR¹⁷⁸ and FKM fluoroelastomer¹⁷⁹.

In every instance, strength and modulus were increased with retention of elongation to break. In some cases the elongation to break was actually improved. This latter effect is rare and highly sought after. The small, easy to disperse particles give a homogeneous material that does not contain imperfections and that is why elongation to break is retained or even improved. Thermal stability can be enhanced as well. In the case of FKM a 25°C increase in thermal stability was noted¹⁷⁹. In EPDM low loadings of halloysite increased thermal stability as measured by TGA.

Material	100% Modulus (MPa)	(E' ₀ -E' _∞) Modulus (MPa)	Tensile Strength (MPa)	Elongation to Break (%)
FKM gum	2.5	7.45	4.5	197
+5 phr Halloysite	3.0	8.50	6.2	217
+10 phr Halloysite	3.4	13.91	6.8	205
+20 phr Halloysite	3.6	15.48	7.3	200

Table 10 Halloysite reinforcement of FKM fluoroelastomer¹⁷⁹

When used in EPDM at 100phr, a V0 fire-retardant material was obtained in addition to a ~3 fold improvement in modulus and almost 10 times greater strength than the control¹⁷³ (Table 11).

Material	M100 Modulus (MPa)	Tensile Yield Strength (MPa)	Elongation to Break (%)	UL 94 Classification
EPDM Unfilled	1.07	1.32	151	Unclassified
+5 phr Halloysite	1.16	1.94	223	Unclassified
+10 phr Halloysite	1.21	2.21	241	Unclassified
+15 phr Halloysite	1.24	2.85	299	Unclassified
+30 phr Halloysite	1.52	4.19	361	V-2
+50 phr Halloysite	1.85	5.42	400	V-1
+70 phr Halloysite	2.22	8.15	506	V-1
+100 phr Halloysite	2.99	12.86	613	V-0

Table 11 Halloysite in EPDM reinforces, increases elongation to break and provides FR¹⁷³

Halloysite was compared to silica, a common elastomer reinforcement. The halloysite outperformed the silica in every respect showing better modulus, strength and retention of elongation to break. When the halloysite was combined with an organosilane coupling agent the improvements were even more pronounced.

Material	200% Modulus (MPa)	300% Modulus (MPa)	Tensile Strength (MPa)	Elongation to Break (%)
Natural Rubber	0.83	1.12	14	1496
+10 phr Silica	1.03	1.03	12	996
+10 phr Halloysite	1.12	1.54	18	1270
+10 phr Halloysite + silane	1.24	2.18	15	1050

Table 12 Halloysite in natural rubber outperforms traditional reinforcements¹⁷²

In polyacrylamide hydrogels¹⁸⁰ strength, modulus elongation and compressive strength all benefited from the halloysite. Halloysite/poly(sodium acrylate-acrylamide) composites showed good humidity controlling properties¹⁸¹.

Halloysite as a Halogen-Free Fire Retardant

Fire-retardancy is demanded in a wide variety of plastic products. Formerly it was possible to add a low amount of brominated fire retardant to achieve the desired FR rating. In recent years, legislation has banned the use of some brominated fire retardants and it is expected that the remaining ones will follow suit.

The demise of the brominated FR agents has precipitated a drive to other solutions and mineral-based alternatives have come to the fore. Aluminium trihydrate (ATH) and magnesium hydroxide (MDH) dominate the market. Both work by releasing water in the event of a fire where high temperature triggers the release. Because ATH gives off water at around $\sim 220^{\circ}\text{C}$, it cannot be used in polymers processed above that temperature. ATH is therefore used in polyethylene and EVA, predominantly in cable formulations. ATH cannot be used in PP as that is processed above the point where ATH begins to release water. Attempts to use ATH in PP result in foaming where the water vapor forms unwanted bubbles. Therefore MDH is used for PP because that does not liberate water until above $\sim 320^{\circ}\text{C}$. MDH is significantly more expensive than ATH but is used for PP as no alternative exists.

Most engineering polymers such as PET, PA6, PA6,6, PBT, polysulfone and PEEK are processed well above the maximum allowable temperature for ATH or MDH. It is well-known that halloysite gives off water when heated to above 400°C (Figure 7) and it has attracted global interest as a natural, halogen-free fire retardant for PE, PP, engineering thermoplastics like nylons and polyesters and also for elastomers. Excellent fire-retardance has been reported across that range of materials (Table 13) as expected from the properties of the halloysite. As high surface area filler, halloysite promotes char formation and at high temperature releases water vapor to help quench the fire. The reaction is endothermic so it takes energy away from the fire. It has also been speculated that the high surface area, reactive surface of halloysite enables it to trap small molecules created as the polymer degrades¹⁷³, thereby further increasing the thermal stability of the material as a whole. Lastly, work on halloysite in glass fiber reinforced PET revealed a synergy between halloysite and glass fibers. When either reinforcement was used alone, FR testing produced a low integrity char. However, the combination of halloysite and glass produced a strong, contiguous char, which is beneficial for fire retardancy. This synergy between glass fiber and halloysite was recently confirmed in polypropylene and is expected to apply to other systems such as nylon and PBT, which are important commercial materials.

Of the kaolin group minerals, halloysite was found to have the highest enthalpy of dehydroxylation compared to both kaolin and kaolinite and dickite^{182,183}. Halloysite from the Dragon Mine is especially suitable as a fire retardant because it has exceptionally high energy absorption even compared to other halloysite samples¹⁸³.

Plastic Type	Mechanical Enhancement	Cycle Time Reduction	Clear Film	Flame Retardance
PE	✓	✓	✓	✓
PP	✓	✓	✓	✓
EVA	✓	TBD	✓	✓
PA6	✓	TBD	TBD	✓
PA12	✓	✓	TBD	✓
PVC	✓	TBD	✓	✓
PLA	✓	TBD	✓	✓
Epoxy	✓	TBD	TBD	✓
EPDM	✓	TBD	TBD	✓

Table 13 Halloysite is an effective halogen-free flame retardant in many systems

The wide applicability of halloysite as a fire-retardant is a combination of the following effects:

- Released water above 400°C to quench the flame
- Endothermic decomposition removes heat from the fire
- Char formation due to high catalytic surface area
- Synergy with glass fiber further improves char integrity
- The lumen traps volatile combustion products

Halloysite has been successfully compounded into polymers processed at very high temperatures. The TGA of halloysite shows water loss onset at just over 400°C. However, a high pressure DSC study revealed that the decomposition temperature strongly depends upon pressure¹⁸⁴. Extrusion and injection molding are performed at significant pressure such that the water vapor release temperature may be increased from 400°C to 500°C or even more. Other factors such as particle size and degree of structural order influence the water release¹⁸⁵.

Cone calorimetry shows how effective halloysite is in reducing the peak heat release rate (Figure 17). In this instance PP is depicted but the same has been seen for EVA, LLDPE, EPDM and other host matrices. The halloysite functions as a synergist or even as a stand-alone fire retardant where V0 rating can be achieved in most cases.

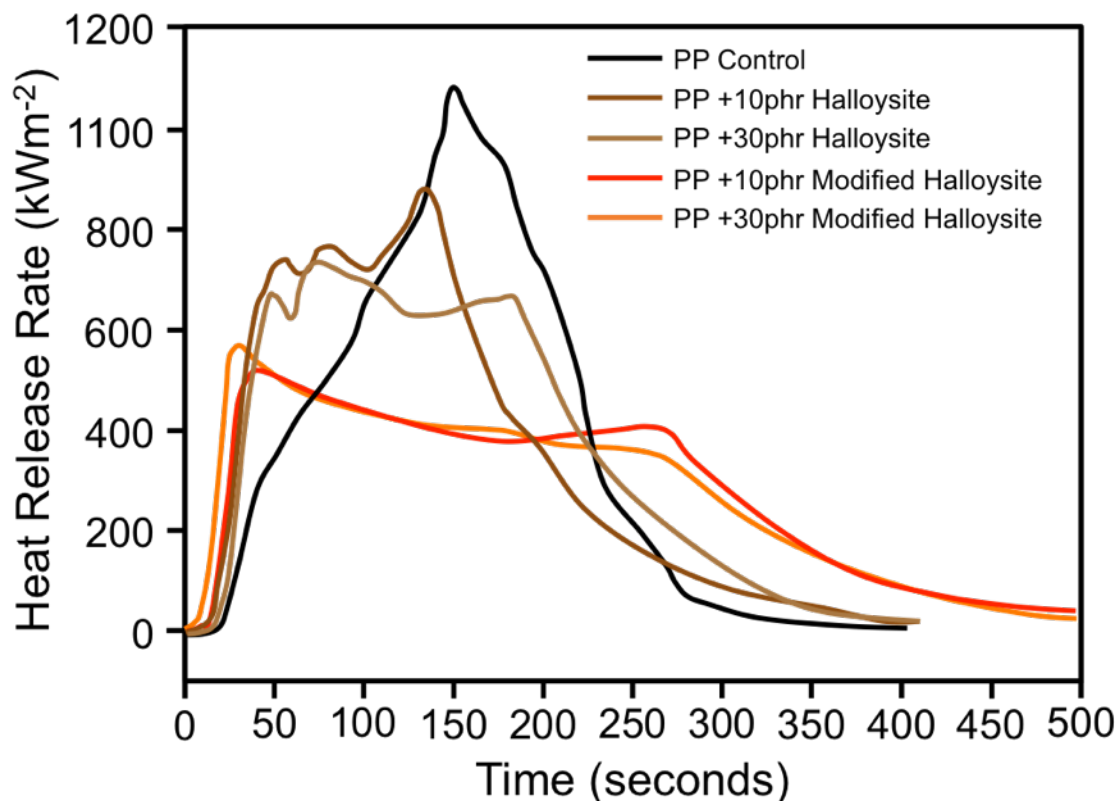


Figure 17 Cone calorimetry for Halloysite in Polypropylene¹⁴⁵

For polymers like polycarbonate that have some degree of intrinsic FR, only a small addition of <5% halloysite can take the rating from V2 to V0 while retaining transparency and good mechanical properties. This was recently patented and commercialized by Samsung Cheil Industries.

The hollow tubes can be loaded with FR synergist. So, for example liquid fire retardants normally plasticize polymers causing strength and modulus to drop. By adding the liquid FR inside the tubes, one can retain the FR effect and reinforce the polymer. This technology has been used to formulate glass-filled PET for high performance plastic pallets. Where RDP, a liquid FR is used with halloysite to give better properties. More information on slow-release and encapsulation using halloysite can be found under a dedicated section.

In an earlier section the excellent reinforcement in PVC was shown. The same can be said for the fire performance.

“The addition of HNTs led to a remarkable reduction in the smoke production rate, the total smoke production and the peak heat release rate.”¹⁵⁴

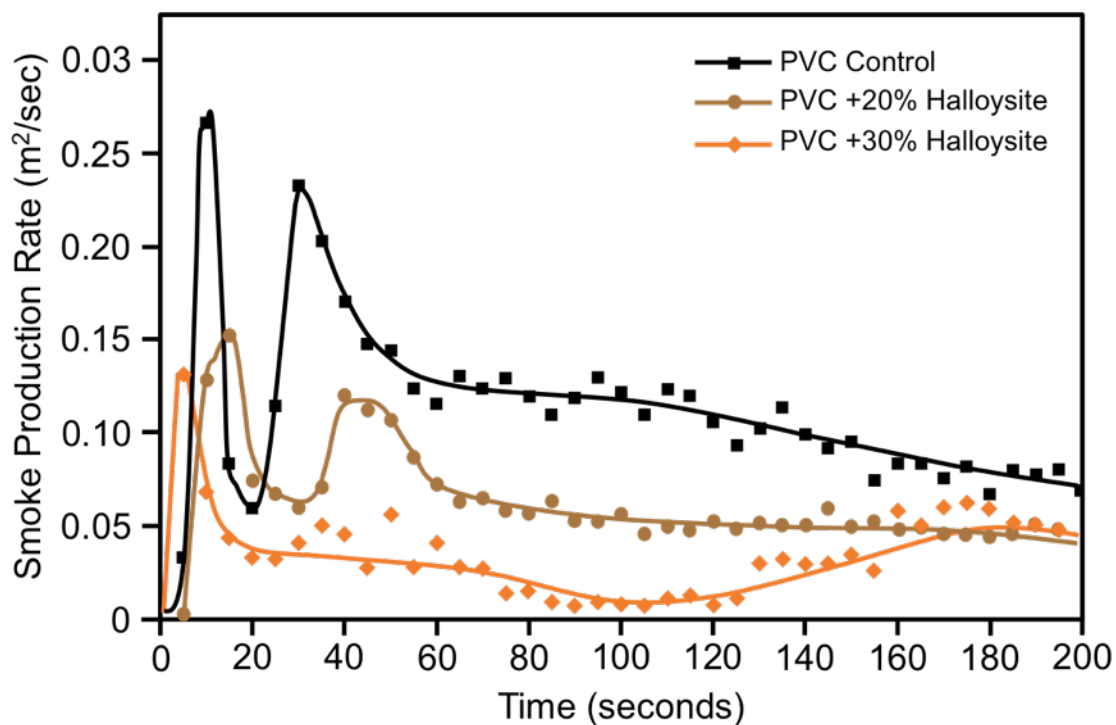


Figure 18 Smoke suppression upon addition of Halloysite to PVC¹⁵⁴

Halloysite forms a strong char and suppresses smoke formation. This led people to investigate the possibility of using halloysite as a partial replacement for antimony trioxide (ATO). ATO works in the gas phase but because halloysite forms a strong char that blocks the gas, substantially less ATO is needed. Reported ATO reductions are in the range 50-75% with halloysite substituting the ATO on a 1:1 basis by weight. Other advantages are in the mechanical properties and much lower cost.

Halloysite for Controlled-Release of Actives

The use of halloysite for the controlled-release of active substances has been demonstrated and patented. Potentially, almost any type of active can be used. Examples include:

- Drugs^{38,186-192}
- Fragrances¹⁹⁴
- Moisturizers¹⁹³
- Antioxidants¹⁹⁴
- UV stabilizers¹⁹⁴
- Corrosion inhibitors¹⁹⁵⁻¹⁹⁹
- Antimicrobials⁷⁷
- Cross-linkers
- Anti-statics
- Lubricants
- Pesticides¹⁹⁴

The list is far from all-inclusive, but gives an idea how broad the applicability is. The US Navy holds patents for the loading of and release from the tubes²⁰⁰. A subsequent patent proposed loading more than one active ingredient in such a way as to provide release of one active and then the other²⁰¹. Other workers showed that end-stoppers (Figure 19) can be applied to control the release rate from the tubes¹⁹⁷. The release effect has been recently reviewed^{202,203}.

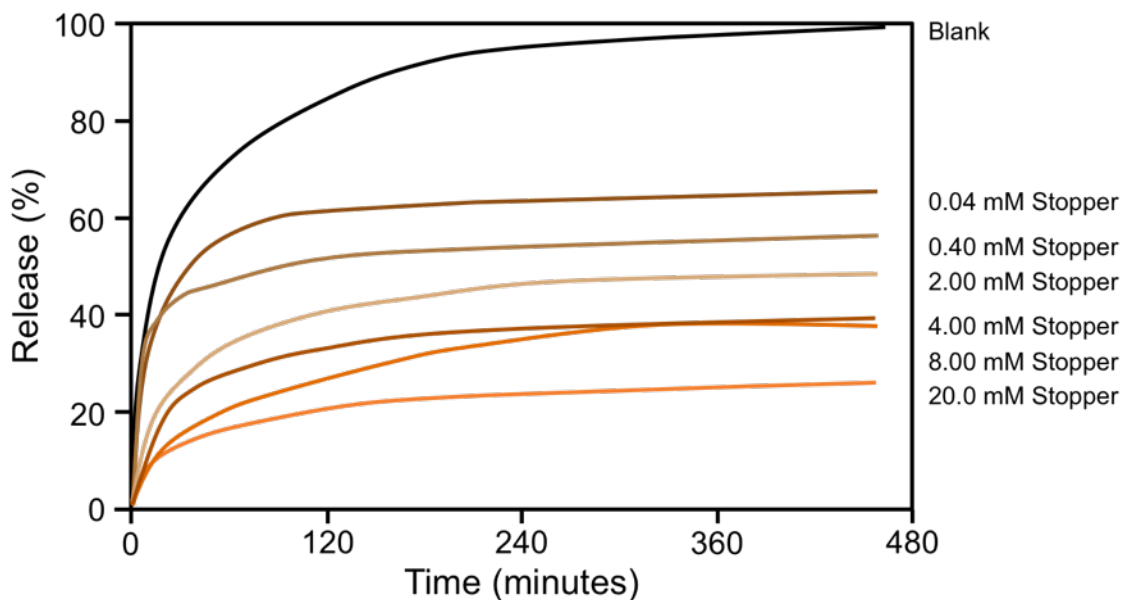


Figure 19 Use of end-stoppers to control release rate of benzotriazole corrosion inhibitor¹⁹⁷

The controlled release effect is applicable to areas including the cosmetics, agrochemicals, polymers, coatings and medical industries.

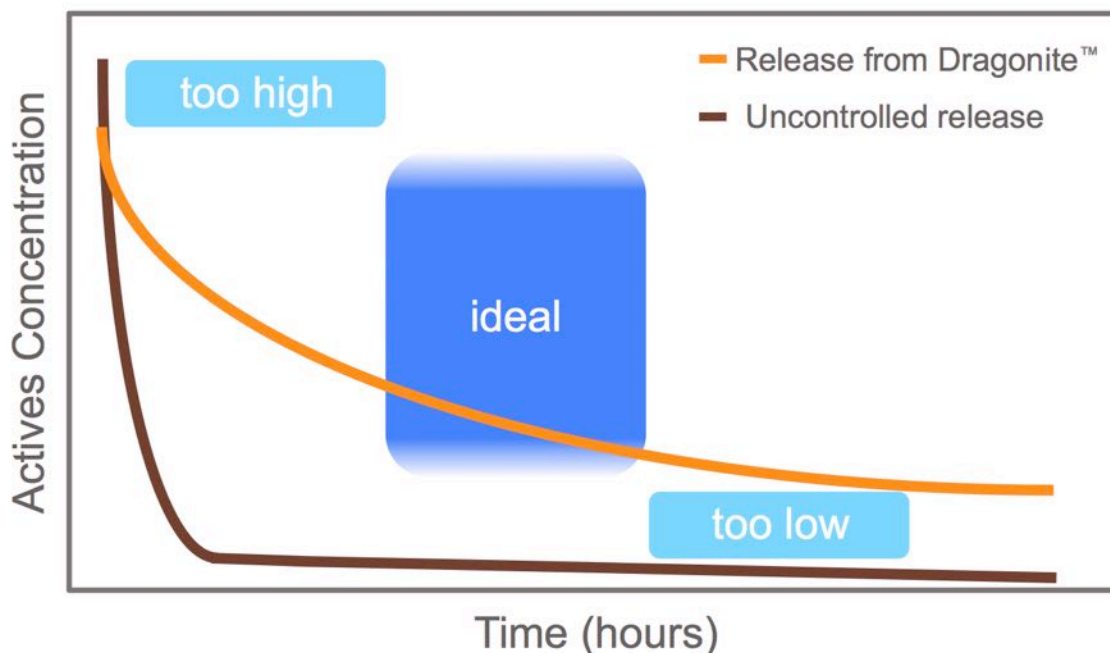


Figure 20 Controlling release rate allows optimal efficacy

Too high of an active concentration is wasteful and may lead to side effects whereas too little active is ineffectual. By controlling the release rate, it is possible to maintain the ideal concentration leading so you can get better results using less active ingredient (Figure 20).

The halloysite tubes are hollow (Figure 21) and the porosity of Dragon Mine Halloysite is particularly high at 20 volume percent²⁰⁵ of the total tube volume. This gives a large capacity for loading active ingredients. The loading procedure is as simple as mixing halloysite and the liquid active and applying a strong vacuum to pull the air from the lumen which then allows the active ingredient to flow inside the tube. Solid actives can also be dosed by melting them, dissolving the active, or making an emulsion. Once inside the tube, the ingredients are held there by capillary forces and slowly released over an extended time driven by a concentration gradient.

It is important to note that this type of release is very different to that from a zeolite. Zeolites work by complexing with molecules so you need to have just the right sized opening and also a specific interaction between the zeolite and the molecule. So zeolites are limited in their scope because you need to choose the right one for your chosen active and some active molecules are simply too large to fit within a zeolite pore which is in the 0.1-2 nm range. The lumen in halloysite is large enough to accept virtually any type of molecule (Figure 22). Typically small molecules are similar in size to Glucose, which has a molecular mass of 180 Daltons. Recent work showed that acid etching is selective to the inside of the tube increasing the lumen diameter and thus the maximum amount of active that can be loaded up to 40%, comparable to polymer microcapsules⁵⁰. Organosilane treatments can be bound inside the tube lumen to improve loading of dyes for example²⁰⁴. The rate of release was adjusted using

pH and also by compaction of the loaded halloysite into pellets. This latter procedure significantly slowed release due to diffusion effects.

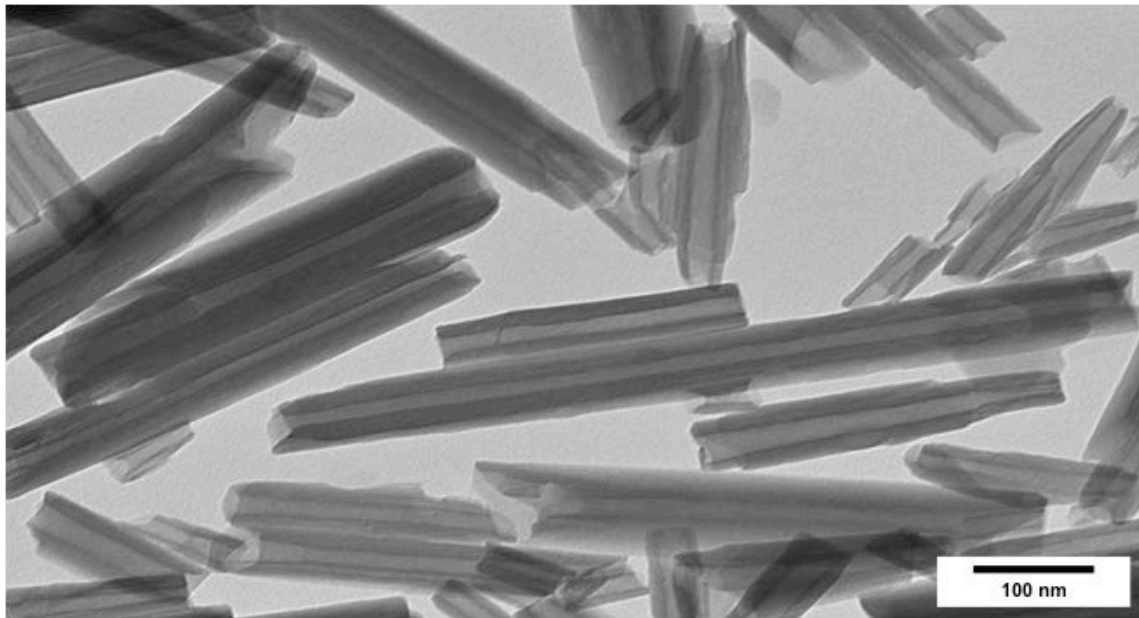


Figure 21 TEM of Dragon Mine Halloysite showing hollow nature of the tubes

Unlike zeolites, the halloysite tube can accept much larger molecules including polymers like Hemoglobin. Furthermore, there is no need for the molecule to have a specific interaction with the tubes, so any type of molecule can be incorporated. This makes halloysite far more versatile than zeolites for controlled-release. The largest molecule loaded inside the tubes so far is the enzyme urease²⁰⁵ with a molecular weight of ~480 000 Daltons and with a molecular diameter of ~5nm.

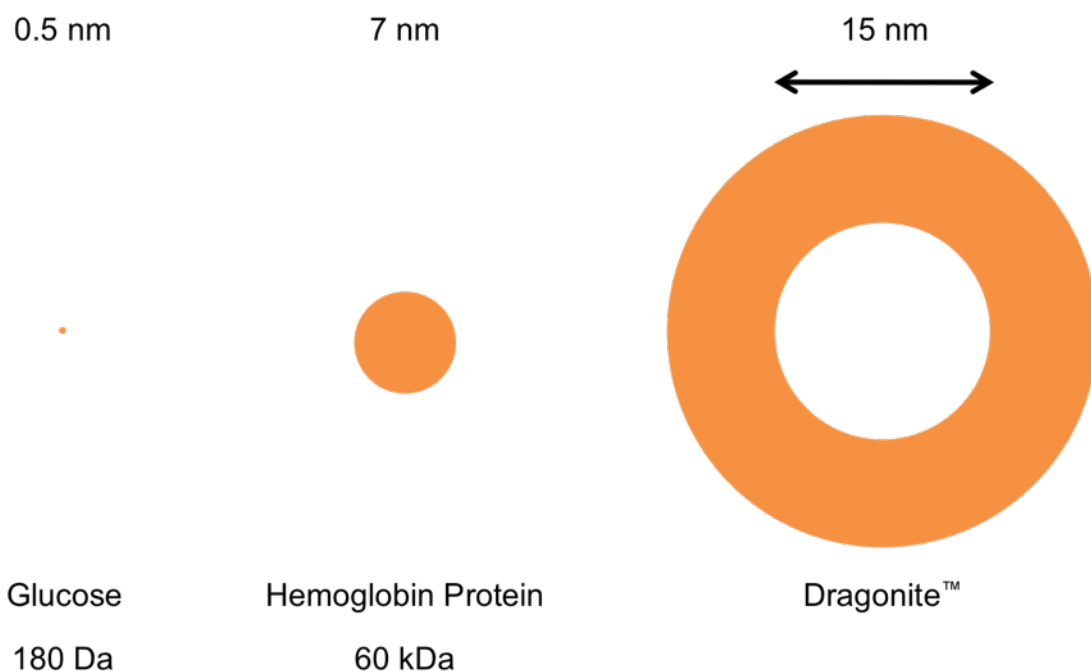


Figure 22 The size of molecules compared to the halloysite tube opening

Compared to zeolites, halloysite has the following advantages:

- Accepts any size of molecule (zeolites are limited to small molecules)
- Works with all types of molecule (no chemical interaction with tube is needed)
- Reinforces the material it is added to (plastics, coatings, elastomers, etc.)

The active ingredient can even be loaded into the tubes from aqueous solution and still remain inside the tubes after washing with water. This has been demonstrated in the case of glycerol¹⁹³.

With polymer microcapsules one needs a trigger to release the active whereas halloysite needs no such trigger enabling release right away. Whereas polymer encapsulants are limited by the temperature and pH stability of the actives and matrix, halloysite tubes are stable to over 900°C⁷⁰ and from pH 0 to pH 14⁴⁸ making them very versatile.

Coatings and Adhesives

In previous sections we have seen that halloysite is a universal reinforcement for thermoplastics, thermosets and coatings. As coatings and adhesives consist of a thin layer of thermoplastic, thermoset or elastomer, it comes as no surprise that halloysite is effective as a reinforcement for them as well.

There are some additional requirements on adhesives and coatings compared with bulk materials. The most obvious one is that they must have good adhesion to the substrate. Coatings bond to one substrate whereas adhesives bond to two substrates, which may be alike or dissimilar.

In coatings advantages include:

- Improved strength and modulus while retaining ductility
- Better adhesion to the substrate
- Corrosion inhibition both for pure halloysite¹⁹⁹ and when halloysite is used to deliver a corrosion inhibitor¹⁹⁵⁻¹⁹⁹ such as a benzotriazole
- Small particles and easy dispersion enable high gloss when desired
- Accelerated cure of UV curable coatings

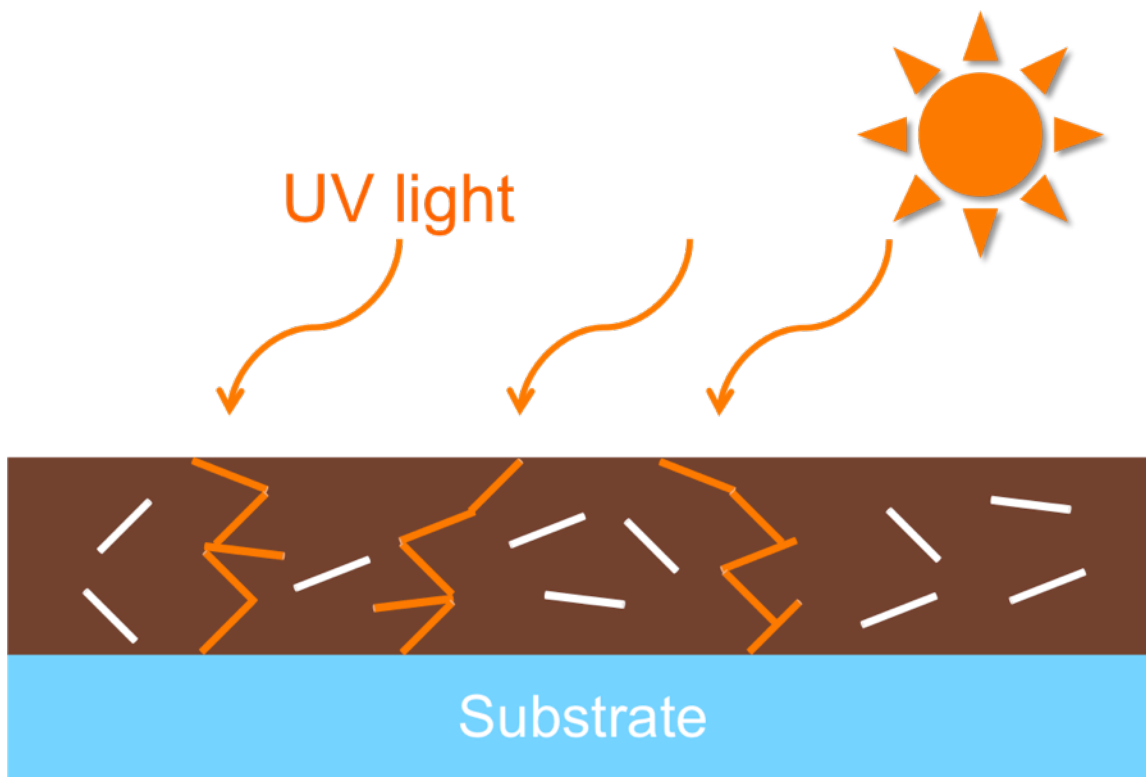


Figure 23 Halloysite acceleration of UV cure through a percolated network (in yellow)

The last point is a good illustration of the value halloysite can bring. Pigmented UV curable coatings are not easy to cure because the pigment absorbs the UV light thereby preventing it from penetrating into the coating. As the UV cannot reach beyond the surface the coating remains soft and tacky with poor mechanical properties. The standard solution to this is to add some amorphous silica particles which, being UV transparent, can help conduct the UV light into the coating. However, silica presents some challenges in use. Firstly, spherical particles do not percolate well (form a path). They are also abrasive due to high Mohs Hardness. Lastly, silica is not effective at reinforcing the mechanical properties of the coatings.

Halloysite shows advantages in all three areas. The anisotropic, elongated particles make for a good pathway to conduct the UV light (anisotropic particles percolate well). halloysite is non-abrasive with a low Mohs Hardness. Lastly, halloysite is very effective at reinforcing the coating and prevents cracking in latex paints²⁰⁶. One might wonder whether other clays would be equally effective in this application but it turns out that halloysite is the only one found to be UV transparent^{63,64}. The UV curing effect has been verified commercially with the customer noting a substantial improvement in adhesion as well as to the other advantages outlined above.

Halloysite has also proven effective in adhesives. Only one publication exists so far¹⁹¹, customers have reported remarkably good performance in a number of adhesive systems and with a wide variety of chemistries. At this stage it is not possible to give details, but performance is said to exceed that possible with any other mineral or filler. For those interested in the rheological properties of halloysite suspensions several publications exist²⁰⁷⁻²¹¹.

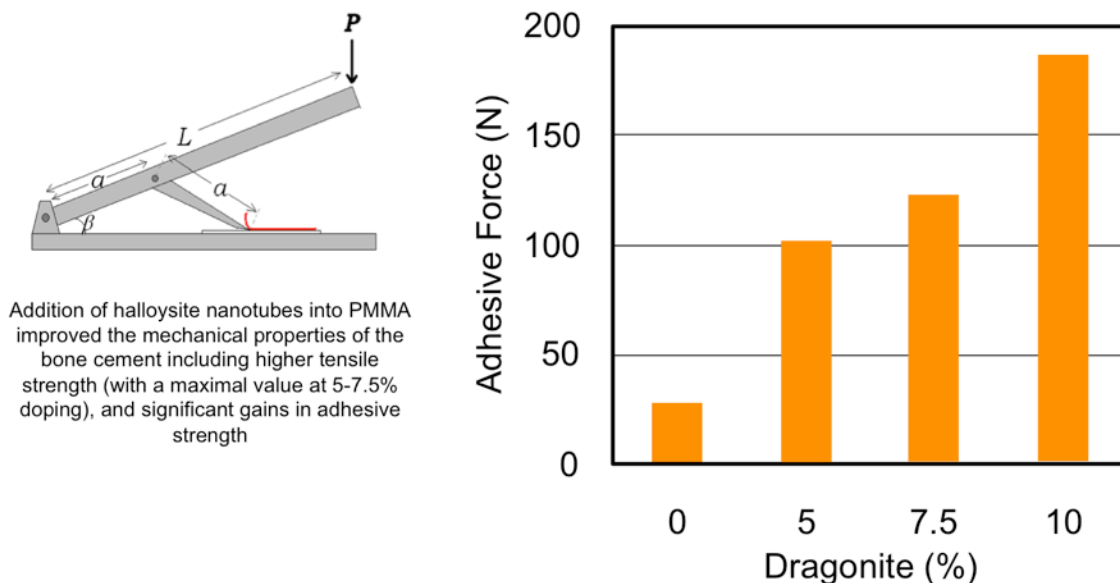


Figure 24 Halloysite dramatically improves adhesion while providing controlled release

Modification of Halloysite

Surface Treatment and Adsorption

Due to the way that the sheets roll to make halloysite the outside of the tube is silica-like and the inside is analogous to alumina. Therefore the surface chemistry of the inside and outside of the tube is markedly different. The inside of the tube has a high density of aluminol groups, which can be seen for example by FTIR and Raman spectroscopy. In contrast, the outside of the tube is relatively inert with some silanol groups at defects but not enough to be detected by spectroscopic means.

The affinity of halloysite to adsorb organic compounds has been well studied and an overview is presented here, as this information is useful, for example, when one wants to surface treat halloysite to improve adhesion to a polymer matrix.

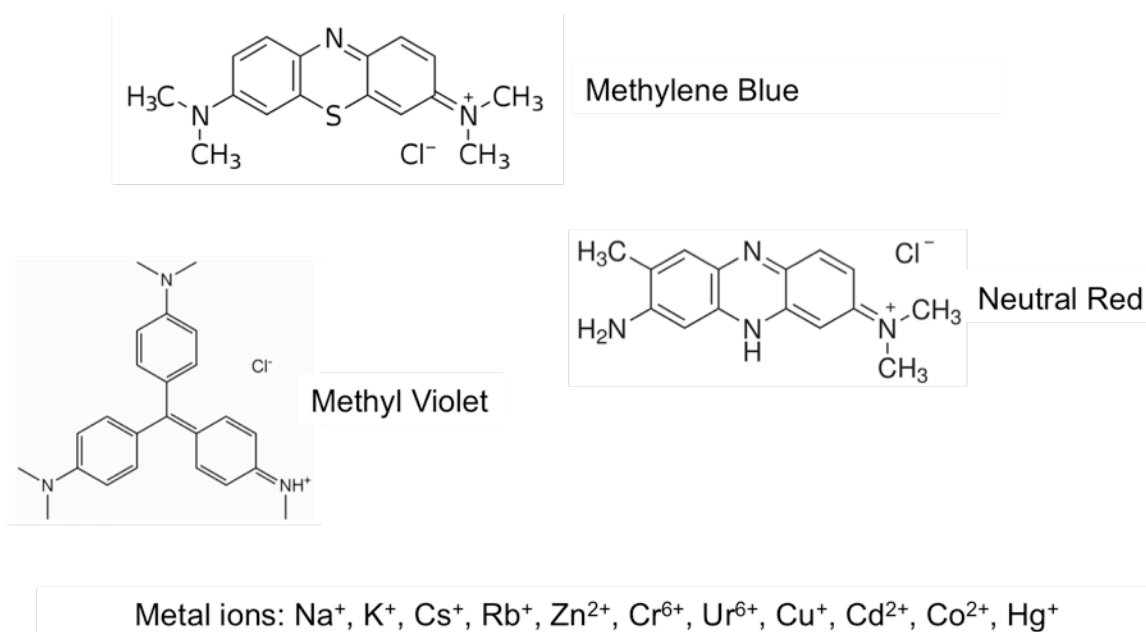
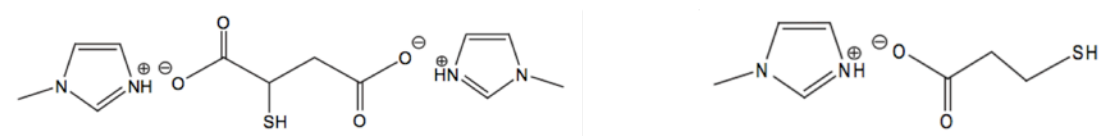


Figure 25 Cationic dyes and metal ions reported to adsorb onto halloysite²⁴⁶⁻²⁵¹

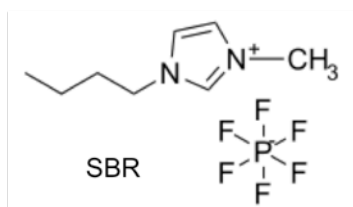
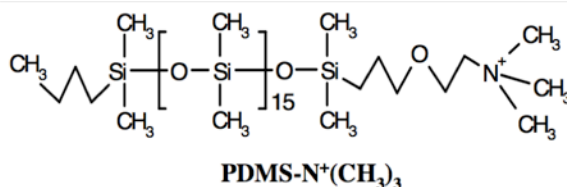
Many cationic species have been shown to adsorb including several dyes and a wide range of metal ions (Figure 25). It has been suggested that this would be useful for remediation, i.e. to chelate toxic and radioactive metals or to adsorb dyes left dissolved after industrial processes.

Similarly, several types of cationic surface treatment have been applied to halloysite (Figure 26). The cationic moiety adsorbs onto the mineral surface and the rest of the molecule is solubilized in the surrounding matrix to improve dispersion of the particles. In many cases added dispersant is not required but the option does exist for those needing a level of dispersion higher than that for untreated material. In each case the name of the corresponding publication is given.

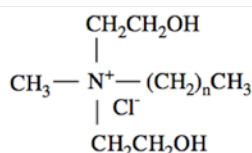


Functional thiol ionic liquids as novel interfacial modifiers in SBR/HNTs composites

A new way to disperse aluminosilicate clays in poly (dimethylsiloxane) matrix



Adsorption of Ionic Liquid onto Halloysite Nanotubes: Mechanism and Reinforcement of the Modified Clay to Rubber

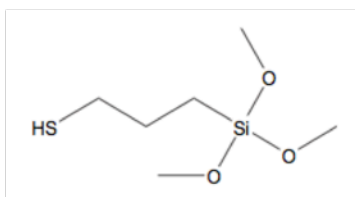


Crystallization behavior and Mechanical properties of polypropylene/halloysite composites

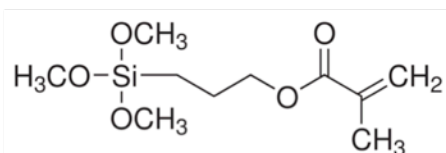
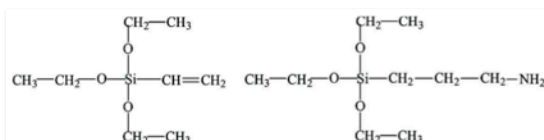
Figure 26 Cationic surface treatments reported for halloysite^{89-91,143}

Organosilanes are commonly used as dispersants and coupling agents for mineral fillers. These have also been reported to work on halloysite (Figure 27). This provides a very versatile route to modification because so many organosilane types are available. They have been reported to bind inside the lumen²⁰⁴.

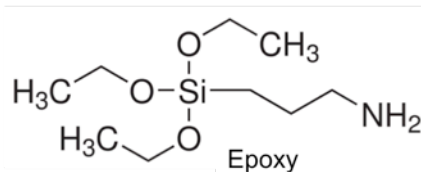
Functional thiol ionic liquids as novel interfacial modifiers in SBR/HNTs composites



New Hybrid Materials based on Modified Halloysite and Unsaturated Polyester Resin



Structure and Performance of Polyamide 6/Halloysite Nanotubes Nanocomposites



Experimental Damping Studies of FRP Hybrid Nanocomposites with Nano Reinforcement

Figure 27 Organosilanes reported to be effective on halloysite^{86-88,91}

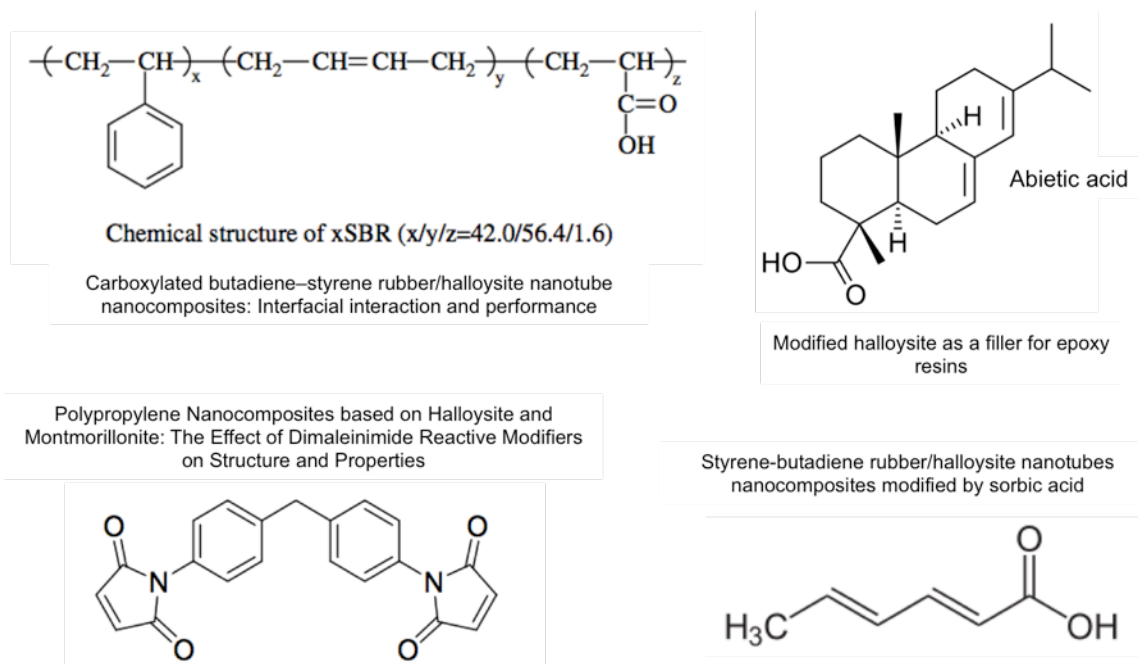


Figure 28 Unsaturated acids used as coupling agents on halloysite^{93-95,169}

Other than organosilanes the other commonly employed coupling agents are the unsaturated acid types. These have proven effective in several articles. One can therefore expect that other analogous molecules such as maleated polybutadiene would also be efficacious.

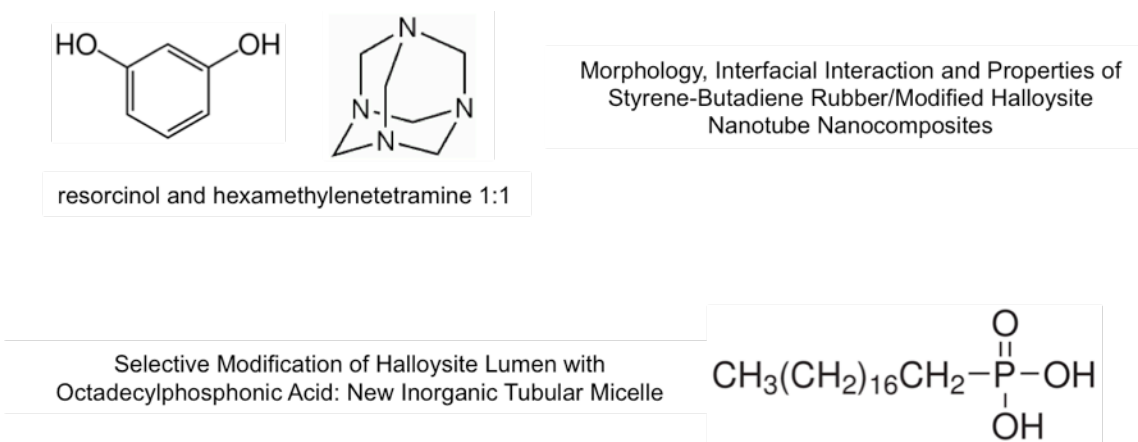


Figure 29 Assorted other reported surface treatments^{97,212}

Other chemistries are also applicable. Octadecylphosphonic acid was shown to selectively react with the Al-OH groups inside the tubes leaving the outer surface unmodified²¹². This imparted a hydrophobic nature to the inside of the tubes so they acted like micelles enabling them to adsorb hydrophobic molecules such as ferrocene. Benzothiazole sulfide was grafted onto PP and that was used as a coupling agent giving better dispersion and strength in PP¹⁴⁰.

Intercalation of Substances Between the Sheets

Much work has been done in recent decades to intercalate organic molecules in between the sheets of platy clays because for those clays, intercalation is essential in order to get good performance from them. By interposing up to 50 weight percent organic surfactant the sheet layers are separated and the inter-sheet forces reduced such that mechanical force can be used to peel the sheets apart. This separation of the sheets increases aspect ratio and surface area giving corresponding advantages in the effectiveness of the plates as reinforcements for plastics for example. Complete exfoliation is in practice not possible and so the theoretical potential of the platy clays has never been achieved¹³⁶.

In the case of halloysite the situation is very different. The tubes as they occur in nature, already have a high surface area and aspect ratio making them ideal for reinforcement. This means that there is no need to intercalate the material. Surfactants are not needed to achieve dispersion either as halloysite disperses readily without them. Nor is high shear required.

Although intercalation is not needed from a dispersion perspective, quite a bit of research has been done for other reasons. For example, intercalation in halloysite provides a way to give controlled release (note this is different from controlled release from the lumen) and it may also help in tuning the halloysite chemistry for certain applications for example where it may be advantageous to replace the inter-layer water with something else. Metal salts²¹³ (K^+ , Rb^+ , Cs^+) or ammonium salts²¹⁴ are effective intercalants and can be incorporated either from solution²¹⁵ or simply by dry grinding of the salt and halloysite^{216,217}. The intercalation behavior is characteristic for halloysite and can be used to help distinguish it from other minerals^{218,256-258}.

The other type of intercalants are small, highly polar molecules including formamide²¹⁹, monohydric alcohols⁴⁰, glycerol⁴⁰, diethylamine⁴⁰, nitromethane⁴⁰, urea^{220,221}, potassium acetate^{221,222,223} and hydrazine hydrate^{224,255} amongst others. The paper by McEwan⁴⁰ is particularly detailed in reviewing previous work and in correlating molecular structure with ability to intercalate.

In all cases it is found that intercalation of 10Å type halloysite is effective and proceeds to completion on a timescale of minutes or hours. In contrast, the 7Å type of halloysite is not as receptive and can only be partially intercalated at best³⁶.

Interestingly, 10Å is converted to 7Å upon heating through the irreversible loss of some of the bound water. If the 10Å is first intercalated, e.g. with glycerol then the complex formed is resistant to heating and retains its 10Å interlayer spacing.

Electrically Conductive Halloysite

Although halloysite is intrinsically insulating⁹, it can be made conductive for applications where that would be beneficial. For example, RFI shielding and ESD applications require some conductivity. Two approaches have been reported in the literature. Deposition of metal

(nickel^{76,78} or silver⁷⁷) and coating the surface with intrinsically conductive polymers such as polyaniline⁷⁹⁻⁸² and polypyrrole⁸³. Electrorheological fluid has also been produced using polyaniline coated halloysite²²⁵.

Magnetic Halloysite

Magnetic particles are useful in several areas including, magnetic data storage, toners and inks for xerography and magnetic resonance imaging²²⁶. In many cases fibrous particles are preferred over spherical ones and to that end cobalt nanoparticles have been deposited onto halloysite²²⁶. The result was uniform deposition of 3-7nm cobalt particles displaying better magnetic properties than bulk cobalt metal.

Another group coated halloysite with 50 weight % iron oxide to produce magnetic particles²²⁷. These were then used to adsorb dyes from water. A magnet was then applied so that the dye-coated particles could be removed leaving the purified water and also enabling the particles to be regenerated and reused. They concluded that this magnetic separation approach is advantageous compared to alternatives such as centrifugation or filtration and provides an attractive method to remove dyes and heavy metals from contaminated water.

Environmental Remediation

The high surface area, surface chemistry and tubular nature of halloysite make it ideally suited to remediation including water purification and clean up of oil or chemical spills.

Water purification

Halloysite has been shown to have a high affinity for specific metals including copper, lead, cobalt, arsenic, zinc, iron, lithium, sodium and potassium²²⁸. Other workers looked at reaction of halloysite with a wide the alkali metals sodium, potassium, rubidium and caesium²²⁹⁻²³². Other studies showed adsorption of copper and cadmium^{233,234}, zinc^{235,236} lead⁶⁸ and cobalt^{237,238}. Even uranium can be adsorbed²³⁹. In that latter study it was concluded “halloysite type clay has affinity for high uranium concentrations and may be utilized for nuclear waste repositories”. Modification of halloysite has been shown to increase its binding capacity for certain metal such as copper^{240,241} and chromium (VI)^{242,243}. The interaction of halloysite with seawater has also been reported²⁴⁴. The sea water increased the cation exchange capacity of the halloysite markedly from 11 to 47 meq/100g.

It has been noted that halloysite is unusual in being an amphoteric adsorbent, i.e. able to adsorb both anions and cations. The reason being that the sheets that form halloysite are chemically different on each side. The outside face of the sheet is similar to montmorillonite and has a negative charge whereas the inward facing layer resembles an α -hydroxide and has a net positive charge²⁴⁵.

As well as the demonstrated affinity for metals, halloysite can also adsorb organic compounds including cationic substances such as dyes^{227,246-251} and surfactants^{252,253}. Various other types of chemical including 5-amino salicylic acid²⁵⁴ can also be adsorbed.

In addition to surface adsorption, certain small molecules can be taken up in between the sheets, a process referred to as intercalation. Molecules studied include nitromethane, methanol, acetonitrile, acetaldehyde, ethylene glycol, acetone, 1,3 propanediol and ethanediamine⁴⁰. It was found that intercalation is best achieved on the 10Å type halloysite. Once the sheets have the 7Å spacing, intercalation is difficult or impossible. Hydrazine hydrate²⁵⁵, formamide²⁵⁶ and potassium acetate²⁵⁷ can also be intercalated and a comparison of the three²⁵⁸ has been made in an attempt to distinguish between halloysite and kaolinite based on their intercalation responses.

Gas scrubbing

As well as water remediation, halloysite has proven effective in removing toxic substances from contaminated gas streams. To date work has been done to show that halloysite can remove dioxins and heavy metals from flue gas²⁵⁹. Adsorption of hydrogen sulfide has also been demonstrated through loading halloysite with potassium permanganate where the high porosity of the halloysite was shown to be advantageous²⁶⁰. Another paper evaluated ways to remove odor from contaminated air and found halloysite to be highly effective²⁶¹. Ammonia adsorption on untreated and heat treated halloysite has been investigated²⁶² where the

ammonia accessible surface area was between 47 and 132m²g⁻¹ depending on the thermal treatment used. Gas adsorption tests including N₂, O₂, CH₄, CO, CO₂ and C₂H₂ were conducted²⁶³ and halloysite was found to be significantly selective towards CO₂ and C₂H₂.

Oil clean-up

A study showed the adsorption of the liquid hydrocarbons hexane, cyclohexane and benzene²⁶⁴. All three adsorbed, but it was shown that benzene had a specific interaction whereas the other two, non-polar molecules did not. Given the demand for better oil-spill clean-up solutions, the efficacy of halloysite for marshland oil-spill remediation was tested. Halloysite was shown to be very effective at wicking oil out of the sub-surface and was also highly effective in deep-water conditions. The EPA were so impressed with the results that they have entered into a Cooperative Research & Development Agreement (CRADA) to further develop this application²⁶⁵. This is particularly noteworthy given that the EPA has tens of thousands of applications and decided to select only halloysite for further work.

Catalysts

Halloysite was used commercially for decades as a petroleum cracking catalyst where Dragon Mine material was used due to its high surface area and purity¹. Since then, work has continued on using halloysite in catalytic processes as a support material and as a catalyst. Examples include the esterification of lauric acid²⁶⁶, the interesterification of sucrose polyesters in high yield²⁶⁷, the firing of agricultural biomass²⁶⁸, the immobilization of metalloporphyrins for oxidation²⁶⁹, the isomerization of α -Pinene to Camphene²⁷⁰, the polymerization of styrene^{271,272} and the depolymerization of polystyrene to give the monomer^{273,274}.

A very interesting development is the use of halloysite as a template for the synthesis of other types of nanotubes. For example, it has been demonstrated that one can deposit particles of TiO_2 onto the surface of halloysite providing a simple, inexpensive and readily scalable route to TiO_2 nanotubes²⁷⁵⁻²⁷⁷. The initial work was done on low surface area halloysite. More recently the authors have reinvestigated using another halloysite, which showed much higher activity due to larger surface area. Other workers have shown that unmodified halloysite can be used for the photocatalytic removal of tetrachloroethene²⁷⁸ and also for the thermal treatment of hydrofluorocarbons²⁷⁹. Co_3O_4 nanoparticles deposited onto halloysite were very effective for the photocatalytic degradation of methyl blue under UV light compared to halloysite alone, Co_3O_4 alone or a physical mixture of the two²⁸⁰. The explanation for the efficacy may come, in whole or in part, from the UV transparency of the halloysite which would be expected to help conduct UV light and thus promote catalysis throughout the specimen.

One paper demonstrated the deposition of Vaterite needles, a polymorph of calcium carbonate, inside of the lumen²⁰⁵. As shown previously, other metal^{76-78,226,227} and metal oxide nanoparticles can be deposited on halloysite. Such materials may also prove useful with regard to catalysis. One group has demonstrated that silver nanoparticles deposited onto halloysite are effective for the catalytic reduction of 4-nitrophenol²⁸¹. Likewise, nano gold particles were deposited onto halloysite and were found to be highly active for the selective cyclohexene oxidation to 2-cyclohexene-ol and 2-cyclohexene-one²⁸². FeNi and BFeNi nanoparticles were deposited onto halloysite²⁸³ where the FeNi showed nearly 100% conversion of toxic phosphene (PH_3) gas into yellow phosphorous and hydrogen at 420°C.

Polymerization has also been accomplished with the aid of halloysite. Atom transfer polymerization to produce PMMA has been reported using halloysite as the catalyst support²⁸⁴. Halloysite has also been used as a catalyst for the synthesis of PLA¹⁶¹. The authors noted high conversion and the biocompatibility of the material as advantages of this synthesis method.

Intellectual Property

Based on the previous sections, it is clear that halloysite is not only unique and interesting, but has high commercial potential. Customers keen to take advantage of the performance gains want assurance that there is freedom to practice in their selected field. While that can only be determined on a case by case basis, some general comments are possible.

Firstly, there is a huge amount of information on the performance of halloysite in the public domain in the form of papers and expired patents. At the time of writing there are over 2000 publications and 400 patents. This prior art means that there is indeed freedom to practice in a wide variety of technical areas. Fortunately, while the potential of halloysite was recognized decades ago, creating prior art, there was limited commercialization because there was no large commercial source of the pure material at that time. With the entrance of purer products, companies are now able to take advantage of this unique mineral.

Halloysite Properties Overview

Property	Value
Chemical formula	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$
Chemistry	Al_2O_3 37.73% SiO_2 43.39%
Loss on Ignition 1000°C	18.00%
Molecular weight	294.19 Daltons
CAS Registry Number	1332-58-7
Density	$2.54 \pm 0.05 \text{ gcm}^{-3}$
Flexural modulus of tube	130-150 GPa
Compressive Strength	$>1500 \text{ GNm}^{-2}$ ($>300\,000 \text{ psi}$)
Refractive Index	1.534
Specific Heat Capacity	$0.92 \text{ kJkg}^{-1}\text{K}^{-1}$
Thermal Conductivity	$0.092 \text{ WK}^{-1}\text{m}^{-1}$
Thermal Diffusivity	$5.04 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$
Tubular shape retained until	$>900^\circ\text{C}$
CTE (- and = directions)	10.0 ± 1.5 and 6.0 ± 2.0
Transparency	Colorless, UV transparent
pH in water	6.4 - 7.2
pH Stability Range	1-13 (slowly etched at 0 & 14)
Cation Exchange Capacity	$\sim 10 \text{ meq/100g}$
Particle morphology	1 micron long (average), 50nm across with 15nm diameter hole
Surface area	$65\text{-}120 \text{ m}^2\text{g}^{-1}$

Table 14 Halloysite properties overview

HALLOYSITE COMPOUNDING GUIDELINES

Quick Start Guide

Halloysite is an easy material to process as long as some simple steps are taken. Halloysite has been compounded at loadings from 1 to 60 weight %.

High quality compounds can be made in all thermoplastic materials, examples already proven include: LLDPE, EVA, HDPE, PP homopolymer, PP copolymer, PVC, PA6, PA6,6, PA12, PET, PLA, PS, PEEK, elastomers and thermosets.

Proven incorporation methods:

- Thermoplastics – Twin-screw extruder, Buss Kneader (Single Screw with mixing element e.g. Maddox type can also be used but is not recommended).
- Elastomers (SBR, EPDM, Natural rubber, FKM) - Two-roll mill
- Polyurethane – Planetary centrifugal mixers e.g. THINKY® ARV-310 or SpeedMixer™
- Epoxies – Tri-shaft high viscosity mixer (e.g. Myers)

Please note the following tips:

- **Pre-dry the halloysite at 110°C for 1-2 hours to remove 1-3% surface moisture and use immediately or store protected from moisture**
- Dose the halloysite in the main hopper / feed throat to give adequate time for wet-out (side feeding is not recommended)
- Use a twin screw extruder with a high L:D to give sufficient residence time (recommended L:D is 36:1 or higher)
- Use vacuum venting especially if the halloysite was not pre-dried or when adding to moisture sensitive polymers like polyesters and polyamides

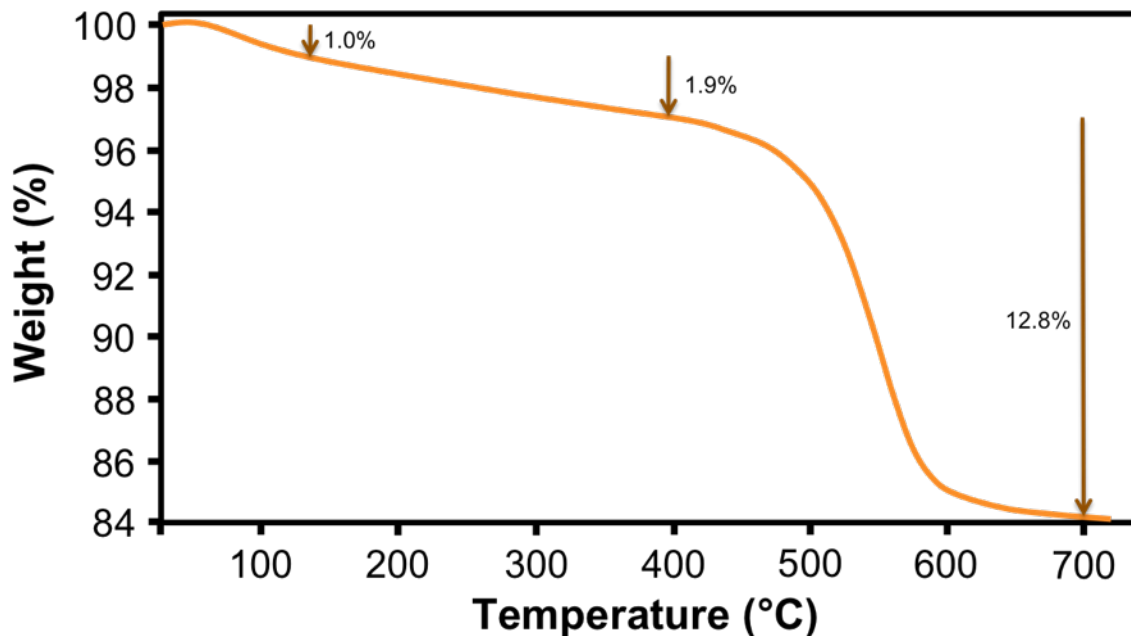
Further details are provided later in the guide.

Moisture and Bound Water

The shape and chemistry of the tubes are stable to very high temperatures. The weight observed in the TGA is due to removal of structural water from between the rolled sheets from which the tubes are made.

Failure to address the surface moisture will result in bad mechanical results caused by bubbles in your final material

The TGA of halloysite shows the loss of surface moisture around 100°C. The material is then stable up to well over 400°C at which point bound water is liberated (see TGA). This is part of the reason for the excellent fire-retardancy provided by halloysite.



There is a slight water loss between 100 and 400°C. Therefore, if you are processing plastics at high temperature (300-400°C), it is recommended to pre-dry the halloysite at or near your intended processing temperature. If that is not possible, then venting under vacuum can be used to remove any water vapor that could otherwise lead to bubbles.

Screw design

Some shear energy input early on is needed to disperse the halloysite. The screw should be designed to give additional residence time once clay is dispersed. Co-rotating twin-screw extruder with minimum 36:1 to 40:1 L/D is preferred. As an example, an experimental study (ZE 25, 40:1 L/D) used the following screw profile:

Main feed – addition of 2/3 of resin and all of the clay

5 D – conveying

5 D to 6 D – kneading and mixing elements ending with a neutral or reverse kneading block.

3rd- or 4th barrel zone – addition of the remaining 1/3 of resin

5D conveying

4 D to 6 D kneading blocks starting with a gear element to distribute melt before it enters in mixing elements, and ending with reverse kneading block.

4D conveying or venting

2D small flight kneading block

The remainder is conveying using a shorter pitch conveying element.

Temperature profile

Use a reverse temperature profile to provide quick melting, removal of surface moisture and to facilitate wetting. Use the standard processing temperature for the resin type or slightly higher.

Screw speed and feed rates should be selected to provide plenty of residence time. Lower screw speeds (longer residence time) have worked better than very high screw speeds.

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