Halloysite Nanotubes in Polymers

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Abstract

Halloysite Nanotubes (HNT™) provide a new avenue for the preparation of nanocomposites. Halloysite is a naturally occurring member of the kaolin family of aluminosilicate clays. Its uniqueness is that it exists predominantly in a tubular form with lengths of up to 10 microns and diameters of up to 400 nm rather than the deck of cards platy form of essentially all other clays.

Well behaved dispersions of HNT in nylon-6, polypropylene, TPO and several varieties of PE have been obtained by standard melt processes. In all cases, improved physical performance has been realized for molded parts.

HNT have also been dispersed in polymer latexes and dispersions at quite high loadings. These polymer and clay dispersions have been coated and produce coatings with useful performance properties.

Key words: halloysite, nanocomposite, nanotube, clay

Introduction

Polymer nanocomposites are an area of intense research and development due to their potential to provide stronger and lighter materials and parts. Unfortunately, it has proven hard to produce finished parts that deliver this potential with a cost and the robust productivity required for critical uses. Clays are a class of nanomaterials that have received a great deal of attention. [1] While the particles of a typical clay are far from nano-sized, the particle can be separated into its individual component sheets by a combination of chemical, thermal and mechanical steps. These two dimensional sheets provide a very high surface area to weight ratio which improved the performance of polymers that they were compounded with, particularly nylon. Despite the improved performance obtained in typical platy clay nanocomposites; their utility has continued to be limited. Separating the platy clay particles into their individual sheets is a difficult process that can alter the materials balance of the melt formulations or in the extreme requires in situ polymerization of the monomer in the presence of the clay.

Halloysite is a naturally occurring member of the Kaolin family of aluminosilicate clays. Halloysite can occur in several structures but predominantly exists as a tubular structure believed to be the result of hydrothermal alteration, or surface weathering of other aluminosilicate minerals. [2], [3] Halloysite nanotubes (HNT™) do not require large amounts of chemical modification or complex chemical processes such as intercalation and exfoliation in order to produce stable nanoparticle clay dispersions in the melt. This makes it possible to obtain performance improvements without the complexity and processing cost associated with platy clays.

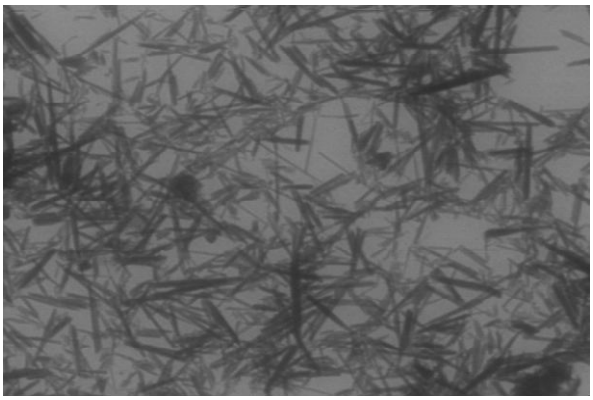

Figure 1 TEM of halloysite at 2600 X magnification.

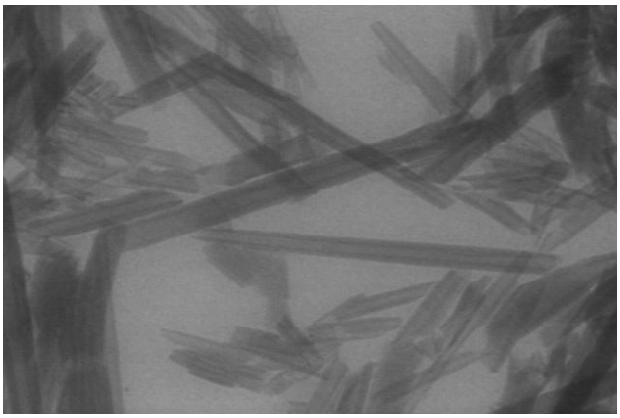

Figure 2 TEM of halloysite at 25000X magnification

Our results for nylon/HNT and polypropylene/HNT polymer nanocomposites indicate that an increase in modulus and strength is obtained with little reduction in elongation. NaturalNano has prepared well-dispersed HNT polymer concentrates which are commercially available under the name Plexmer™ at HNT concentrations of up to 50%.

Additionally, stable acrylic polymer latex/HNT dispersions were prepared to concentrations as high as 30% HNT. Coatings made from these latex formulations exhibit a ten fold increase in storage modulus, while maintaining key properties such as transparency and tack.

Experimental Work

The scope and property improvements seen by Toyota in their work with platy clays in nylon for injection molded parts [4] caused us to begin our nanocomposite work with nylon. The composites were typically prepared by melting the nylon pellets in the early part of the extruder and feeding the desired amount of halloysite onto the melt at a later hopper. The halloysite was milled to an extremely fine, near white powder that flows and handles like flour. Both the polymer and the halloysite were dried to discourage degradation of the nylon. The composite strand was passed through a water bath and chopped into pellet form for direct use or to be let down for injection molding.

Figure 3 is a 20,000X magnified SEM image of the end of a frozen strand of a 30% halloysite composite in nylon-6. Individual tubes can be seen as well as small clusters of tubes.

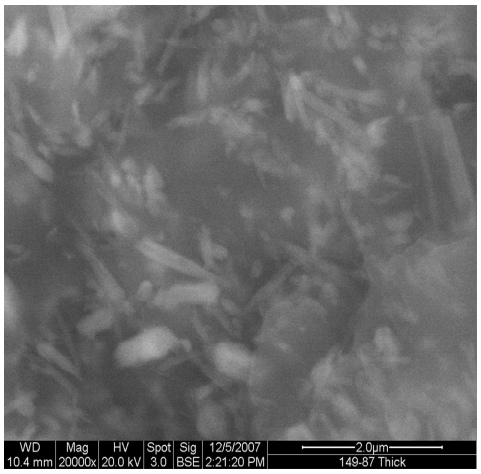

Figure 3 SEM of 30% halloysite in nylon-6.

Figure 4 shows that the tubes are oriented within the flow while remaining dispersed. Micrograph 4a was taken across the strand while 4b is taken along the length of a fractured strand.

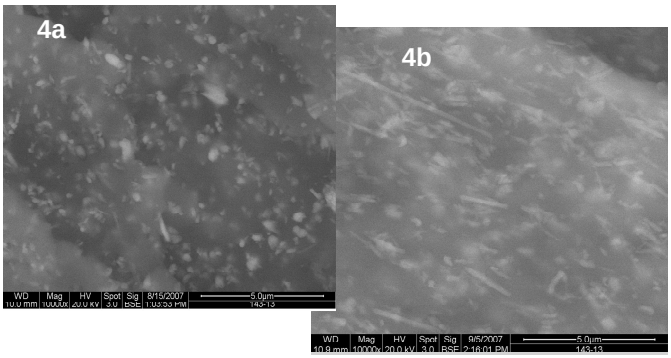

Figure 4 SEM of 20% halloysite in nylon-6 when fractured in the cross direction (4a) or along the strand (4b).

Properties \ Composite	Nylon 0% HNT	Nylon 2% HNT	Nylon 4.1% HNT	Nylon 5.1% HNT	Nylon 10.2% HNT	Nylon 3.8% HNT2	Nylon 4.7% HNT2	Nylon 9.4% HNT2
Modulus of Elasticity, psi	322000	438000	455000	456000	466000	448000	474000	516000
Elongation at Break, % (2in/min)	91.1%	35.8%	31.3%	41.4%	16.9%	68.5%	42.5%	39.0%
Tensile Modulus, psi	407000	457000	464000	481000	495000	477000	502000	572000
Gardner Impact, in.lb	>160	140	140	120	120	>160	>160	80

Table 1 HNT-Nylon Nanocomposite Physicals.

Testing bars were prepared from the extruded pellets by injection molding. HNT generally improved physical performance but it was especially effective at producing parts which have good ductility, impact resistance and resistance to flex fatigue. The improvement in physical performance can be obtained at low levels of incorporation and while maintaining good elongation properties.

Two different halloysite samples are shown in Table 1. HNT1 is a shorter tube than HNT 2. HNT1 has an average tube length of about 1.2 microns while HNT2 averages slightly less than 5 microns. The tensile performance of the long tubes is preferred but at some expense in impact and fatigue.

A potential disadvantage for HNT is that the addition of HNT increases the mold shrinkage for nylon injection molded parts compared to the nylon itself. However, this brings a significant opportunity for mixing HNT with the more normal talc or glass fiber fillers in the composites.

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Composites with talc or glass fibers, will have large improvements in tensile properties but may suffer from very low elongation at break, poor Gardner impact and too little shrinkage. A composite containing both fillers in low amounts can produce an excellent set of final properties as shown in Table 2

% HNT in B3K nylon	% GF in nylon	tensile mod (psi)	flex modulus (psi)	mold shrink (%)
0	0	407000	322000	0.92
5.1	0	481000	456000	1.60
10.2	0	495000	466000	1.76
10	5	600000	449000	1.00
5	7.5	581000	415000	0.65
0	15	731000	524000	0.30

Table 2 Mixed Composites of HNT and glass fibers in nylon.

The mold shrinkage can be dialed in by controlling the ratio and amount of the two fillers. Reducing glass fiber loadings can dramatically improve the processing and esthetics of the finished parts while the HNT keeps the mechanical properties quite high.

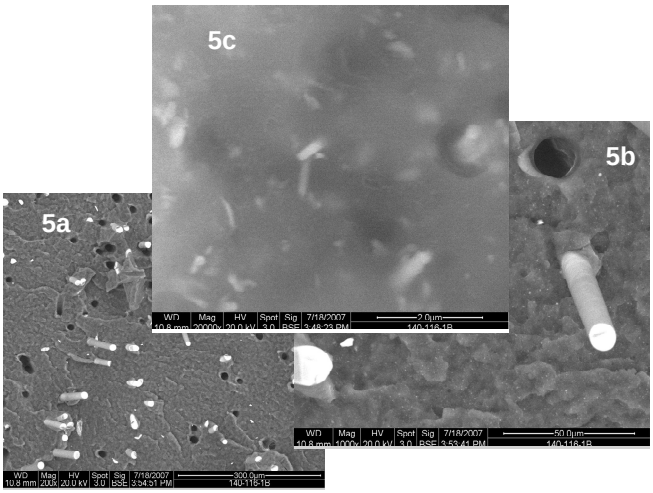

Figure 5 SEM images of mixed composites of halloysite and glass fibers in nylon-6. The large difference in size can be recognized by the different magnifications needed to see the two types of fillers. 5a at 200X, 5b at 1000X and 5c at 20000X.

Polyolefins similarly form composites using melt technology with improved physical performance but the impact is not as large as for nylon. As with platy clays it is difficult to get complete dispersion and more clay is needed to get large effects. Figure 6 includes data for HNT composites with a polypropylene homopolymer and a propylene copolymer. In both cases the flex modulus improves while some elongation to break remains. Similar results have been observed for a variety of polyethylenes and TPO's.

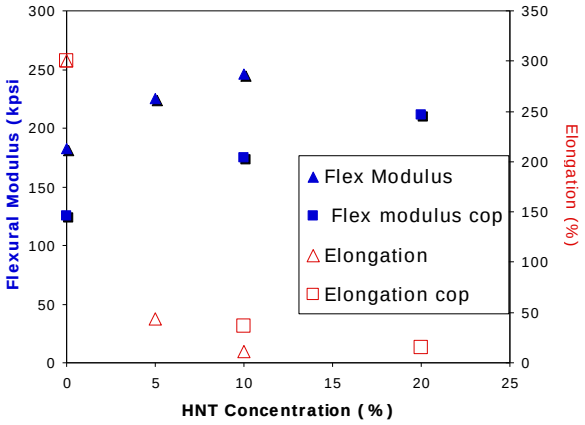

Figure 6 Flexural Modulus and Elongation at break for HNT composites in polypropylene and a polypropylene copolymer.

As the polypropylene extrusions were being made it became obvious that the addition of halloysite to the polymer melt made it easier to process. Temperatures could be dropped or outputs increased. Dry blended samples of halloysite in INEOS H12F-00 were prepared and extruded under the same input and output conditions using the same screw and temperature profile. As seen in Table 3, less torque was required as more HNT was added.

Percent HNT	0	10	20	30
Extruder Torque (%)	85.8	69.5	64.1	63.2

Table 3 Extruder torque as a function of adding HNT to polypropylene.

Composites of HNT have also been prepared by dispersing the milled and treated halloysite with polymer latexes and emulsions. Significant mixing is required but not enough to harm the polymer system. The subsequent filled fluids may be coated and dried in the normal way to give coatings which have improved physical properties. Figure 7 contains information about the change in modulus produced by putting various amounts of HNT and platy clay into an

acrylic polymer dispersion and coating it onto a substrate. When HNT were added to the acrylic dispersion, the modulus of the coating rose significantly while it dropped when even a small amount of a platy clay was added. In fact 5% platy clay was the maximal amount that could be placed in a stable dispersion while the HNT went easily to 20% percent of the total solids.

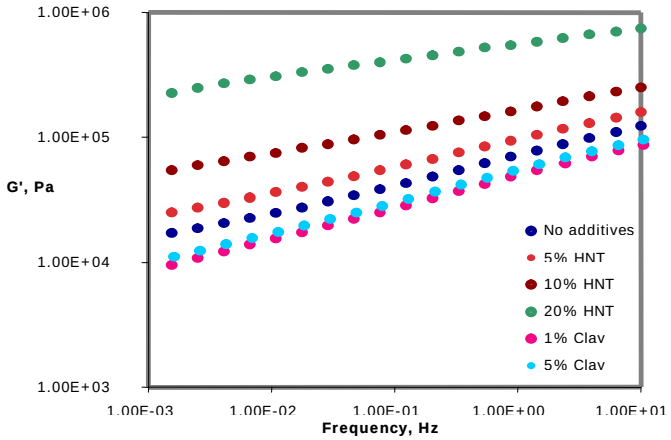

Figure 7 G' modulus for MG 0580 latex coatings with varying amounts of HNT or platy clay.

Since the coatings of this polymer latex could function as a pressure sensitive adhesive, the HNT filled coatings were also evaluated as an adhesive. Formulations were prepared containing 40% polymer and 10% clay within the latex. Coatings were drawn down onto PET using a 20 mil coating knife and air dried. Remarkably, the coatings remained tacky even at higher levels of HNT up to 20% HNT. A measured strip of the coated PET was cut and pressed with a weighted roller onto an uncoated strip of PET. The strips were peeled apart on a Tinius Olsen H5KT. The peel forces reported in Table 4 for composite coatings on PET show that the compositions were not only tacky but they formed bonds that were considerably stronger than the polymer itself. On the other hand, one of the two platy clays tested crashed out and the other made adhesion much worse.

Clay added to Rhoderm 5600 Latex	Strength (N)	Failure Mode
HNT1	31.8	cohesive
HNT2	28	cohesive
Latex alone	26.9	cohesive
Veegum T	N/A	N/A
Bentonite	4.1	adhesive to uncoated PET

Table 4 Peel strengths for composite coatings from acrylic polymer latexes with HNT and platy clays

Summary

Halloysite nanotubes were formulated in the melt and via polymer dispersions to form polymer nanocomposites which produced objects with useful and unusual properties.

Acknowledgements

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