

BIODEGRADABLE POLYMER/HALLOYSITE NANOCOMPOSITES

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Matthew C. Hartline, B.S.

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BIODEGRADABLE POLYMER/HALLOYSITE NANOCOMPOSITES

Committee Members Approved:

Luyi Sun, Chair

Clois E. Powell

Todd W. Hudnall

Approved:

J. Michael Willoughby
Dean of the Graduate College

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ABSTRACT

BIODEGRADABLE POLYMER/HALLOYSITE NANOCOMPOSITES

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Matthew C. Hartline, B.S.

Texas State University-San Marcos

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SUPERVISING PROFESSOR: DR. LUYI SUN

Biodegradable polymer/halloysite nanotube (HNT) nanocomposites have been found to have superior mechanical properties over that of the neat polymer. Two extremes of biodegradable polymers have been made into halloysite containing nanocomposites, from the very rigid, brittle poly(lactic acid) (PLA) to the very ductile poly(vinyl alcohol) (PVOH). Both nanocomposites utilized relatively low loadings of halloysite to realize improved mechanical properties over that of the neat polymer.

The Young's modulus of PLA increased by 35% with a 10 wt.% loading of washed halloysite. Gains of 47% were seen at 5 wt.% loadings of sodium dodecyl sulfate (SDS) treated HNT. The incorporation of SDS treated HNTs into PLA nanocomposites showed increased tensile strength at yield and Young's Modulus over that of the

PLA/peroxide washed HNT nanocomposites. Almost no change in the thermal degradation was observed for any of the samples.

The PVOH/HNT/montmorillonite (MMT) nanocomposites showed increased tensile strength over that of the neat PVOH samples. The Young's Modulus was improved by 71% with the addition of 9.0% HNT and 1.0% MMT, while maintaining transparency of the thin film. The decreased strain at break (40% lower than neat PVOH) was to be expected, as the addition of a very stiff nanoparticle to a very ductile material will reduce the elongation under tensile stresses. The addition of smectic clay (MMT) to a PVOH/HNT nanocomposite further improved the mechanical properties of the thin film, with no reduction in optical transparency.

The improvements in mechanical properties of PLA/HNT and PVOH/HNT/MMT will expand the usefulness of PLA and PVOH for new applications, especially where high mechanical performance and environmentally friendly biodegradable products are desired.

CHAPTER I

HALLOYSITE NANOTUBE NANOCOMPOSITES

1.1 Introduction

Halloysite is a naturally occurring aluminosilicate, which has the formula $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ where n is 0 or 2 (Figure 1).¹ Aluminosilicates can occur in agglomerates, spheroids, sheets, or in hollow, tubular shapes.² Halloysite is most commonly found in a hollow, elongated tubular shape, but other shapes have been reported.² The shape of halloysite nanotubes (HNTs) is similar to that of carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs). Some representative scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of HNTs are shown in Figure 2 (next page).

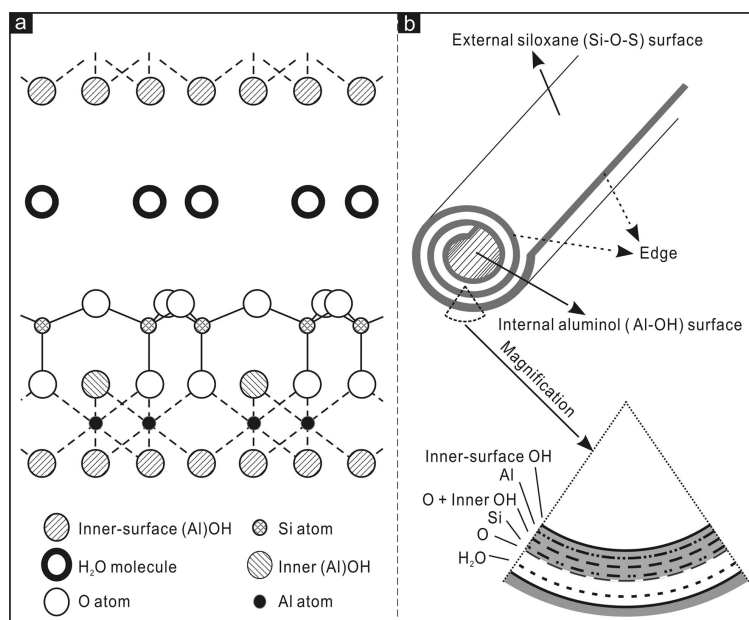


Figure 1. Molecular and physics structure of HNT. (reprinted with permission from Yuan, et al.³ copyright 2008)

High Purity deposits of HNTs can be found in New Zealand and the United States of America.² Each individual deposit has its own unique length/diameter (L/D) ratio, with lengths averaging between 1 and 3 μm , and diameters ranging from 100 to 300 nm.⁴

With HNTs' unique shape, structure, and high stiffness, HNTs have found widespread applications, in fine china and porcelain products, time-release capsules filled with additives for paints, lubricants, sealants, household foods, personal products, pest repellents, pharmaceuticals, catalysts, fillers in nanocomposites, polymers, plastics, high tech ceramics, and molecular sieves.²

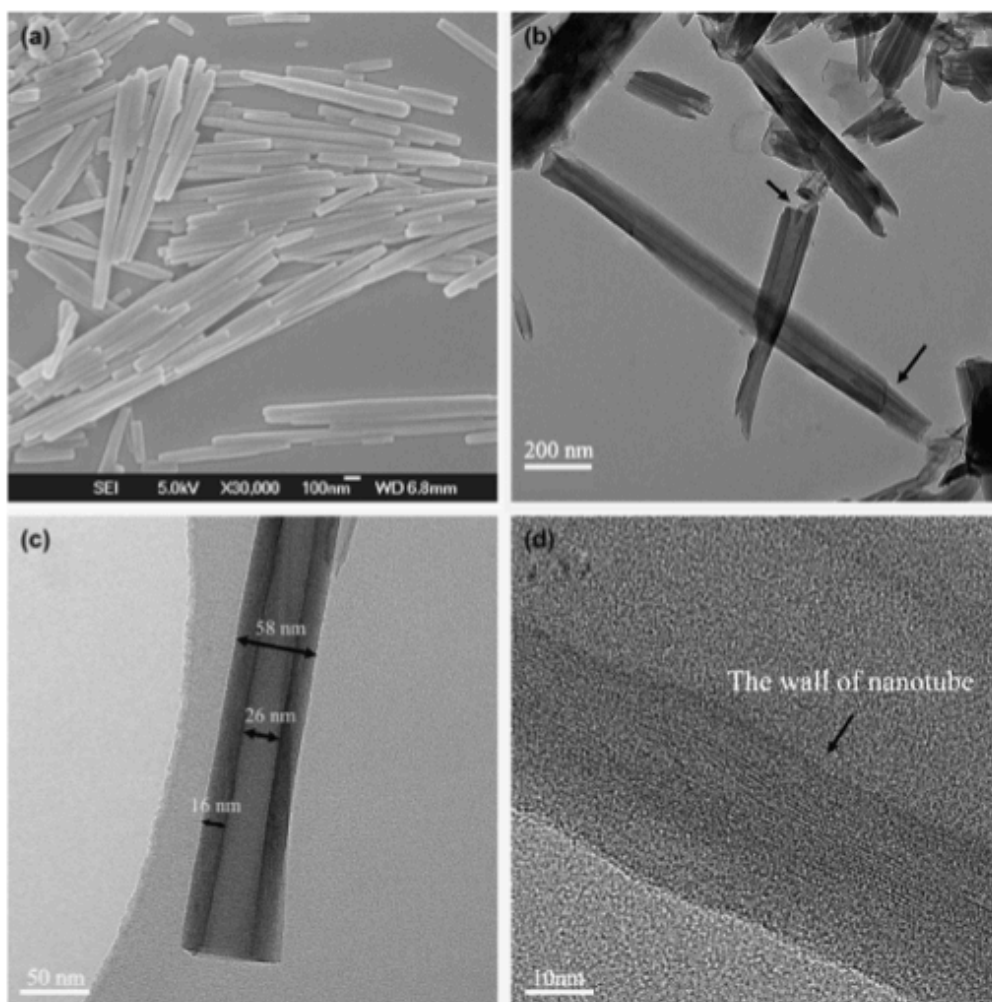


Figure 2. Microscope images of HNTs: (a) SEM image of HNTs; (b-d) TEM images of HNTs showing their tubular structure and wall thickness. (reprinted with permission from Ye, et al.⁵ copyright 2007)

1.2 Structure of HNT

HNTs have an outer surface comprised of a silica sheet, and the inner surface is comprised of an alumina sheet (Figure 3). This largely non-polar exterior and polar interior give HNTs the ability to be internally loaded with charged molecules. The non-polar surface allows HNTs to be easily dispersed into many polymer systems. The rigid HNTs become a good candidate for increasing the stiffness of polymers. The hollow tubular volume can be filled with chemicals. Filled HNTs can be released to facilitate use in many unique applications in biomedical fields. The inner water molecules of the hydrated halloysite are loosely held, which makes dehydration easy.⁶

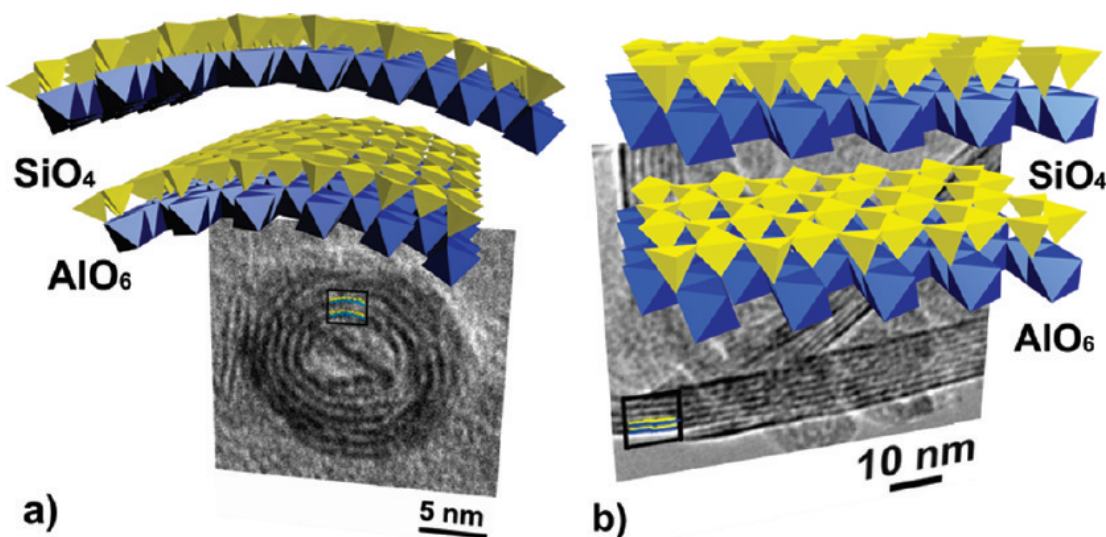


Figure 3. Comparison of a) Halloysite to b) Kaolinite. (reprinted with permission from White, et al.⁷ (copyright 2012))

HNTs are a natural product. The structural imperfections are common.² The most common imperfections are groups on the outer surface instead of the silica. The density of the silanol groups is relatively low overall, but the density was found to increase after hydrogen peroxide treatment.⁸ Other impurities include replacement of the Al^{3+} by Fe^{3+} in the octahedral inner sheet, and replacement of the Si^{4+} with Al^{3+} on the outer

tetrahedral sheet.² The substitution leads to disruptions in the structure, which reduces the efficiency of the packing, changes the inner diameter of the nanotube, and results in a lower modulus of the overall nanotube.^{7,9}

Below pH 8.5 the inner surface's lumen is positively charged. Negatively charged molecules can be loaded into HNTs.¹⁰ This behavior is also apparent when the HNT is incorporated in nanocomposites, leading to biocompatible nanocomposites for further functionalization.¹⁰

Synthesis of nanoscrolls from kaolinite nanosheets have been produced by intercalation of guest species into kaolinite and simultaneous swelling with solvents.¹¹ The final product is very similar to halloysite.¹¹

Figure 4, next page, shows the FTIR spectrum of HNT. The low intensity peaks at 790 and 750 cm^{-1} are due to the external -OH groups both through out of plane -OH bending and translational vibrations.¹³ The spectrum also contains a broad peak where three distinct peaks are observed in other forms of kaolinite at 1115, 1033, and 1008 cm^{-1} .¹² The peaks are typically the plane vibrations of Si-O-Si (1033 and 1008 cm^{-1}) and the apical vibrations of Si-O (1115 cm^{-1}).¹² The -OH stretching peaks are found at 3694 and 3615 cm^{-1} .¹²

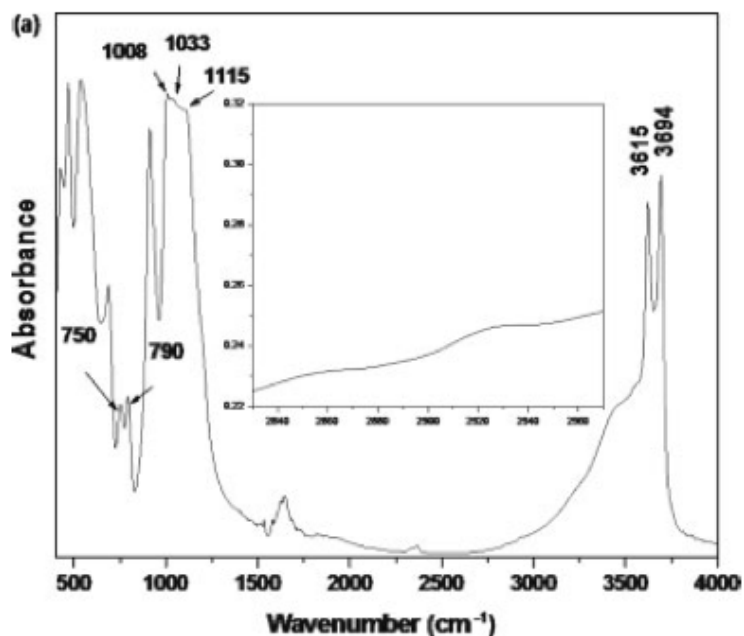


Figure 4. FTIR spectrum for HNT. (reprinted with permission from Shamsi, et al.¹² copyright 2010)

Guimarães et al. performed a study of theoretical single-walled halloysite nanotube models.⁹ The Young's modulus was determined to be between 230-340 GPa, depending on the orientation of overlap of the nanotube (armchair, zig-zag) with the zig-zag having the highest calculated modulus (Figure 5).⁹ Increasing number of layers reduces the Young's modulus due to a higher number of imperfections in the structure.⁹

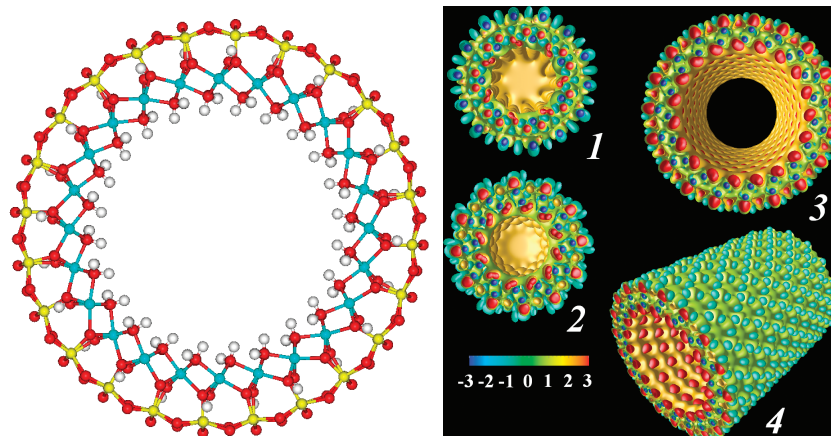


Figure 5. Cross section of HNT and armchair and Zig-Zag Conformations of HNT. Left: Cross section of HNT: white atoms are H, red O, gray Al, and yellow Si. Right: Armchair (1) and zig-zag (2,3,4) conformations of halloysite. (reprinted with permission from Guimarães, et al.⁹ copyright 2010).

1.3 Treatment of HNT

1.3.1 Purification of HNT

As HNTs are a natural product mined from all over the world, natural mineral and organic impurities will be present in the mined samples.^{3, 7} Because of its mined source, halloysite typically needs to be purified of organic contaminants prior to further treatments. The specific method of purification will depend upon the types of impurities present in the raw sample, and subsequent process steps of functionalization or surface modification of the halloysite.

A hydrogen peroxide (H_2O_2) treatment was found to be very effective in removing organic matter from the surface of HNTs.⁸ Meanwhile, the treatment also increased the density of the silanol groups on the outer surface as confirmed by TOF-SIMS, which is beneficial for surface functionalization.⁸ The purification by H_2O_2 can be performed in several variations, but in general, a large quantity of HNT is dispersed in 10% H_2O_2 , and magnetically stirred for 30 minutes, the mixture is then ultrasonicated for 30 minutes, and the HNTs are collected by either filtration or centrifugation.⁸

Another method of purification that has been previously used is to grind the halloysite with water to create a thin slurry, followed by filtration thru a fine mesh sieve (125 μm) to remove any contaminants.¹³ The slurry is then diluted with water, in which the precipitate was collected for further grinding, and any suspended particles are collected by centrifugation and subsequently dispersed in another water solution with 0.5 M tetrasodium ethylenediamine tetraacetate for 24 hours.¹³ The resultant white solid was ground in an agate mortar and pestle.¹³ Further separations were achieved with centrifugation and were monitored until no uncharacteristic shapes were found by SEM,

and then dried at room temperature.¹³ This method yielded 8-10 wt.% based on crude material.¹³

1.3.2 Surface Treatment/Functionalization of HNT

The surface modification of halloysite can help improve its compatibility or even potentially generate bonding sites with polymer matrices, the latter of which has been proven to increase the mechanical properties of the resulting nanocomposites.⁸ Sodium dodecyl sulfate (SDS) and benzalkonium chloride have been used to treat HNTs.⁸ It was found that the SDS treated HNTs could be well dispersed into organic media, but the benzalkonium chloride treated HNTs were only effectively dispersed in certain organic solvents.⁸ SDS was also used to disperse the HNTs in an aqueous solution, which was found to be stable for several days.¹⁴

Phenylphosphonic acid (PPA) was found effective in intercalating into and unrolling HNTs.¹⁵ This changed the normal tubular morphology of the HNTs into a very rigid, partially uncurled halloysite platelet, which showed an improvement in dispersion when compared to that of the untreated HNT.¹⁵

HNTs have been functionalized with many different silanes in order to increase their compatibility with epoxy resins. For a typical silane treatment, in 100 mL 50/50 (vol/vol) solution of ethanol/water, 10 g HNTs is added and mechanically stirred until well dispersed.¹⁶ The pH value is lowered to 5.5 with acetic acid, and in a separate beaker, 2.3 g γ -glycidoxypolytrimethoxy silane is added to another 100 mL of 50/50 ethanol/water and mechanically mixed.¹⁶ The two solutions were combined and mechanically stirred at room temperature for 2 days.¹⁶ The HNTs were then collected by vacuum filtration and put into methanol for 2 h while being stirred, and subsequently

filtered and again a 2 h methanol treatment.¹⁶ The modified HNTs are then vacuum filtered and dried for 6 h at 80 °C.¹⁶ The functionalized HNTs exhibited higher compatibility with epoxy resins, especially the flexural modulus with loadings below 8%.¹⁶

Halloysite treated with γ -methacryloxypropyl trimethoxysilane (γ -MPS) (Figure 6) has been shown to improve dispersion in an EPDM nanocomposite.^{17, 18} The functionalization of HNT with γ -MPS was in a solution of 100 ml of 95% ethanol is adjusted to pH of 5.0 with acetic acid, then 10 mL of γ -MPS is added and stirred for 5 min, followed by 100g of HNTs, then stirred for an additional 15 minutes.¹⁸ The solvent was removed by evaporation at ambient temperature, and any residual solvent is removed under vacuum at 70 °C.¹⁸ The EPDM/ γ -MPS HNT showed an increase in tensile strength and modulus over that of the neat EPDM or that of the EPDM/unmodified HNT nanocomposites.¹⁸

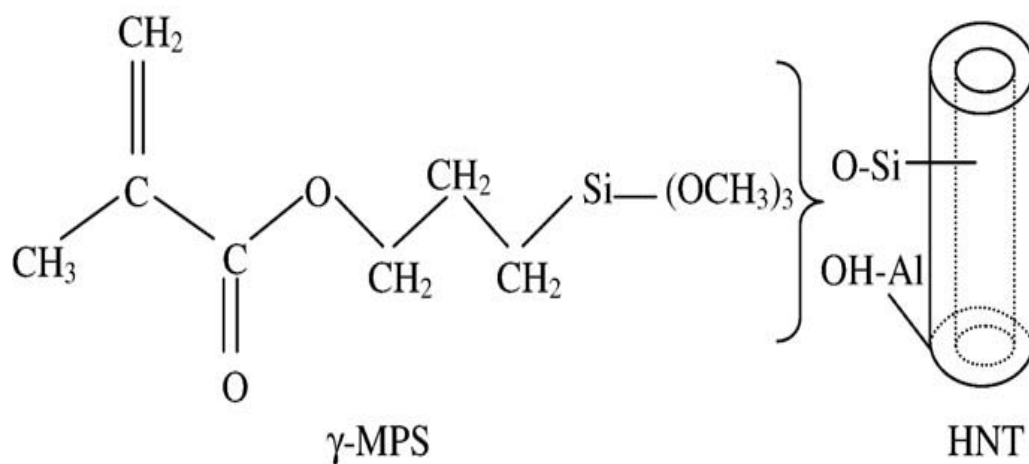


Figure 6. Interaction mechanism between γ -methacryloxypropyl trimethoxysilane (γ -MPS) and HNT. (reprinted with permission from Pasbakhsh, et al.¹⁸ copyright 2010)

1.3.3 Metalization of Halloysite

It was found that halloysite can be metalized by electroless plating first catalyzing the outer surface of the halloysite with acidic palladium chloride and then dispersing the

activated halloysite into a solution of Niposit™ 468 (The Dow Chemical Company) plating bath at an elevated temperature.¹³ This process produced a 20 nm thick uniform nickel coating that can be used for increased mechanical properties in ceramics, an increased bond strength in metal matrix systems, and magnetic alignment of the halloysite in nanocomposites.¹³

1.3.4 Encapsulation Process

Because of its unique hollow tubular structure, there has been much work done to use HNTs as a carrier, a nanoreactor, and a delayed release mechanism for many other purposes.²

The loading of various materials into halloysite has been achieved with great efficiency, due to its completely hollow shape with two open ends.¹⁹ In most cases, the loading process is performed under vacuum, with the halloysite in a saturated solution of the target filler.¹⁹ The process is repeated several times in order to achieve maximum packing efficiency.¹⁹ Once the tubes are loaded, they are dried to drive out excessive solvent, leaving only the target filler. This process can be seen in Figure 7.

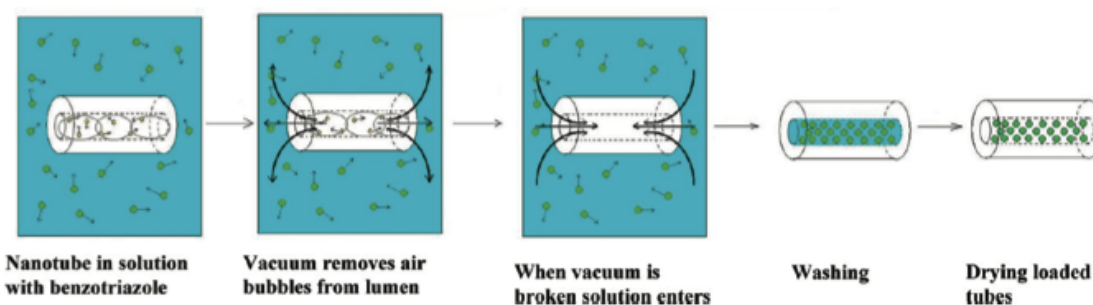


Figure 7. Typical procedures to load HNTs. (reprinted with permission from Abdullayev, et al.¹⁹ copyright 2009)

Once the nanotube has been filled with the desired contents, the nanotube ends can be closed to keep the contents contained. This can be done in several ways. If the filler is capable of making an insoluble complex, the end capping is quite easy. This was

the case with HNTs filled with benzotriazole, which formed an insoluble metal-benzotriazole complex when exposed to a copper (II) solution for only a few minutes (Figure 8).¹⁹ The end-capped nanotubes were then separated by centrifugation.¹⁹

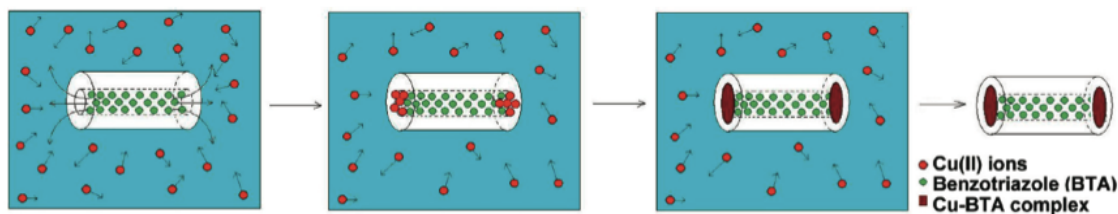


Figure 8. Scheme of end-capping HNTs with insoluble complex. (reprinted with permission from Abdullayev, et al.¹⁹ copyright 2009)

In addition to loading liquid chemicals as described above, other nanomaterials can be loaded into HNTs following specific strategies. Moreover, HNTs can even be used as a template to synthesize special nanostructures. For example, halloysite has been used in the production of silver nanorods by first filling the halloysite nanotube with a saturated solution of silver acetate under vacuum.²⁰ The silver acetate is then reduced by heating, resulting in silver nanorods inside of the halloysite nanotubes (Figure 9).²⁰ This has proven effective for use as a paint filler with antibacterial properties.²⁰

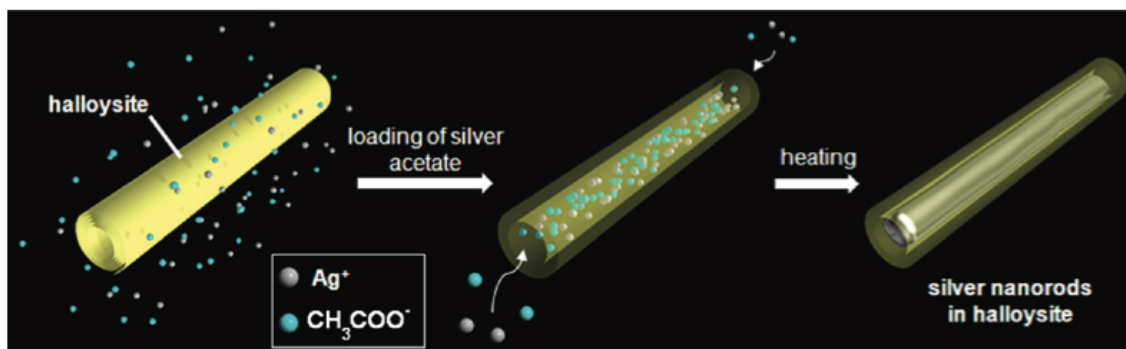


Figure 9. Scheme of halloysite loading for silver nanorods. (reprinted with permission from Abdullayev, et al.²⁰ copyright 2011)

1.4. Preparation of HNT-Based Polymer Nanocomposites

The term nanocomposite is used to describe the combination of organic molecules and the nanofiller with dimensions less than 100 nanometers in at least one dimension.²¹

The advantages of nanocomposites are numerous over traditional composites, including but not limited to enhanced mechanical properties, increased flame retardancy, decreased gas permeability, and increased thermal stability.²² This can be accomplished at low loading levels due to the large surface area and high aspect ratio of the nanoparticles.²² This effect greatly depends on the shape/aspect ratio of the particle, the dispersion of the nanoparticles in the polymer matrix, and the interaction between the filler and the bulk polymer (Figure 10).²²

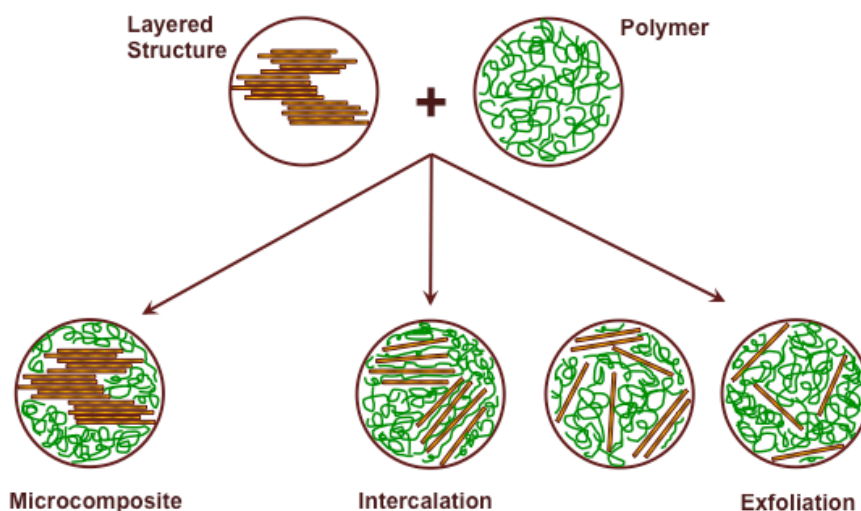


Figure 10. Traditional composite and nanocomposite structure types.

The advantages of the nanocomposite over traditional glass-fiber type reinforcement are not only present in the final product, but also in the processing. A glass-fiber reinforced composite will require different processing than the bulk polymer.²³ The glass-fiber reinforced composite will have a lower melt flow rate, while a nanocomposite, with lower levels of loading will have processing properties much more in line with that of the bulk polymer.²³ With the low loading requirements of a nanofiller, the polymer processing remains largely unaffected.²³

Several approaches have been developed to incorporate HNTs into polymers to prepare polymer nanocomposites, including solution method,^{24, 25} melt mixing,^{22, 26} and in-situ polymerization.^{27, 28}

1.4.1 Solution method

The solution method is probably the most straightforward approach to prepare HNT containing nanocomposites. This approach is particularly suitable for water soluble biopolymers, which typically tend to decompose at relatively low temperatures or even below their melting points, thus excluding the possibility for melt blending.²⁴

For example, pectin/HNT bio-nanocomposites were prepared using a 2 wt% aqueous dispersion of pectin and a pre-determined amount of HNT under magnetic stirring at 70°C. The solutions were then poured into petri dishes and heated at 80 °C for 15 hours, or until all water was evaporated. The films were easily removed and collected.²⁴ In comparison with the pectin/Laponite RD nanocomposites from the same approach, it was found that the deprotonated carboxylic acid groups of the pectin paired well with the lumens of the halloysite, forming very strong interactions. The addition of HNTs improved tensile strength and elongation at break, but degraded other mechanical properties.²⁴ With the solution method, a pectin/HNT nanocomposite was prepared that had mechanical properties rivaling some current plastics.²⁴

Similarly, bio-nanocomposite films were prepared using bovine gelatin and HNT by Voon et al.²⁵ The films was prepared by using a 5 g gelatin per 100 mL of water, 20 g glycerol per 100g gelatin (as a plasticizer), and the desired amount of HNT in 0, 2, 3, 4, 5 g per 100 g of gelatin.²⁵ The films were allowed to dry in atmospheric conditions at 25 °C for 24 h, then they were placed in an oven at 40°C for another 24 h.²⁵ It was found that

the HNT-containing bio-nanocomposites had higher mechanical properties than the bio-nanocomposites containing nano silica prepared via the same approach.²⁵

1.4.2 Electrospinning

Because of the tubular structure of HNTs, researchers explored the spinning of polymer/HNT nanofibers to align the HNTs in the nanofibers to maximize the benefits of HNTs. Electrospinning can be considered a special solution method or an extension of regular solution methods, since it is also based on the same starting mixture. Because of the tubular morphology and ease of dispersion of HNTs, the processing is trivial in regards to electrospinning- no special processing is required for alignment of the HNTs.⁴

Polylactic acid (PLA) can be degraded in the body via acid catalyzed hydrolysis.⁴ To some extent, the hydroxide groups of the halloysite negate the low pH of PLA. The PLA pellets were dissolved in chloroform for 2 hours, where the HNT previously sonicated in N,N-dimethylformamide (DMF) for 15 minutes were added to the solution. The solution was then stirred at 70°C for 2 hours.⁴ A ratio of 3:1 PLA/HNT was used.⁴ With the mixture homogenized, 10 mL of the solution was added to a glass syringe equipped with a 22-gauge needle, with a 22 kV power source and an aluminum foil covered ground plate 15 cm away.⁴

It was found that a 3:1 ratio of chloroform:DMF solution produced bead free nanofibers at a feed rate of 1-4 mL/h (Figure 11 (d) and (e)).⁴ This is primarily due to a higher conductivity of the mixture over pure chloroform⁴. Pure DMF cannot be used due to its low volatility, which created a porous, uneven surface on the nanofiber.⁴ It was also found that by varying the concentration of the HNT, the size of the nanofiber can be controlled, as shown in Figure 11 (f).⁴

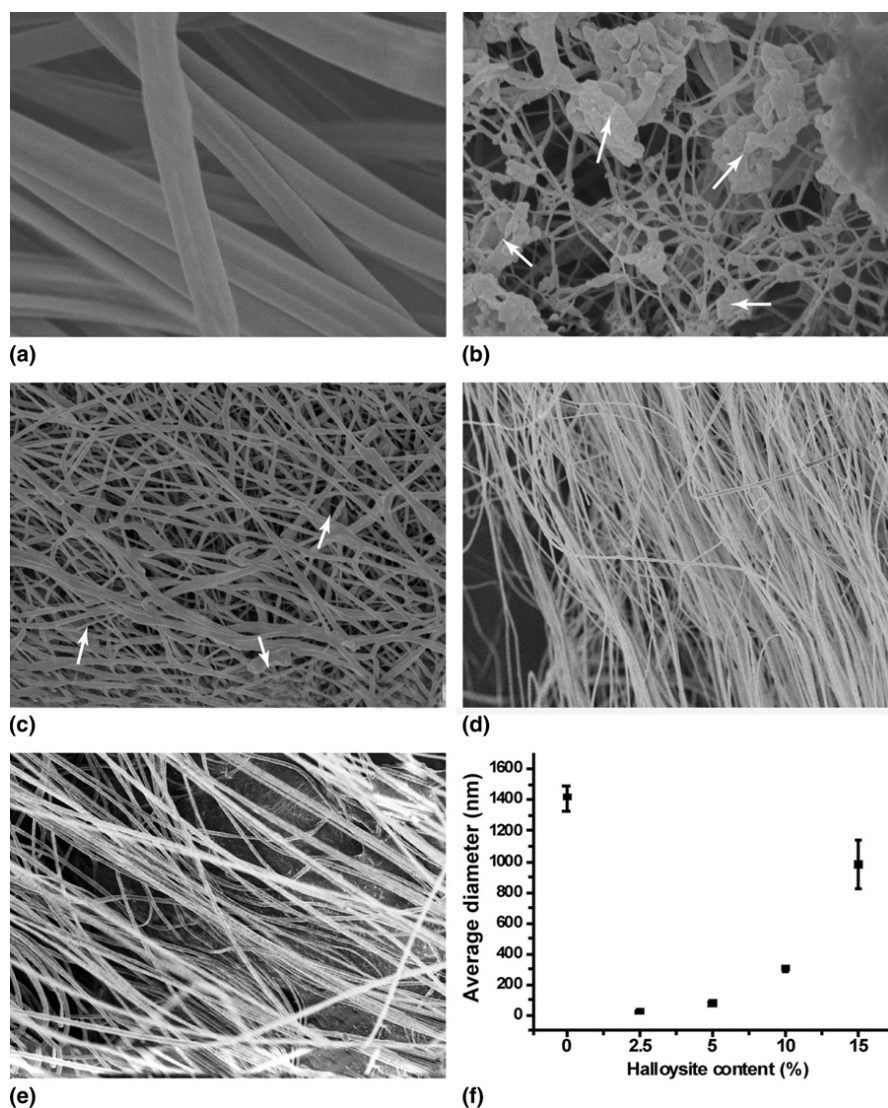


Figure 11. SEM images of electrospun PLA/HNT nanocomposite nanofiber mats. Nanocomposite mats of various concentrations with HNT loading at (a) 0 wt. % (b) 2.5 wt. % (c) 5 wt. % (d) 10 wt. % and (e) 15 wt. % (f) plot of average diameters of nanofibers with respect to HNT loading. Arrows indicate formation of beads in nanofibers. (reprinted with permission from Touny, et al.⁴ copyright 2011)

HNTs encapsulated with medicines were also incorporated into poly(lactic-co-glycolic acid) (PLGA) and subsequently spun into nanocomposite nanofibrous mats (Figure 12).²⁹ The solvent was a 3:1 ratio of tetrahydrofuran (THF): DMF containing 25% w/v PLGA.²⁹ The HNTs were blended (1.23 wt% ratio with the PLGA) into the PLGA/THF:DMF solution for electrospinning at 20 kV with the collection occurring at 15 cm.²⁹ The PLGA/HNT mats were then tested in various MTT assays and cell

cultures.²⁹ The nanofibrous PLGA/HNT mats were effective in slowing the release rate of the encapsulated drug.²⁹

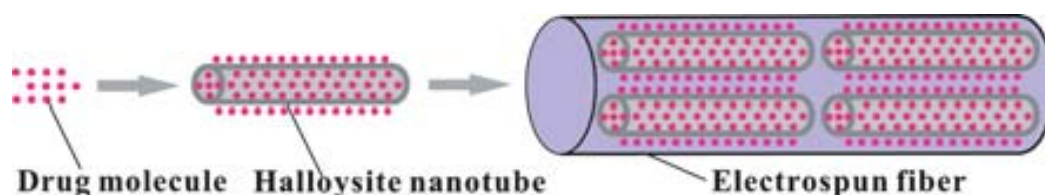


Figure 12. Illustration of drug-loaded HNTs in electrospun nanofibers. (reprinted with permission from Qi, et al.²⁹ copyright 2010)

1.4.3 Melt Mixing

Melt mixing is a popular composite technique for thermoplastics that has transferred well to nanocomposites. The same equipment can be used with only minor changes, such as the need for a lower feed rate of the filler, and equipment changes to help better disperse the nanofiller. The lack of solvent is very attractive in industry, as is the high throughput, but care must be taken to prevent thermal degradation. The variety of techniques that fall under the melt mixing varies greatly in efficiency of mixing, and each technique has its advantages and disadvantages.

Melt mixing has been used to mix wheat starch/HNT nanocomposites.²⁶ A mechanical mixer is used to prepare a blend of 75% starch, 24% glycerol, and 1% glycerol monostearate for 3 hours.²⁶ The blend is then fed into a twin-screw extruder (16 mm screws, 40 L/D at 110-115-120 °C) at the same time as the pre-determined amount of dried HNT to make 2, 4, 6, 8% nanocomposites.²⁶ The product was pelletized and injection molded into testing bars.²⁶ A set of chemically modified-HNTs in 2, 4, 6, 8 (wt.%) were made in the same way, but prior to compounding were treated with benzoalkonium chloride.²⁶

A polyamide 12 (PA12)/HNT nanocomposite was processed with both batch internal mixers (BIM) and a co-rotating twin-screw mini-compounder (TSMC) at 240 °C, and the performance was compared. While both mechanical methods, the TSMC has the advantage of lining up the HNTs in the direction of the shear stresses (Figure 13).²² The TSMC also dispersed the halloysite much more evenly, again attributed to the higher shear force of the TSMC compared to the BIM.²²

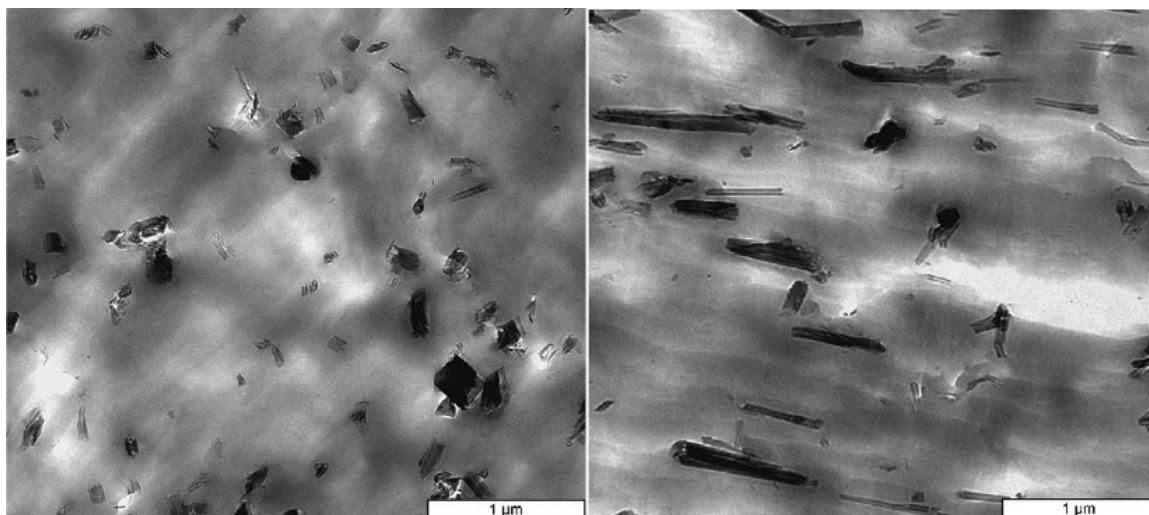


Figure 13. TEM images of PA12/HNTs 10 wt%. Left: cut perpendicularly. Right: cut parallel to the extrusion. (reprinted with permission from Lecouvet et al.²² copyright 2011)

A nanocomposite of xSBR/HNT was prepared with a twin roll mill. A 10 wt% aqueous suspension of HNT and xSBR latex were mechanically stirred for 30 min, then co-coagulated with a 1 wt% solution of calcium chloride, then rinsed until no chloride ions were detected.³⁰ The compound was subsequently dried at 80 °C for 5 h, and then compounded with rubber additives at 150 °C in the twin-roll mill.³⁰

An EPDM/HNT nanocomposite was found to have increased storage modulus over neat EPDM. The EPDM/HNT were loaded with the other compounding agents (zinc oxide, stearic acid, 2-mercapto benzothiazole (MBT), tetramethyl thiuram disulfide

(TMTD) and sulfur (for vulcanization)) into a small scale twin roll mill at 150 °C.³¹ The samples were then compression molded at 150°C until cured.³¹

Similarly, halloysite was treated with γ -methacryloxypropyl trimethyloxysilane (γ -MPS) to improve dispersion in an EPDM nanocomposite. The modified HNTs, EPDM, and other compounding additives were mixed using a lab-sized twin roll mill.¹⁸ The vulcanization and cure time were determined at 150°C using a rheometer, and the samples were further compression molded at 150°C.¹⁸

1.4.4 In situ polymerization

The SDS treated HNTs have been shown to have excellent dispersion in styrene monomers.¹⁴ After purification, the dried HNT was dispersed in an aqueous solution with SDS in 300 mL of deionized water (DI H₂O), and then sonicated for 20 minutes, followed by mechanical mixing for another 20 minutes (Figure 14, next page).¹⁴ The styrene monomer was then added to the round bottom flask, degassed, and mixed at 400 rpm under argon for 18 h at 70-75°C. The resulting material was then washed, dried, and filtered out of the solution.¹⁴ Lin et al found that HNT agglomerates were separated by nanospheres of PS during polymerization, leading to good dispersion of the HNT in the polymer matrix (Figure 15, next page).¹⁴

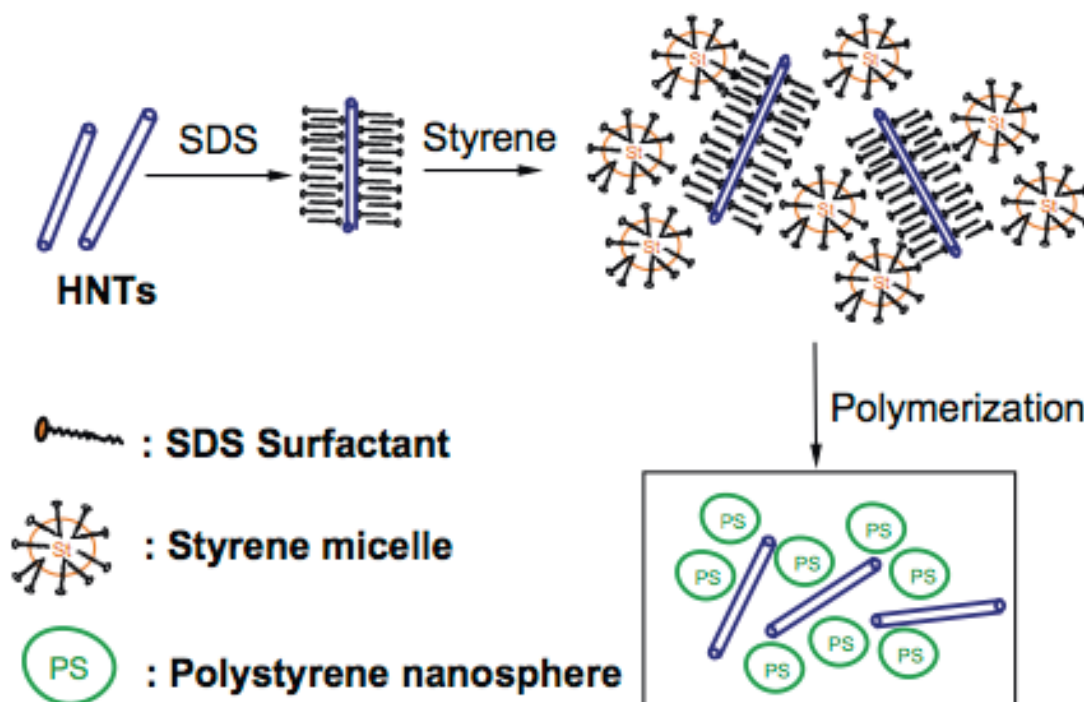


Figure 14. A schematic picture showing the in situ polymerization of styrene in the presence of HNTs. (reprinted with permission from Lin et al.¹⁴ copyright 2011)

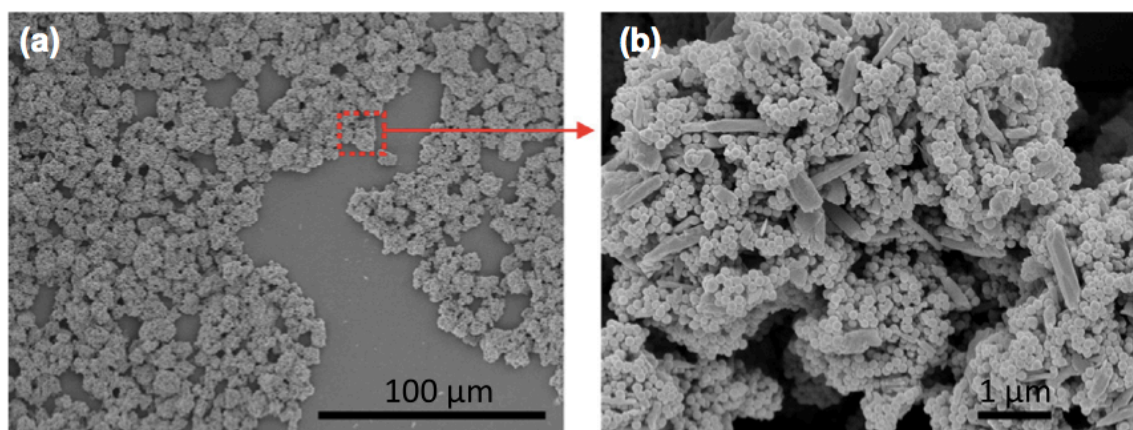


Figure 15. SEM images of PS/HNT nanocomposites. (reprinted with permission from Lin, et al.¹⁴ copyright 2011)

1.4.5 Thermoset/HNT nanocomposites

Crosslinking monomers and curing agents to prepare thermoset based nanocomposites can be considered a special in situ polymerization process, during which

HNTs are dispersed in the mixture of monomers and curing agents after the removal of solvents.

Natural nanotubes have been found to be highly effective in reinforcing epoxy composites. Liu et al. incorporated silane grafted HNTs into epoxy resin to form nanocomposites.¹⁶ The desired amount of HNTs were dispersed in epoxy resin at 70°C and mechanically mixed for 1 h, degassed, then the hardener was added and mechanically mixed for another 10 minutes.¹⁶ The resulting mixture was degassed for 30 min and poured into Teflon-lined steel molds.¹⁶ The epoxy/hardener ratio was 100/40 by weight.¹⁶ The manufacturer's curing schedule was followed, and the molds were then cooled to room temp over 8 h.¹⁶

Another use for HNT nanocomposites is for electronics. An epoxy/cyanate ester resin/HNT nanocomposite was studied for applications in circuit boards, as a low CTE is desired to minimize heat induced damage.²⁸ The general procedure is the same as Liu's previous work.¹⁶ The range of HNT loading ranged from 4 to 12 wt%.²⁸ The cyanate ester resin was chosen because of its compatibility with the HNT's outer silica surface.²⁸

High-impact polystyrene (HIPS) has been used effectively in many automotive and high-impact applications, but its shortcomings are that it absorbs impact by craze formation, which leaves the material weaker for subsequent impacts.⁵ An epoxy/HNT resin could show similar performance without degradation after impacts.⁵ The HNT was dispersed in the epoxy resin at room temperature and stirred at 30 minutes, then the temperature was elevated to 75 °C and stirring was continued for another 2 h.⁵ The mixture was degassed and 4,4'-methylene dianiline (MDA) was added as a hardener with

gentle mixing, and the mixture was poured into a steel mold for curing. The system was pre-cured at 80°C for 2 h followed by a post-cure at 160°C for another 2 h.⁵

The effective use of the shear in a planetary ball mill has been used to evenly disperse HNT into an epoxy matrix prior to the hardener being added.³² The epoxy/HNT mixture was mixed for 25h, with 10 min breaks every 30 mins to prevent overheating, then diluted to the desired ratio mixed with a mechanical mixer at 60°C for 3h.³²

1.4.6 Other methods

Plasma polymerization of styrene has gained use as a high-energy surface for increased interfacial interaction between filler and bulk polymer.¹² First, the HNT was vacuum dried at 80°C for 24 h. The plasma-polymerization is a thin coating of styrene monomer on the halloysite nanotube surface, carried out in a plasma-reactor for 5 min at 5.3 Pa with a plasma power at 20 W. The white HNTs turned pale-yellow after the plasma treatment.¹² The HNT or p-HNT was then mixed with more styrene monomer and polymerized under normal conditions (Figure 16).¹²

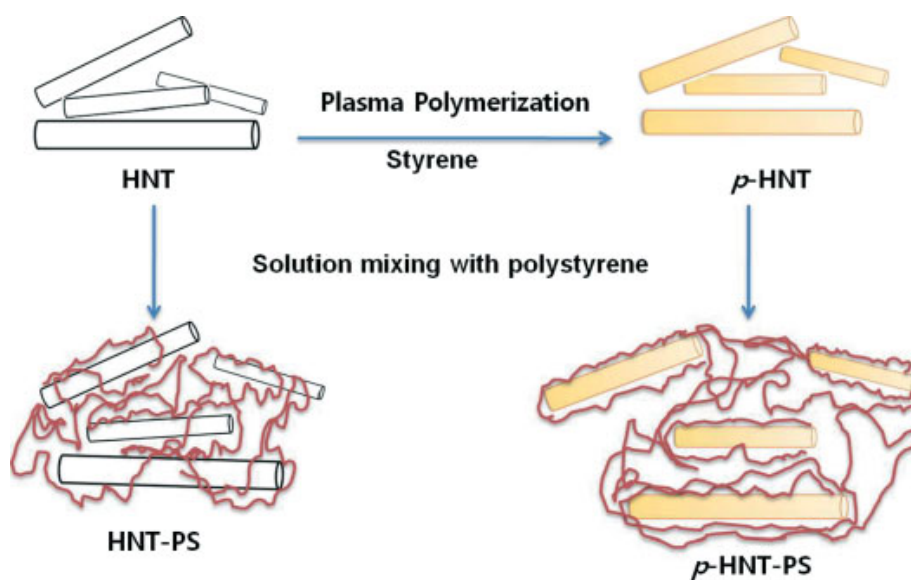


Figure 16. Scheme of plasma treatment of PS/HNTs. (reprinted with permission from Shamsi, et al.¹² copyright 2010)

Supercritical fluid nitrogen (SCF N₂) has also been used as the foaming agent of the mixture of a microcellular poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV)/HNT nanocomposite. The SCF N₂ was injected into the polymer melt, then is injection molded.³³ The expansion occurs at the nozzle (pressure drop) and in the mold.³³ The advantages of microcellular components are that they use less material (lower cost) and can be optimized for increased durability over that of the homo-polymer.³³ It was found that the HNTs were dispersed well into the microcellular components, and that the microcellular PHBV/HNTs composite acted as a rubber, in that crazes were initiated and bridged by the HNTs.³³ This behavior led to an increase in the specific toughness over both the neat homopolymer and of the solid counterpart, while the specific tensile strength was higher in the solid composite counterpart.³³ Also, the interlayer spacing of the HNT was found to be unchanged in both the microcellular and solid composites.³³

1.5. Properties of HNT Based Polymer Nanocomposites

1.5.1 Anti-corrosion and anti-bacterial property

Hybrid sol-gel films are being developed to use as anti-corrosive coatings for aluminum alloys.³⁴ Instead of being capped with an insoluble complex, the nanotubes are entrapped within polyelectrolyte layers (2-mercaptobenzothiazole), which are responsive to damaged areas and their change in pH.³⁴ The sol-gel coating is 1.0-1.2 μm thick.³⁴ Effects of the coating and the 2-mercaptobenzothiazole can be found in Figure 17, next page. Limitations of the loaded HNT for this application are low w/w% (17% maximum) and a slow release rate which limits performance.³⁵

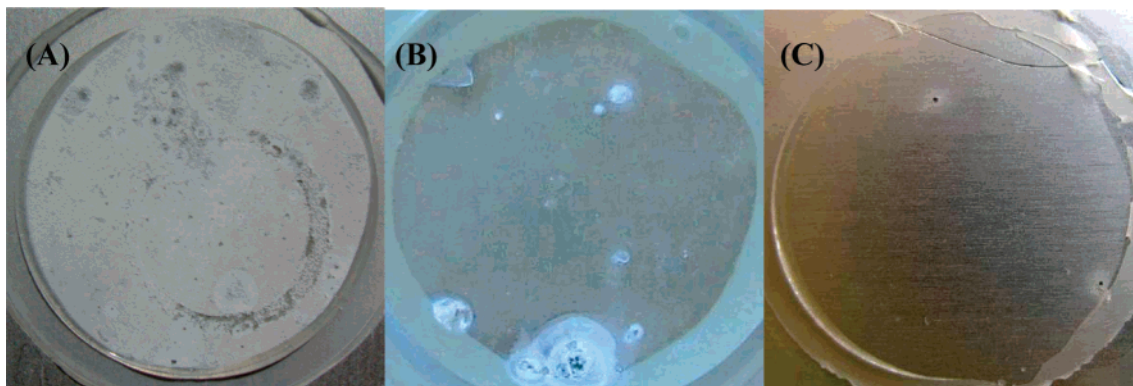


Figure 17. Photos of a 2014 blank after a two week exposure to 0.3 % NaCl. (a) untreated. (b) treated with 2-mercaptobenzotiazole. (c) Alloy treated with hybrid sol-gel halloysite coating. (reprinted with permission from Shchukin, et al.³⁴ copyright 2008)

Loading of HNTs has also been used with a solution of silver acetate to make silver nanorods inside of the nanotubes to provide increased antibacterial performance of painted products (Figure 9, page 10).²⁰

1.5.2 Crystallization of polymers

Using the HNT particles as a site of nucleation for the polyvinyl alcohol (PVOH) film has a significant effect on the properties of the thin films cast from the process. The decrease in T_g (up to 10 °C) was found with the increase of HNT loading, up to 53%.³⁶ The ratio of PVOH/HNTs had little effect on the particle size or distribution; it was found that the HNT tended to coagulate when drying.³⁶ The results of the casting methods and the coagulation methods varied slightly, with the coagulation method showed less nucleation when the casting dried.³⁶ This can be found in Figure 18, next page.

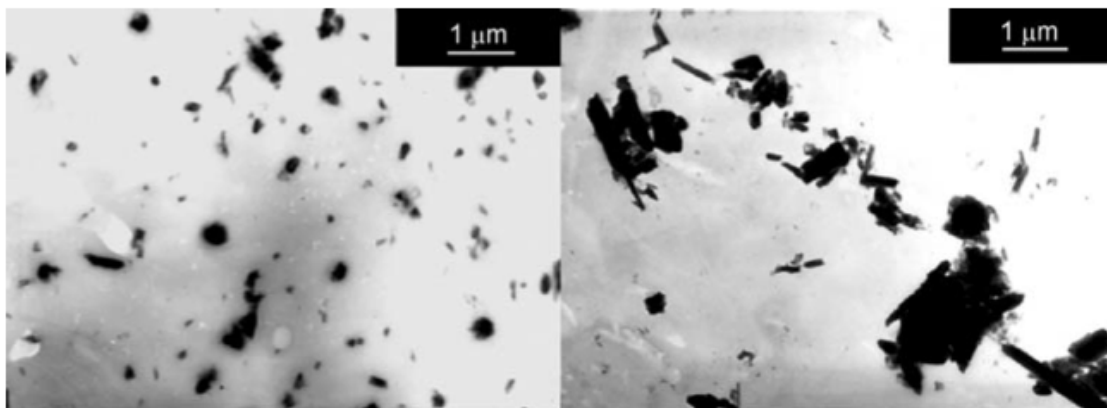


Figure 18. TEM photos of PVOH/HNTs composite films with 2 wt. % HNTs. Coagulation (left) and cast (right). (reprinted with permission from Liu, et al.³⁶ copyright 2010)

As in the HNT/PVOH films, at low HNT concentration, the HNTs act as a nucleation site for crystal growth of the PA12. At higher concentrations, the crystal growth of PA12 is delayed by reduced chain mobility, leading to the formation of much smaller crystallites.²²

The HNTs also act as a nucleation point in isotactic polypropylene for both α -PP and β -iPP, depending on the temperature and the processing conditions.³⁷ It was found that β -iPP was favored under cooling conditions of 115-140 °C, with a maximum at 135 °C.³⁷ No β -iPP was observed outside of that range.³⁷

The addition of HNT to PP has shown to increase the rate of crystallization and temperature at which crystallization occurs, as well as providing a nucleation site for the PP to crystallize.³⁸

1.5.3 Mechanical properties

1.5.3.1 Stiffness and strength

Halloysite nanotubes have been reported to have a similar asymptotic behavior in its Young's modulus when compared to other inorganic nanotubes, with the modulus increasing with an increase in nanotube diameter for single walled halloysite nanotubes,

with multi-layered nanotubes having lower modulus, most likely due to increased imperfections in the multi-walled nanotube structure.⁹ Note that the calculations were performed for the anhydrous form of the halloysite, and may differ for that of the hydrated form.

HNT has been used to reinforce epoxy nanocomposites with great success. With its high modulus, it has been found to bridge crazes/cracks and to stiffen polymer matrices well beyond traditional means even at low loading levels (Table 1).¹⁶ The thermal and mechanical data can be found below in Figure 19.

Table 1. Flexural strength and modulus of epoxy/modified-HNT nanocomposites. (reprinted with permission from Liu, et al.¹⁶ copyright 2010)

Samples	Flexural Strength (MPa)	Flexural Modulus (GPa)
Neat resin	47	3.26
4.0 wt% m-HNTs	100	3.65
8.0 wt% m-HNTs	107	3.85
12.0 wt% m-HNTs	91	3.98

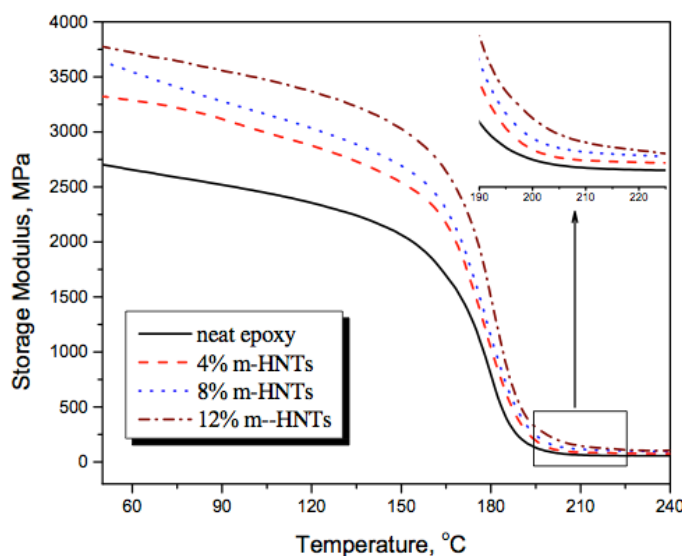


Figure 19. Storage modulus vs. temperature plots of epoxy/modified-HNTs nanocomposites. (reprinted with permission from Liu, et al.¹⁶ copyright 2010)

The use of HNT to increase mechanical properties at low loadings has been well documented. HNT has been shown to improve the tensile strength, tensile modulus, and elongation at break in EPDM/HNT nanocomposites up to 100% phr, with increased values correlated with increased loadings.³¹ The low hydroxyl group concentration on the surface has been attributed to ease of dispersion of HNT into EPDM (Figure 20).³¹ Decreased swelling in toluene was attributed to increased cross linking, which also improved barrier properties, most likely due to the increased tortuous path of the solvent thru the polymer matrix.³¹

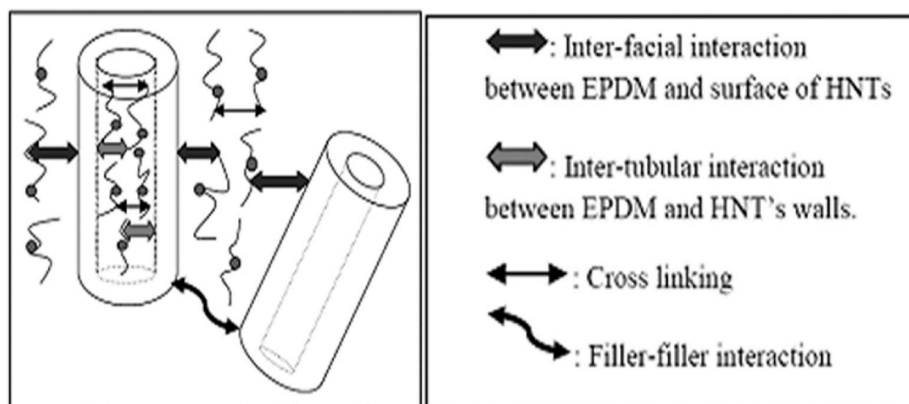


Figure 20. Proposed mechanism of interactions between HNT and EPDM. (reprinted with permission from Ismail, et al.³¹ copyright 2009)

Malic anhydride grafted EPDM has shown increases in tensile strength of 43% were found at 20% phr MAH-g-EPDM/HNT over the neat HNT nanocomposite.¹⁷ It was also determined that the cross linking density of the MAH-g-EPDM/HNT had increased compared to that of the EPDM/HNT.¹⁷

The tensile properties of the full bio-nanocomposite HNT and modified-HNT and wheat starches showed that the deformation mechanism was unchanged in the wheat starch/HNT or wheat starch/modified-HNT nanocomposites, with the typical plastic behaviors maintained.²⁶ However, the significant increases in Young's modulus and

tensile strength were observed, with no noticeable change in ductility.²⁶ It was found that the tensile strength of the untreated wheat starch/HNT nanocomposite rose 28%, while the modified-HNT's tensile strength rose 29% (Figure 21).²⁶

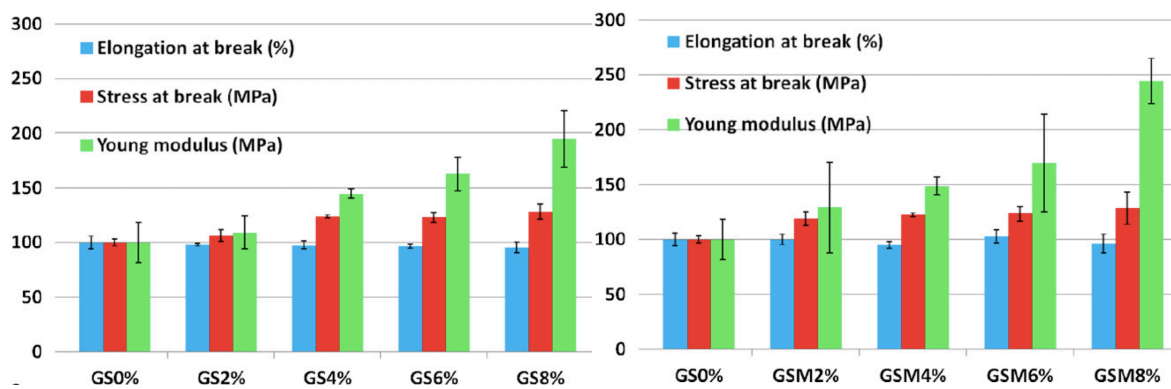


Figure 21. Mechanical testing data of plasticized starch and plasticized starch/HNTs nanocomposites. (left: HNT/wheat starch nanocomposite, right: MHNT/wheat starch nanocomposite. (reprinted with permission from Schmitt, et al.²⁶ copyright 2012)

Halloysite has been functionalized with MAH-g-EPDM (ethylene propylene diene monomer grafted with maleic anhydride) through hydrogen bonding. The mixing of MAH-g-EPDM with HNT and other materials was done with a small-scale two-roll mill at room temperature for 20 minutes.¹⁷ The samples were then compression molded at 150 °C, and left for a time based on their predetermined cure values.¹⁷ It was found that without the maleic anhydride grafting, the halloysite nanotubes cannot interact with the non-polar surface of the EPDM.¹⁷ The strong hydrogen bonding that occurs between the HNT and the MAH-g-EPDM was found to increase the tensile strength to a significant degree except at 100 phr, as seen in Figure 22, next page.

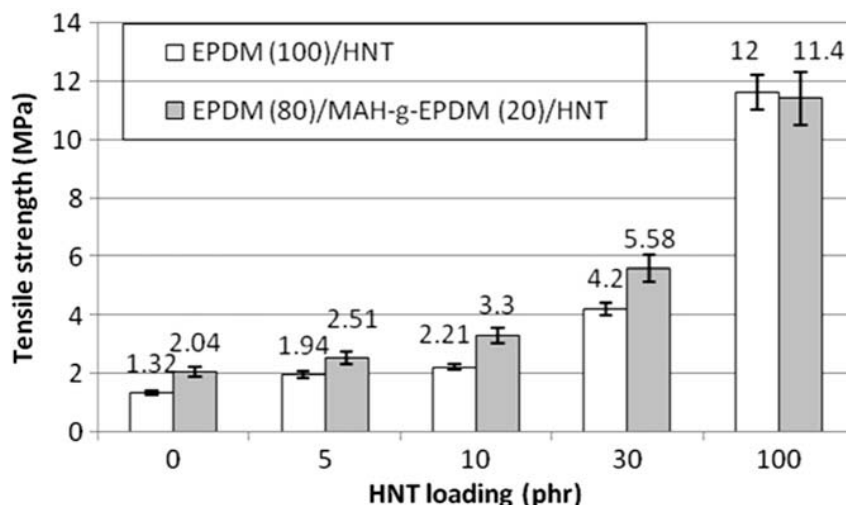


Figure 22. Tensile strength comparison of unmodified EPDM/HNT and MAH-g-EPDM/HNT nanocomposites. (reprinted with permission from Pasbakhsh, et al.¹⁷ copyright 2009)

HNT has been found to provide a nucleation site for the PVOH film, and was found to have a significant effect on the mechanical and thermal properties of the resulting PVOH films.³⁶ Images can be found in Figure 17 (page 22).

In both the batch internal mixer and the twin-screw mini-compounder PA12/HNT nanocomposites, the storage modulus was found to have increased at all temperatures, increasing with HNT concentration, with the greatest improvement shown in the twin-screw mini-compounded nanocomposites.²² This increased performance of the twin-screw mini-compounded nanocomposites is most likely due to better dispersion and the alignment of the HNTs.²² A decrease in T_g was found for both samples at low concentrations, most likely due to reduced chain entanglements of the PA12 chains because of the disrupted chain stacking, but at high concentrations, the PA12/HNT interactions dominated, and an increased T_g was observed, but still lower than that of the neat PA12. The BIM nanocomposites showed increased T_g , most likely due to reduced chain mobility.

1.5.3.2 Fracture toughness

The straight morphology of the HNTs prevents the nanotubes from entangling like carbon nanotubes (CNTs), which makes dispersion of HNTs in viscous liquids much easier than CNTs.⁵ Difficulty occurred in evenly dispersing the HNTs in the epoxy; there were epoxy-rich regions and HNT-rich regions in the final nanocomposites, although even in the agglomerations of HNT the area between the HNTs was still filled with epoxy.⁵ In a SEM study of the fractured surfaces showed some significant pullout of the HNTs, but this was not the fracture arresting mechanism.⁵ The main crack-arresting mechanism was attributed to the formation of many micro-cracks with a length ranging from 100 nm to 1 μm , with the cracks bridged by multiple HNTs (Figure 23).⁵ The formation of these micro-cracks helped to disperse energy of the initial impact, but the bridging of the gaps by the HNTs prevented the formation of larger cracks that would lead to total failure, similar to the craze formation of HIPS (Figure 24, next page).⁵

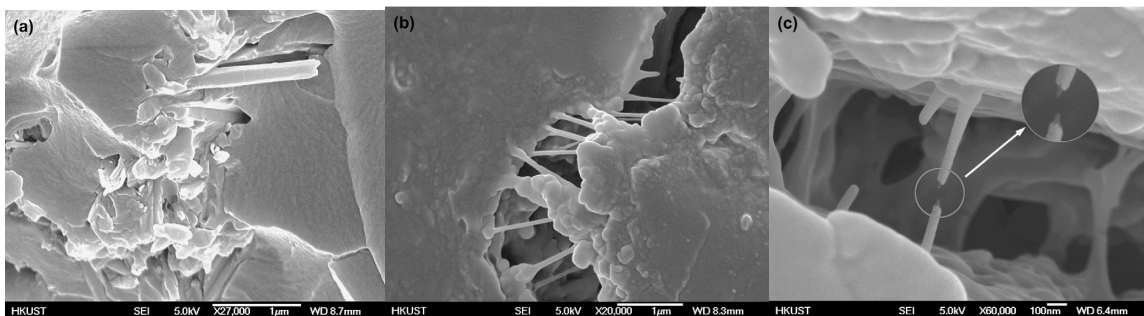


Figure 23. SEM micrographs of fractures of epoxy/HNT nanocomposite. (a) HNT pull-out (b) HNT-rich zone with crack bridging, (c) HNT fracture showing inner layers pulling out from outer layers. (reprinted with permission from Ye, et al.⁵ copyright 2007)

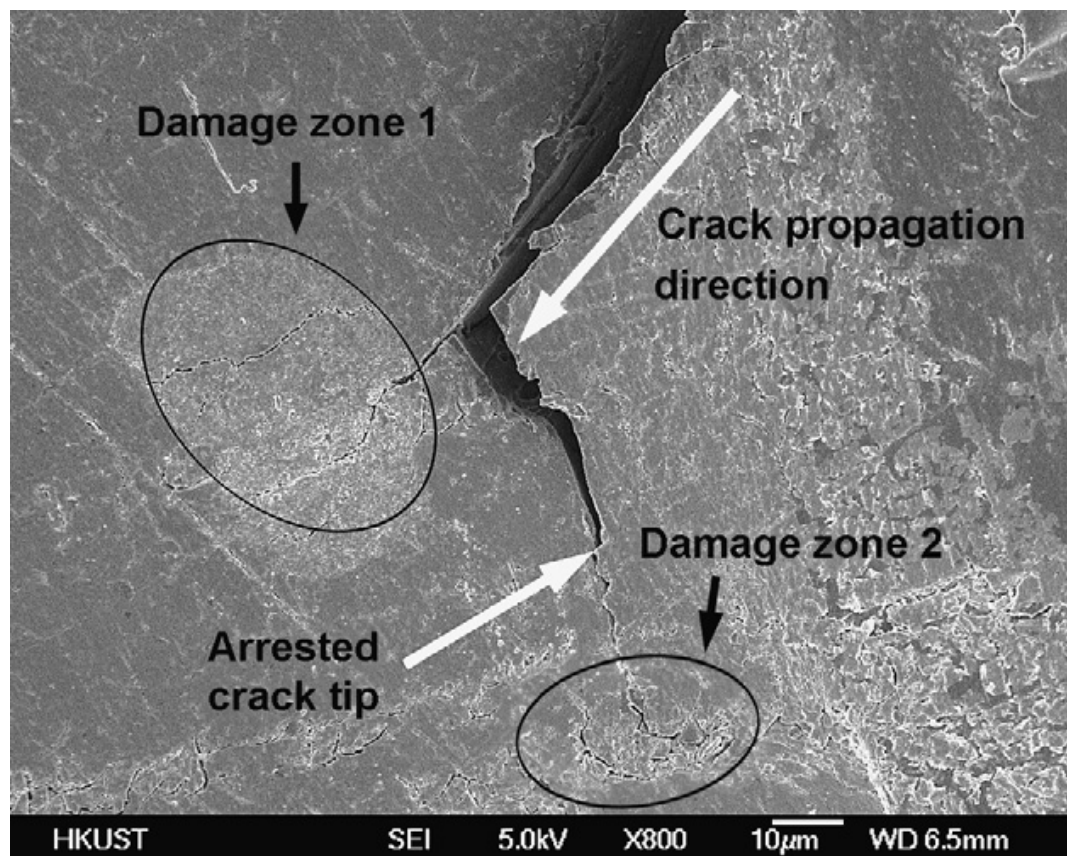


Figure 24. SEM images of crack arresting of a 2.3 wt.% epoxy/HNT nanocomposite. (reprinted with permission from Ye, et al.⁵ copyright 2007)

In typical layered clays, it has been shown that most cracks are initiated by a separation of the interlayers of the clay itself. Halloysite does not show this behavior, most likely due to its strong hydrogen bonding between layers and its tubular morphology.¹⁵

The impact strength of PS/HNT nanocomposites were significantly improved over that of neat PS (by 300% in the 5% nanocomposite).¹⁴ The normal failure mode of PS is initiation of a craze, followed by rapid craze propagation. This typically occurs without much resistance, leading to low toughness. By the addition of HNT to the PS matrix, the stiff HNT can bridge and arrest forming crazes. Three significant behaviors were observed with the PS/HNT nanocomposite: first, a stress build up at the PS/HNT

interface, which lead to the formation of large crazes formed at the same area which were bridged and arrested by nearby HNTs; pullout of HNTs from the surrounding PS most likely due to weak interaction between the PS and HNTs; and plastic deformation of the PS around the embedded HNTs.¹⁴ Similar behavior can be seen in other polymers.

An improvement of almost 300% of the notched Izod impact test of a 5 % wt. PS/HNT nanocomposite over the PS homopolymer was observed by Lin, et. al. (59.1 ± 4.8 J/m to 19.5 ± 3.6 J/m).¹⁴ With additional HNT loading to 10% wt., the performance fell off dramatically to only 35.0 ± 6.9 J/m (Figure 25).¹⁴ It appears that the main crack arresting mechanism is the bridging of cracks by the HNTs. (Figure 26, next page).

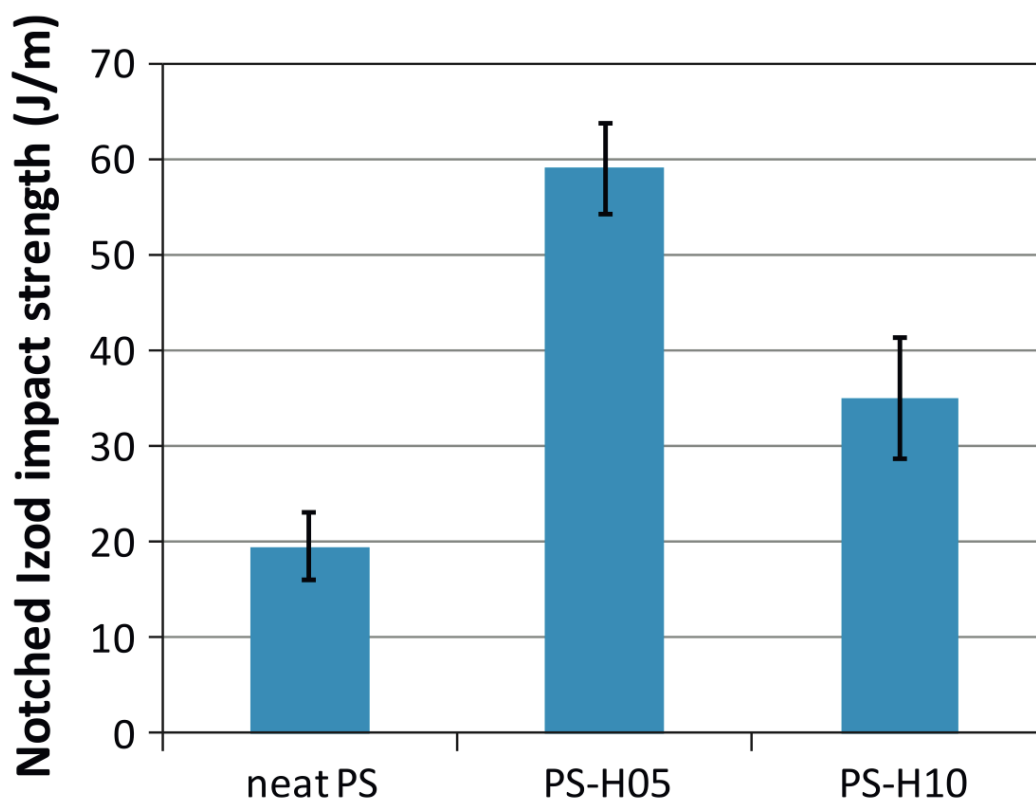


Figure 25. Notched Izod impact strength of PS/HNT nanocomposite and neat PS. (reprinted with permission from Lin, et al.¹⁴ copyright 2011)

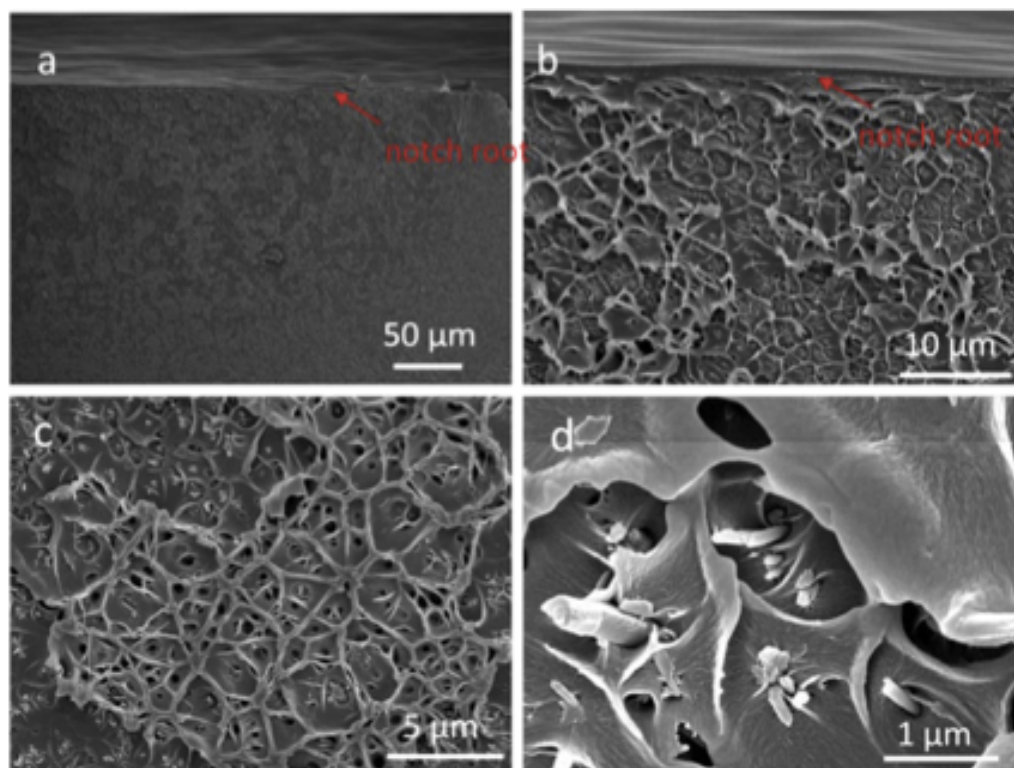


Figure 26. SEM micrographs of the fracture surface of the PS-H05 nanocomposite. (reprinted with permission from Lin, et al.¹⁴ copyright 2011)

The toughening mechanism of epoxy/HNT nanocomposite is attributed to crack bridging, crack deflection, and plastic deformation of the epoxy around the HNTs.¹⁵ This behavior is expected in a very rigid system, with the addition of a stiff nanofiller, regardless of the filler type. With the tubular morphology of the HNT, it was easily dispersed into the viscous epoxy. Some of the HNTs were partially unfolded due to the intercalation of phenylphosphonic acid (PPA).¹⁵ The unfolding of the HNT led to an increased surface area, which leads it to further improvements in barrier properties and increased epoxy-halloysite interactions. However, the PPA-intercalated HNT/epoxy matrix showed decreased tensile strength and modulus over the untreated epoxy/HNT nanocomposite, but the PPA-intercalated epoxy/HNT showed an increase in the fracture toughness over the untreated HNT-epoxy.¹⁵ Both the neat epoxy and the PPA-intercalated

epoxy/HNT showed unstable crack propagation, but all epoxy/HNT nanocomposites showed improved performance over the neat epoxy. The HNT-containing composites showed an increase in the roughness over the neat epoxy matrix, which shows that the crack propagation was deflected by the presence of rigid nanoparticles. However, if the HNTs are not well dispersed, the HNT agglomerates will initiate crack formation, leading to decreased toughness. It was shown that plastic deformation of the epoxy around the HNT was the main source of reinforcement.¹⁵ It was also shown that micro-cracks were present perpendicular to the crack direction, showing that the HNT did act as a stress riser in the nanocomposite (Figure 27).

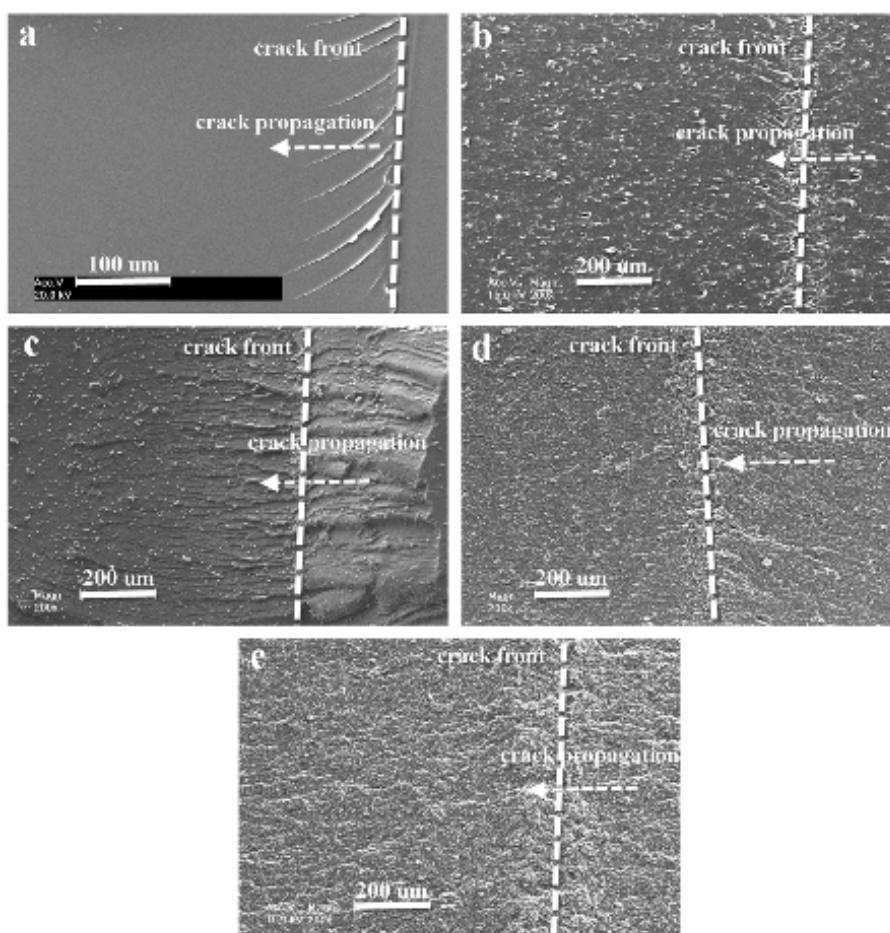


Figure 27. SEM images of epoxy and epoxy/HNT fracture specimens. (reprinted with permission from Tang, et al.¹⁵ copyright 2011)

Halloysite has been found to reduce the cracking of latex films during the drying process.³⁹ The formation of cracks and crazes are normally a part of the drying process, formed to relieve mechanical and tensile stresses induced by the drying process, specifically the shrinking process (Figure 28).³⁹ Similar behavior has been seen when HNTs were loaded into paint, as an increase of the paint tensile strength was observed (Figure 29).²⁰

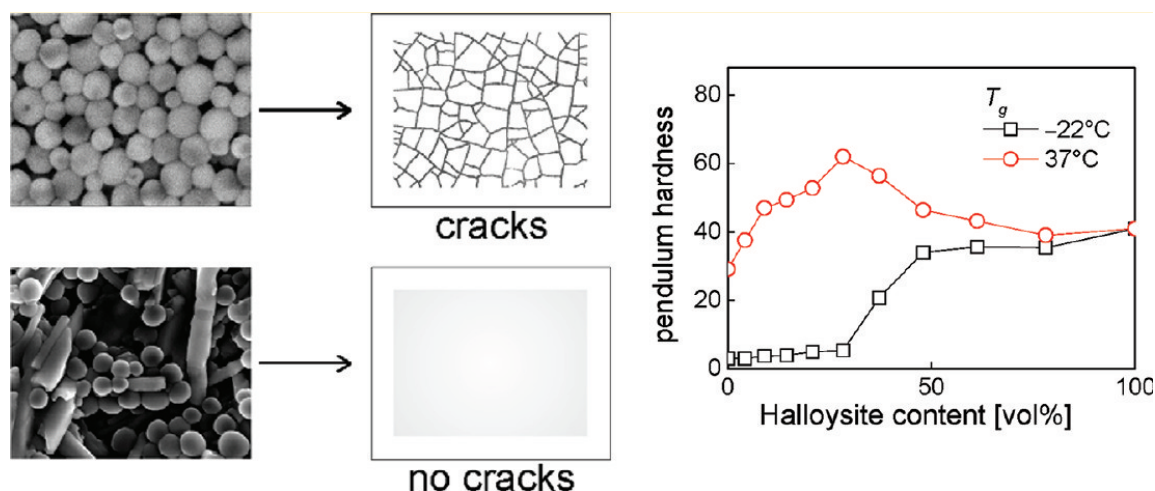


Figure 28. Effects of HNT on drying in latex films. (reprinted with permission from Qiao, et al.³⁹ copyright 2012)

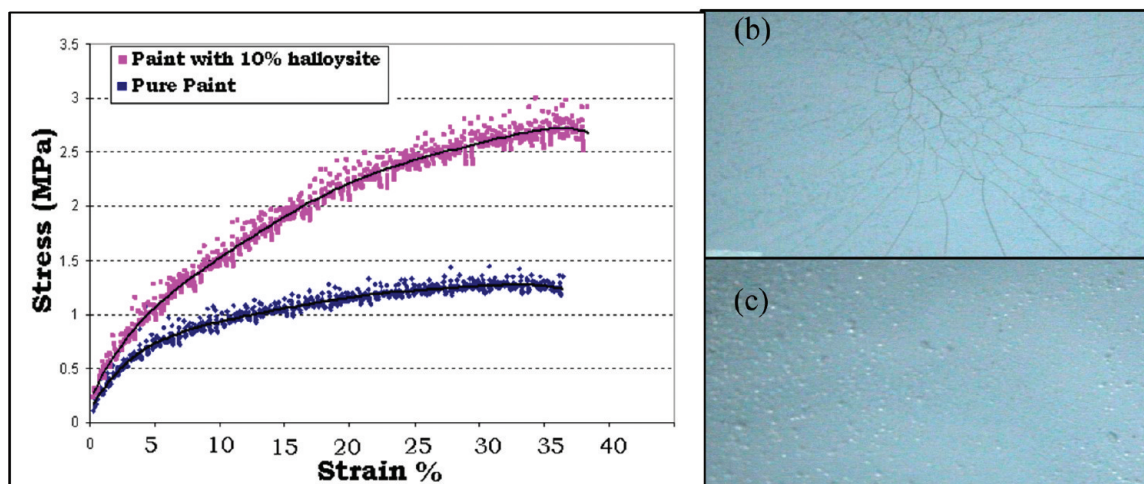


Figure 29. Stress/strain curve of paint/HNT nanocomposite (a), pure paint (b), and HNT/paint nanocomposite with 10% HNT. (reprinted with permission from Abdullayev, et al.²⁰ copyright 2011)

1.5.4 Thermal properties

1.5.4.1 Glass transition temperature

Among the most critical properties that affect the physical characteristics of a polymer is the glass transition temperature (T_g).⁴⁰ The ability for the individual polymer chains to move determines the bulk polymer's amorphous or crystallinity, which determines how rubbery or glassy a polymer acts in a given application. The interfacial interactions between the polymer chain and a nanoscale filler, such as halloysite nanotubes, can change greatly from the properties of the bulk polymer.⁴⁰

1.5.4.2 Thermal stability

The random nature of the HNTs in the batch internal mixer prepared nanocomposite led to an increased thermal stability (12°C), most likely due to improved barrier properties over that of the twin-screw mini-compounder prepared nanocomposite, but in both cases the thermal stability of the nanocomposites were superior to that of the neat PA12.²² By improving the barrier properties of the composite, the internal region of the composite is delayed in degradation. It has been hypothesized that HNTs improve the thermal stability of composites by absorbing the volatile parts of the composite into the nanotube, delaying its release.²² While not as effective as a two-dimensional clay, it still provides some increase in thermal stability, either in absorption of the evolved gas into the hollow tubular structure, or by agglomerates creating a heat-shielded region.

PHBV has several known issues, such as a narrow processing window (20 °C) and poor mechanical properties, and poor thermal stability, but interest is still high due to the hydrophobic biodegradable nature of the polymer. Many shortcomings can be overcome with the addition of plasticizers and other additives, but the low molecular

weight additives tend to migrate to the surface over time, leading to brittleness and the same issues as the product ages. The addition of HNT lead to an increase in thermal stability.¹⁴ The improvement in the HNT based nanocomposite was attributed to the organic vapors becoming trapped inside the nanotubes, and the ability for the HNT to absorb heat within the nanocomposite.¹⁴

HNT has shown improvements in thermal stability, reduction of cell size, and increased cell density of the Poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV)/HNT nanocomposite when compared to that of a neat PHBV sample.³³ The interlayer spacing of the HNT remained unchanged, even after incorporation into the PHBV nanocomposite system, and furthermore the HNTs were well dispersed within the nanocomposite.³³ The addition of HNT showed a decrease in the average cell size of the microcellular components, and increased the density of the composite.³³

CHAPTER II

POLY(LACTIC ACID)/HALLOYSITE NANOTUBE NANOCOMPOSITES

2.1 Introduction

Poly(lactic acid) (PLA) is a biopolymer derived from the ring opening polymerization of lactide (Figure 30).⁴¹

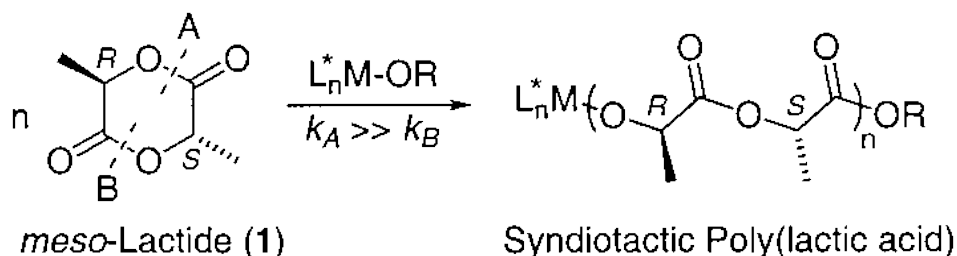


Figure 30. Scheme of ring opening polymerization of *meso*-Lactide. Catalyst is a Lanthanide metal- organic catalyst. (reprinted with permission from Ovitt, et al.⁴¹ copyright 1999)

PLA can be atactic, syndiotactic, isotactic L- or D-poly(lactic acid) (usually referred to as PLLA or PDLA).⁴¹ The accepted mechanism for the ring opening polymerization is a cleavage of the oxygen-acyl bond by a catalyst, usually a metal alkoxide.⁴¹ Most commonly used is tin (II) ethylhexanoate (Sn(Oct)₂) due to high molecular weights and low polydispersity.⁴²

PLLA can be processed much like poly(ethylene terephthalate) (PET), by blow molding, clear films, and injection molding.⁴³ PLLA has a T_g of 60 °C, which is unusually high for a thermoplastic, and a T_m of 130 to 180 °C, which is lower than most thermoplastics.⁴³ These two conditions together create a rather narrow processing window, and depending on the cooling, PLLA can form α , β , or γ crystalline regions.⁴³ The α -crystalline regions

are formed either in the melt or by cold crystallization, β -crystalline regions are formed by drawing or spinning the polymer at high temperatures, and γ -crystalline regions are formed by epitaxial crystallization.⁴³

PLA has been found to have performance similar to polyethylene and polystyrene, with much faster biodecomposition and lower environmental impact.⁴⁴ Decomposition of PLLA results in a mixture of optically active L-lactide and D-lactide monomers and oligomers under low temperatures, but this can be pushed to favor L-lactide at higher temperatures (90% L-lactide if the temperature is above the T_m of PLLA).⁴⁴

PLA has been a very attractive bioplastic for use in agriculture, biomedical devices, and as packaging materials due to its easy compostability and biocompatibility.⁴⁵ Grafted PLLA has been shown to be biocompatible.⁴⁶

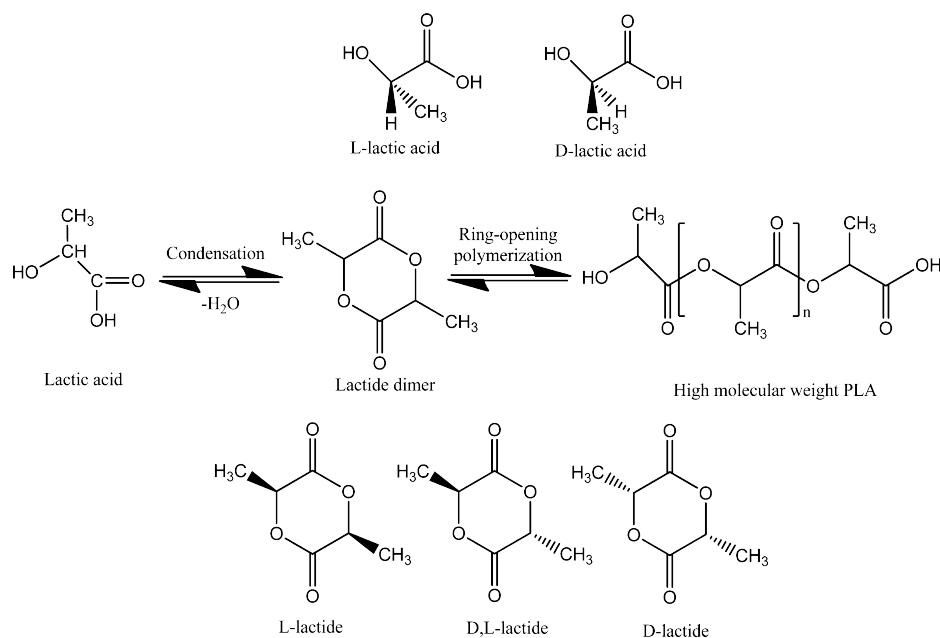


Figure 31. Stereoisomers of lactic acid, synthesis of PLA, and diastereoisomeric forms of lactides. (reprinted with permission from Ray, et al.⁴⁷ copyright 2012)

PLA-clay nanocomposites have shown great promise as biodegradable nanocomposites, as the PLA is easily degradable, and the residual clay is benign to humans and the environment (Figure 31).⁴⁷ At the end of a HNT/PLA nanocomposite

product's life, the PLA will degrade into CO_2 , H_2O , and clay.⁴⁷ Biodegradation of PLA/Clay nanocomposites has been shown to occur at a higher rate than that of neat PLA (Figure 32).⁴⁷

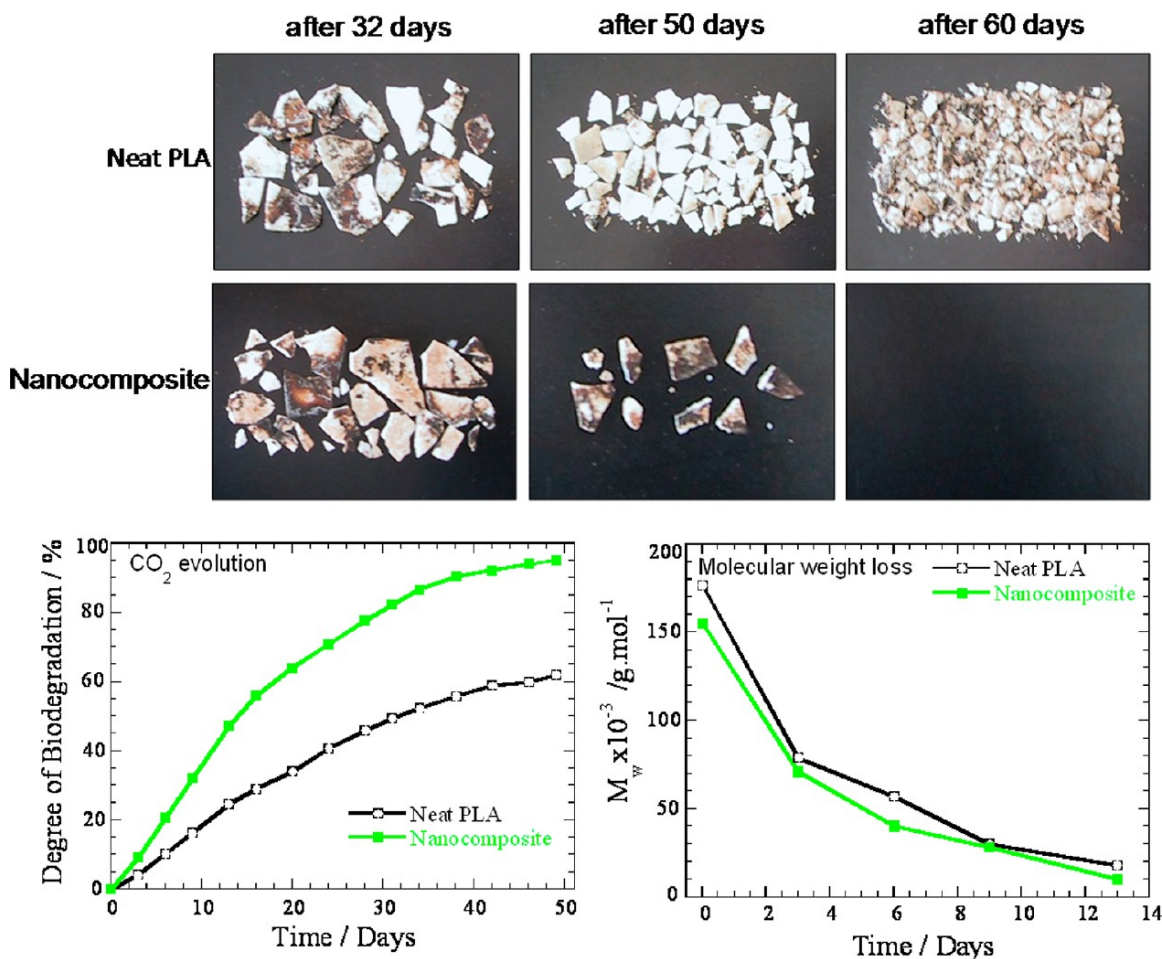


Figure 32. Biodegradation of neat PLA versus PLA/Clay nanocomposites. (reprinted with permission from Ray, et al.⁴⁷ copyright 2012)

Melt-extrusion or melt-blending are more environmentally friendly than other methods and of interest to industry due to a lack of solvents and its compatibility with existing production equipment.⁴⁷ Good nano-level dispersion of the HNT with no degradation of the PLA is key to a successful PLA/HNT nanocomposite.⁴⁷ Functionalization of the surface of the HNT increases the interaction between the HNT

and the PLA, as does copolymerization of the PLA with groups with high affinity for the silica surface of the HNT.⁴⁷

Halloysite nanotubes have been used as substitutes for carbon nanotubes (CNTs) and boron nitride nanotubes due to their low cost and unique surface chemistry, which allows them to be preferentially internally loaded with a filler.^{48, 49} Halloysite is found in natural deposits around the world, and its processing is limited to mining and drying the halloysite clays, keeping cost low.⁴⁸

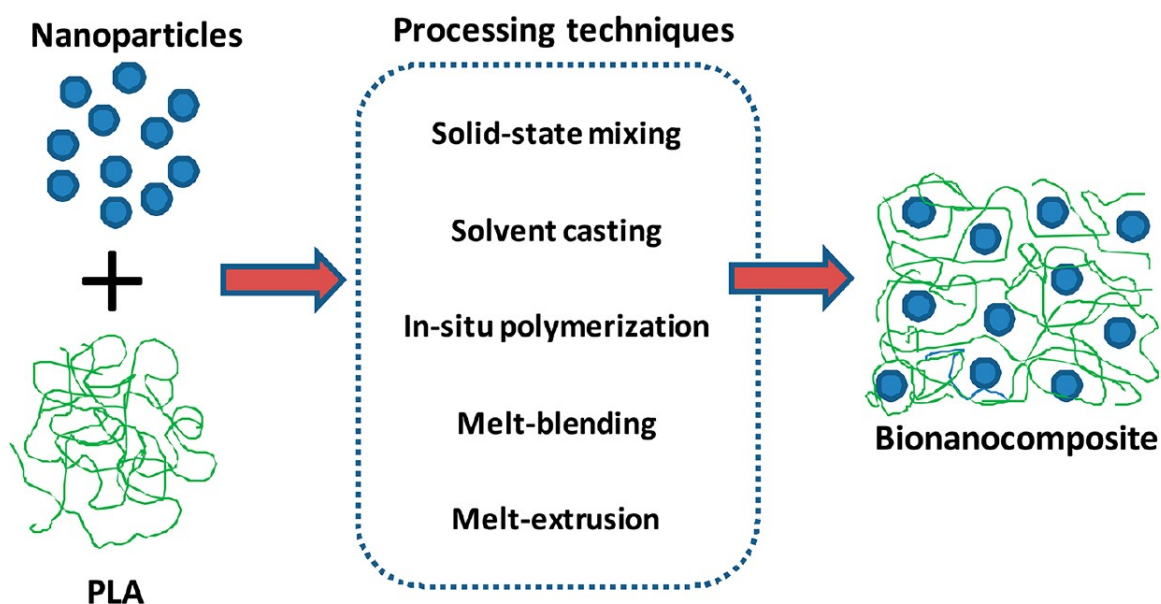


Figure 33. Methods used to prepare polymer nanocomposites. (reprinted with permission from Ray, et al.⁴⁷ copyright 2012)

Simply putting a nano-clay and a polymer together does not necessarily form a nanocomposite (Figure 33). Sometimes either the polymer or clay must be functionalized in order to compatibilize it with the other species to truly form a nanocomposite, and one must properly exfoliate and/or disperse the clay filler into the polymer (Figure 34, next page).²¹ One advantage HNT has over other nanofillers is that it increases strength without loss of ductility.⁴⁵

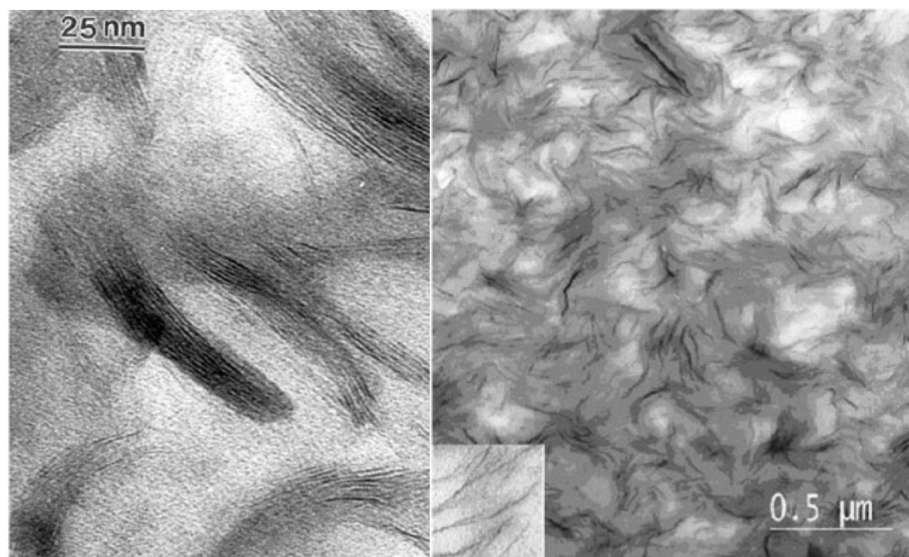


Figure 34. TEM images of intercalated composite (left) and exfoliated nanocomposite (right). Inset shows magnified images of exfoliated clay layers. (reprinted with permission from Chen, et al.²¹ copyright 2004)

While two-dimensional nanoplatelets, such as montmorillonite (MMT) have received much interest recently, one-dimensional nanofillers have had the spotlight for years. The primary difficulty with two-dimensional inorganic clays is the exfoliation process. Montmorillonite and kaolinite clays have high aspect ratios, but difficulty dispersing them during nanocomposite processing has lead to limited uses.²³

2.2 Experimental

2.2.1 Materials

Halloysite was received from Applied Minerals INC (1415:JM). Sodium dodecyl sulfate (SDS, $\geq 98.5\%$) was received from Sigma-Aldrich. Poly(lactic acid) was received from NatureWorks, LLC and is general purpose grade 4042D. Hydrogen peroxide was purchased from CVS pharmacy, 3% H_2O_2 . The PLA 4042D and Halloysite were dried for 24h in a vacuum oven at 60°C prior to any processing.

2.2.2 Purification of HNT

The raw HNT was then treated with a 3.0% H_2O_2 solution, magnetically stirred for 30 minutes, ultrasonicated for 30 minutes, and then filtered with a mesh filter to remove organic contaminants. The small amounts of ferrous contaminants were removed during this process with a neodymium magnet prior to filtration. The resulting solid was then placed in a petri dish and dried at 80°C for 24 hours. The HNT was then placed in a vacuum oven at 60°C overnight, and the remaining solid was ground with an agate mortar and pestle before any further treatments.

2.2.3 SDS treatment

SDS is well known to stabilize dispersions in polymers, and is used extensively in industry as a general-purpose surfactant due to its low cost (Figure 35). Previous studies have utilized SDS to emulsify HNT and facilitate a homogeneous mixture during aqueous polymerizations.¹⁴ The resulting emulsions have shown success in improving the overall properties and homogeneous nature of the PP/HNT nanocomposites, with an increase in the impact resistance of the PP/HNT nanocomposite over that of the neat PP.¹⁴ The use of a rigid filler has been well documented to increase the modulus of an already stiff polymer.⁴⁷

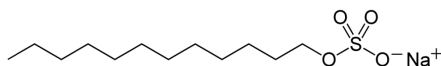


Figure 35. Sodium dodecyl sulfate

After the H_2O_2 purification, the sample was treated with a 1.0 wt.% sodium dodecyl sulfate (SDS) solution. The HNT-SDS was then centrifuged, supernatant liquid discarded, and the resulting solid was triple rinsed with DI before being dried in an oven at 80°C for 24 h, then further dried in the vacuum oven at 40°C overnight. The resulting HNTs can be seen in Figure 36, next page.

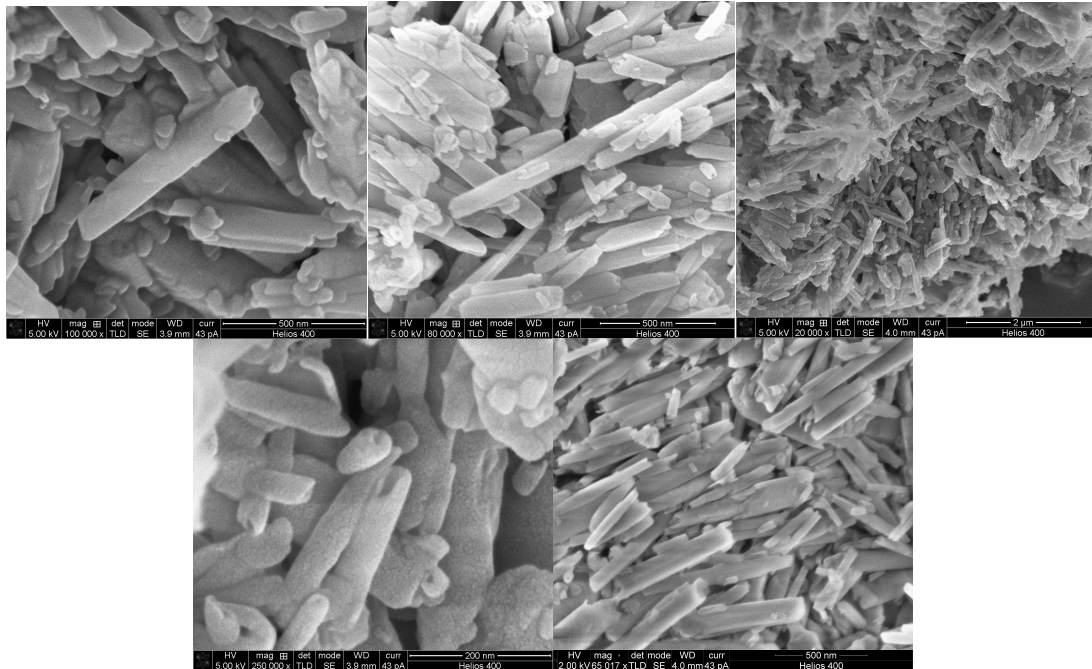


Figure 36. HNTs after SDS treatment (HNT-SDS).

2.2.4 Compounding

All compounding was done with the HAKKE MiniLAB II, with co-rotating screws (Figure 37). Temperatures were set to 185 °C with a 3 minute cycle time and a rotating speed of 200 RPM. It is imperative that thorough mixing occur to promote the best physical and mechanical properties of the nanocomposite, but without mechanical damage of the nanofiller itself, or degradation of the PLA matrix.⁴⁷



Figure 37. Twin-screw extruder (Hakke MiniLAB II internals).

Samples were then pelletized and injection molded with the Hakke MiniJet into type I test bars with a chamber temperature of 210 °C, mold temperature of 80 °C, an injection pressure of 600 bar for 5 seconds, and a post pressure of 350 bar for 3 seconds.

2.2.5 Characterization

Thermal stability of the nanocomposite was evaluated by thermogravimetric analysis and differential scanning calorimetry. TGA samples were tested using the TA Instruments Q50 under a 60.00% air/40.00% argon atmosphere. DSC was performed using the TA Instruments Q200, using aluminum DSC pans.

Mechanical tensile testing was performed using the Instron 5500 with Bluehill software.

Scanning electron microscopy (SEM) images were collected using the field emission-SEM (FE-SEM) from FEI (Helios Nanolab 400).

2.3 Data and Analysis

2.3.1 Thermal analysis

2.3.1.1 Thermal Gravimetric Analysis

The small difference between the as-received (raw) HNT and the H₂O₂ treated HNTs illustrates that the H₂O₂ treatment is effective in removing the organic contaminants off of the HNTs prior to further treatment. It appears that less than 1% of the total weight of the HNTs was due to organic contamination. Figure 38, next page, supports that the hydrogen peroxide treatment did not affect the thermal decomposition temperature of the HNT.

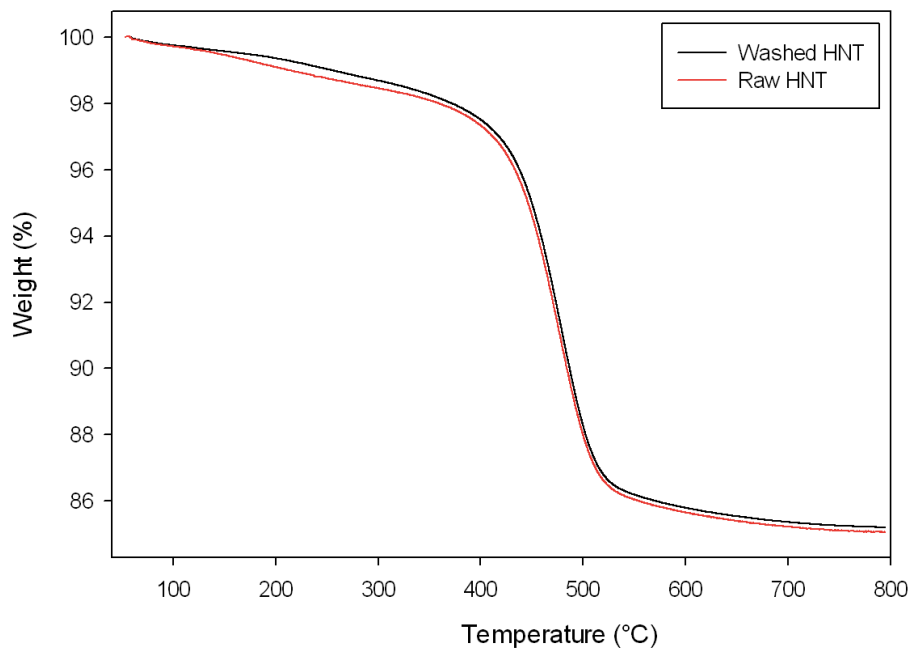


Figure 38. TGA thermogram of as-received (raw) HNTs compared to peroxide treated HNTs.

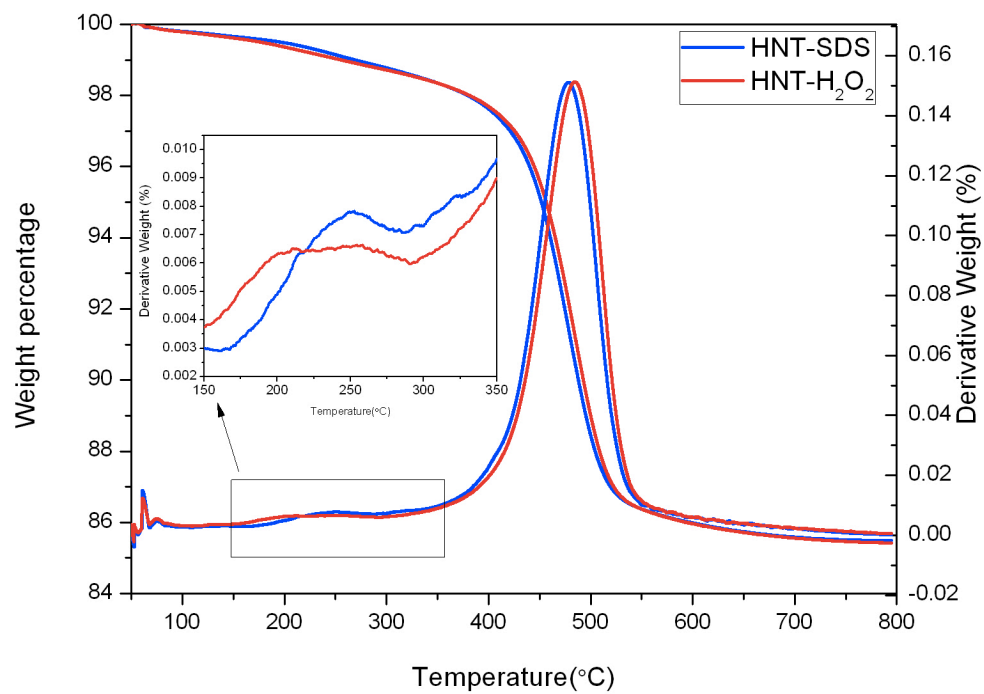


Figure 39. TGA thermogram of HNTs after hydrogen peroxide treatment and post-SDS treatment, and derivative weight percent curves. Inset shows addition of SDS onto HNTs.

Figure 39, previous page, shows that only a small amount of SDS was added to the HNTs. This SDS treatment did not greatly affect the thermal behavior of the HNT. SDS has been

HNT has been associated with an increase in thermal stability, reported in various other polymer nanocomposite systems.^{5, 14, 33} Figure 40 showed little change in behavior due to the addition of up to 10% HNT into the PLA in our system. Other methods should prove to be more definitive, as TGA is not the only method of thermal analysis with respect to thermal stability or flame retardancy.

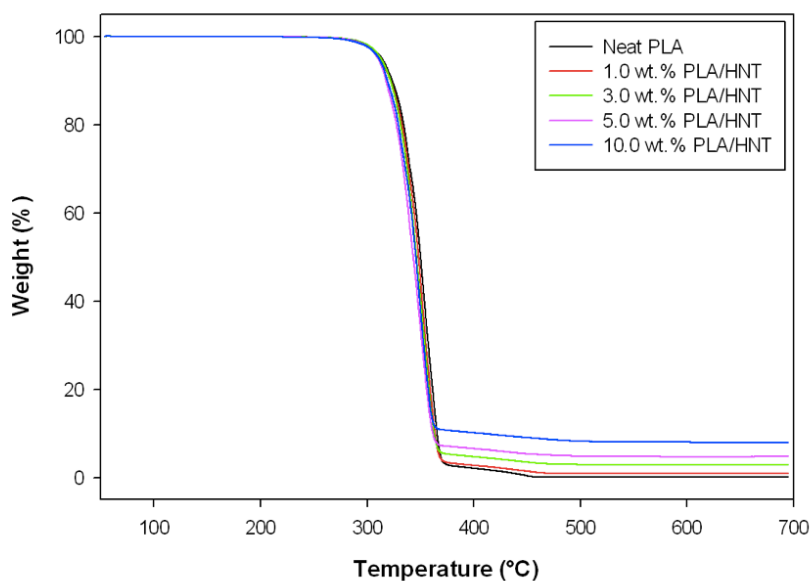


Figure 40. TGA thermograms of PLA/HNT nanocomposites.

Overall, The actual HNT loadings were found to be close to their nominal loading values based on the weight percent remaining in the TGA curve of the respective

PLA/HNT nanocomposites. The addition of HNT to the PLA has shown less than a 2 °C change in the beginning of decomposition. This was not entirely unexpected, as the torturous path model states that a large, flat plate will decrease permeation more than a smaller, one dimensional tube as the flow must be around the object and the clay-polymer interface region.⁵⁰

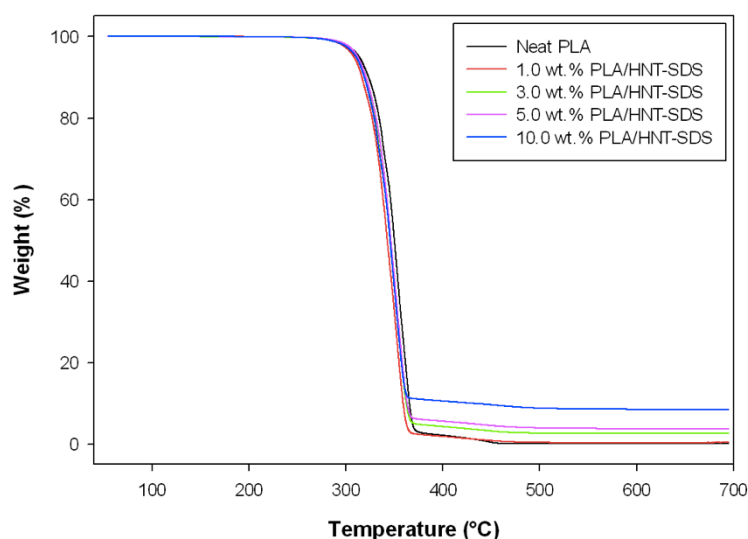


Figure 41. TGA thermograms of PLA/HNT-SDS nanocomposites.

The consistent behavior of the TGA curves with the peroxide treated and the SDS-treated HNT nanocomposites showed that the SDS did not greatly affect the thermal degradation of the nanocomposite, and that only a small amount of the SDS was on the surface of the HNT (Figure 41). By keeping the concentration of SDS low, plasticizing effects of the SDS in the nanocomposite can be kept to a minimum.

2.3.1.2 Differential Scanning Calorimetry

The addition of HNT to the PLA did not change the glass transition temperature (T_g) or melting temperature (T_m) compared to that of the neat PLA (Figure 42). The crystallization temperature (T_c) of PLA is typically difficult to see with a DSC, as it occurs very slowly, on the order of magnitude of minutes instead of seconds when compared to that of polyolefins.⁵¹

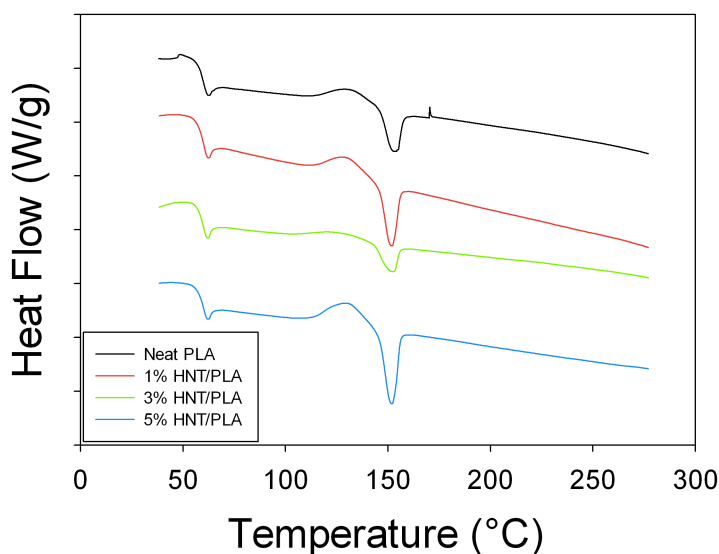


Figure 42. DSC curves of PLA/HNT nanocomposites.

The T_g of neat PLA and all PLA/HNT nanocomposites tested occurred at 58 ± 1.0 °C and T_m occurred at 152 ± 1.2 °C. The variance in the height of the T_m peak is related to the difference in the heat capacity between that of the PLA and the HNT.

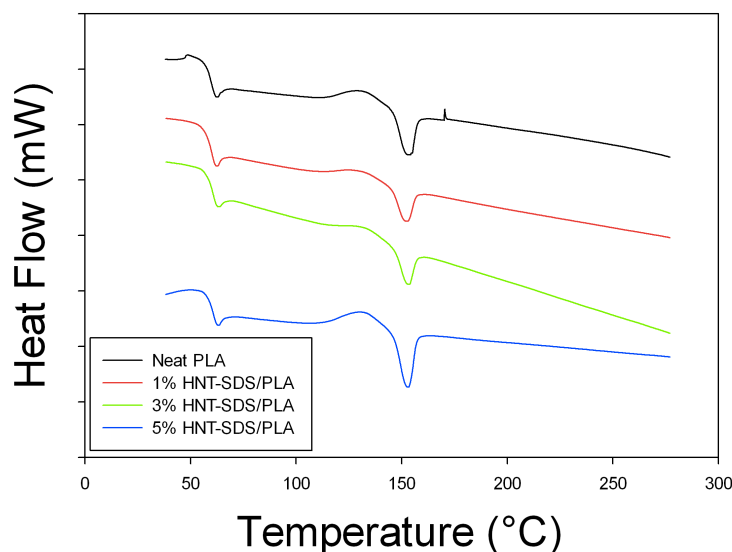


Figure 43. DSC curves of PLA/HNT-SDS nanocomposites.

The T_g of neat PLA and all PLA/HNT-SDS nanocomposites tested occurred at 57.5 ± 1.0 °C and T_m occurred at 152 ± 1.2 °C (Figure 43). The difference between the neat PLA, PLA/HNT, and PLA/HNT-SDS treated nanocomposites is minimal.

The differences between the PLA/HNT and PLA/HNT-SDS samples were minimal, as the T_g and T_m remained largely unaffected by the addition of SDS to the nanocomposite. This was to be expected with the very low concentration of SDS added to the HNT during the SDS treatment (1 wt.%).

2.3.2 Mechanical Properties

The PLA/HNT nanocomposites all show increased Young's Modulus follow the expected trend that the Young's Modulus of a stiff polymer should increase with the loading of a rigid nanoparticle, and the elongation at yield should decrease with further loading of an inelastic filler. The stress-strain curves presented in Figure 44, next page, are one sample that was most average of the dataset, but not a composite of all data, and does not perfectly match the mean data presented in Table 2, next page.

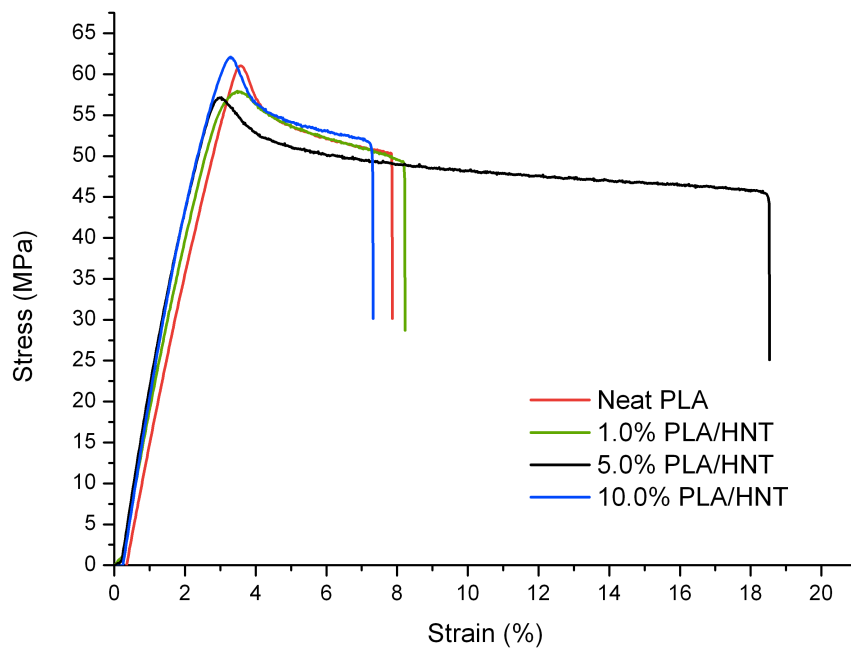


Figure 44. Stress-strain curves of PLA/HNT nanocomposites tensile testing.

Table 2. Mechanical data from PLA/HNT nanocomposites.

	Young's (MPa)	Modulus	Tensile Stress at Yield (MPa)	Elongation at Yield (%)
Neat PLA	1962±85		69.2±0.45	4.47±0.18
1.0 wt.% PLA/HNT	2077±69		67.1±1.2	4.18±0.11
5.0 wt.% PLA/HNT	2281±171		64.1±1.8	3.45±0.35
10.0 wt.% PLA/HNT	2661±154		62.7±0.7	3.37±0.14

For the PLA/HNT nanocomposites, a trend of increased modulus with increased loading of HNTs into the PLA was observed. Also, the tensile stress at yield decreased as the HNT loadings were increased, which was to be expected with a very rigid polymer and a stiff nanofiller. The decrease of elongation at yield was to be expected, as the rigid HNT's would disrupt the packing structure of the PLA, which decreased the ability of the PLA to stretch with applied stress.

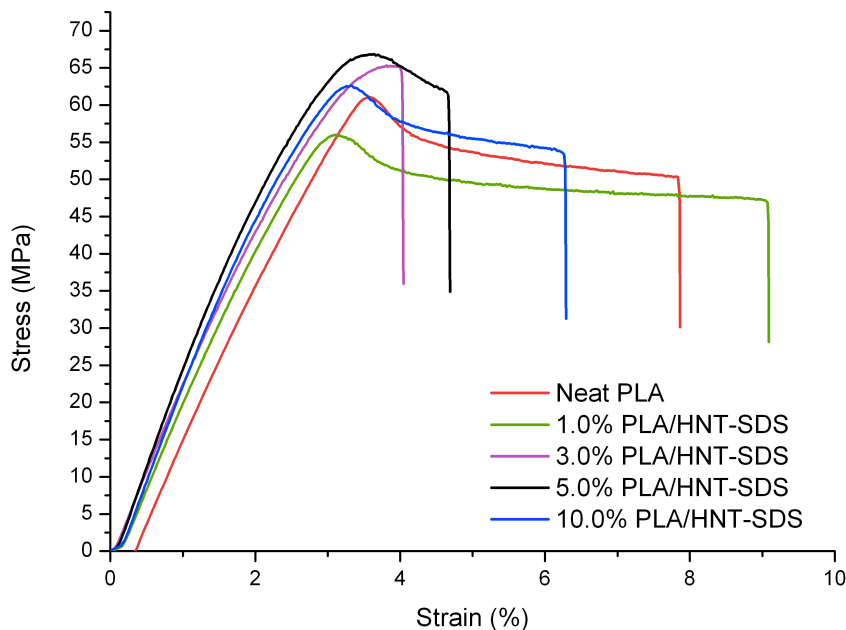


Figure 45. Stress-strain curves of PLA/HNT-SDS nanocomposites tensile testing.

The PLA/HNT-SDS sample showed further improvement over the performance of the PLA/HNT nanocomposites in Young's Modulus, but even more reduction in the elongation at yield, up to 5 wt.% loading of HNT-SDS into the PLA (Figure 45, above, and Table 3, below). The decrease in overall performance of the 10 wt.% can be attributed to the increased SDS concentration in the nanocomposite, as the SDS was on the HNT surface.

Table 3. Mechanical data for PLA/HNT-SDS nanocomposites

	Young's Modulus (MPa)	Tensile Stress at Yield (MPa)	Elongation at Yield (%)
Neat PLA	1962±85	69.2±0.5	4.47±0.18
1.0 wt.% PLA/HNT-SDS	2388±55	56.1±0.4	3.15±0.04
3.0 wt.% PLA/HNT-SDS	2556±35	57.9±1.7	2.92±0.10
5.0 wt.% PLA/HNT-SDS	2893±246	60.0±1.8	2.86±0.09
10.0 wt.% PLA/HNT-SDS	2580±80	62.2±0.4	3.31±0.03

When comparing the PLA/HNT and PLA/HNT-SDS nanocomposites, increased Young's Modulus comes with decreased elongation at yield. Plasticity of the PLA/HNT-SDS appears to not have been an issue, as the elongation at yield is lower than that of the PLA/HNT nanocomposites, but with an increased Young's Modulus. Further studies should be performed to verify the toughening mechanism of the system.

2.3.3 SEM imagery

The SEM images in Figure 46 shows evidence that the HNTs are well dispersed and agglomerates are not present to any significant degree. The primary crack arresting mechanism for a rigid polymer/HNT nanocomposite system is the bridging of cracks by the high-modulus HNTs, which eventually leads to fracture of the HNT.⁵

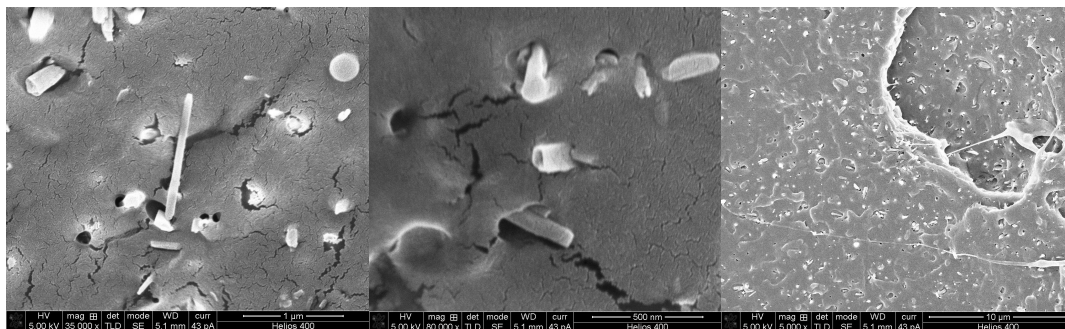


Figure 46. SEM images of 5% PLA/HNT-SDS.

The termination of cracks by HNTs can be seen in the first two SEM images (Figure 46), and the formation of new cracks at the PLA/HNT interface can be seen. Further studies need to be performed to verify the fracture-toughening mechanism of the nanocomposite.

2.4 Conclusions

In conclusion, several PLA/HNT and PLA/HNT-SDS nanocomposites were made using a twin-screw extruder and injection molder to adequately disperse the HNTs in the PLA. The stiffness of the polymer was improved through the addition of HNT and HNT-

SDS to the PLA. Young's Modulus was improved by 35% in the 10.0 wt.% PLA/HNT nanocomposite, while improvements of 47% were seen in the 5.0 wt.% PLA/HNT-SDS nanocomposite. The thermal decomposition of the nanocomposite is largely unaffected by the addition of HNT and HNT-SDS (TGA and DSC), which was expected as the long, narrow HNT particle will only minimally affect the heat transfer when compared to that of larger, two-dimensional nanoparticles. The improvements in the mechanical properties will allow the use of PLA for new applications, expanding its usefulness as a biodegradable polymer.

CHAPTER III

POLY(VINYL ALCOHOL)/HALLOYSITE NANOTUBE NANOCOMPOSITES

3.1 Introduction

Poly(vinyl alcohol) (PVOH) has been used primarily for thin films and fibers due to its excellent mechanical and physical properties.⁵² It is widely available commercially, in many different molecular weights, degrees of hydrolysis, and tacticity.

Due to the high surface area to volume ratio of nanoclays, even at low loading levels, a high fraction of polymer-clay interphase is present.⁵³ PVOH/montmorillonite (MMT) nanocomposites have shown large increases in strength and stiffness with loadings below 5%.^{54, 55} However, re-aggregation often occurs upon drying.⁵⁴ However, the same trend is observed in PVOH/HNT nanocomposites, as the water concentration decreases, the PVOH is no longer soluble, and aggregation becomes a problem.³⁶

Most natural smectic clays are known for their stable suspensions in water due to their hydrophilic surfaces once exfoliated.⁵³ This technique can be used to form stable suspensions of polymers during drying, and is very helpful during thin film processing and electrospinning.⁵³ Halloysite does not form the same stable suspension in water. Halloysite has a neutral outer surface and only limited areas of the HNT are negatively charged (ie; the ends of the alumina sheet and inner surfaces).¹⁴ Small defects in the outer silica sheet a negatively charged regions, but the overall concentration of these regions is low.⁸

These defects only account for a small percentage of the overall outer surface, and do not significantly alter the behavior of the HNTs.⁸

3.2 Experimental

3.2.1 Materials

Halloysite was received from Applied Minerals INC (1415:JM). The Poly(vinyl alcohol) (PVOH) was from Kuraray America Inc., MOWIOL 8-88, with MWT of 67000. Montmorillonite used was Cloisite Na⁺ from Southern Clay Products. All water used was deionized. Hydrogen peroxide was purchased from CVS pharmacy, 3% H₂O₂. Potassium iodide (KI) was from Fischer Scientific, 100%.

3.2.2 Purification of Halloysite

The procedure for purification of halloysite from organic residues is outlined in Chapter 2 of this work.

3.2.3 Suspension of HNT and MMT in water

The ability of HNTs to form suspensions in water was studied with 0.50 and 1.0 wt.% HNT/water concentrations, and to ensure that the H₂O₂ treatment did not affect the stability of the HNT in water, MMT was used to assist the HNT in suspending, with ratios of 0:1; 1:2; 1:1; 1:0.5; 1:0.25; 1:0.1; 1:0 (HNT:MMT) for the 0.5 wt.% HNT dispersions and 0:1; 1:1; 1:0.5; 1:0.25; 1:0.1; 1:0 (HNT:MMT) for the 1.0% HNT dispersions. The HNT was measured out in powder form, while the MMT was used in a 1.0% aqueous dispersion that was ultrasonicated immediately prior to sample preparation to ensure even dispersion. Samples were prepared in clean, dry 20 mL vials, with total solution weights of 12 grams. Pictures were taken periodically to observe the settling

effects on the dispersions over time. Once they were set up, they were not disturbed for the duration of the study.

3.2.4 Preparation of PVOH/HNT/MMT Thin Films

A 10.0% solution by weight of PVOH was made by heating 720.00 g of water in a round bottomed flask in a stirred water bath to 91.0 °C, then slowly adding 80.00 g of PVOH to the stirred solution. The solution was covered and continuously stirred for the next 3 hours, or until the PVOH was completely dissolved. The PVOH solution was then removed from the heat and stirred without heat until cooled to room temperature, and then transferred to a sealed container for storage.

Thin PVOH/MMT/HNT nanocomposite films were prepared by casting aqueous solutions onto glass. An epoxy border was made to prevent runoff. Dispersions of 1.0 wt.% HNT and 1.0 wt.% MMT were prepared and ultrasonicated just prior to film casting. The dispersions were then added in the correct ratios by mass to beakers (Table 4, next page), slowly stirred for 30 minutes, followed by ultrasonication for 1 hour with a Branson 8510 ultrasonicator. The thin, bubble-free films were dried on clean, dry leveled glass plates for 18 hours in an oven at 35 °C. The samples were then placed into a humidity chamber outlined by ASTM E104-02 with a saturated aqueous solution of KI below the samples to maintain constant humidity. The chamber was found to be 69.0 ± 1.0 % relative humidity. After 24 hours, the samples were die cut using a hydraulic press and cutter into type I test bars with a width of 4.00 mm, a length of 25.00 mm, and a thickness between 0.032 mm and 0.057 mm. The length and width were measured with digital calipers, and the thickness was measured with a digital micrometer. The thickness was accounted for in all calculations. After die cutting, the samples were placed back into

the constant humidity chamber for a further 48 hours prior to testing to ensure equilibrium of PVOH.

Table 4. Relative concentrations of PVOH/HNT/MMT nanocomposite films.

Sample Name	PVOH (wt.%)	HNT (wt.%)	MMT (wt.%)
100/0/0	100	0	0
99/0/1	99	0	1
91/9/0	91	9	0
90/9/1	90	9	1

3.3 Data and Analysis

Thermal stability of the nanocomposite was evaluated by thermogravimetric analysis. TGA was performed using the TA Instruments Q50 under a 60.00% air/40.00% argon atmosphere.

The mechanical testing was performed using the Instron 5500R. All samples were die-cut prior to testing to ensure consistency. The samples were hydrated using the ASTM E 104-02, using an aqueous saturated salt solution of KI in a sealed container for 48 hour prior to mechanical testing. Temperature was controlled at 23.5 ± 1 °C, and humidity was observed to be at 69.0 ± 1.0 % prior to all tests performed.

3.3.1 Halloysite Suspensions in Water

At a concentration of 0.1 wt.%, HNT was found to suspend itself in water for up to one week, however as the concentration approached 1%, more immediate settling of the HNT was observed.

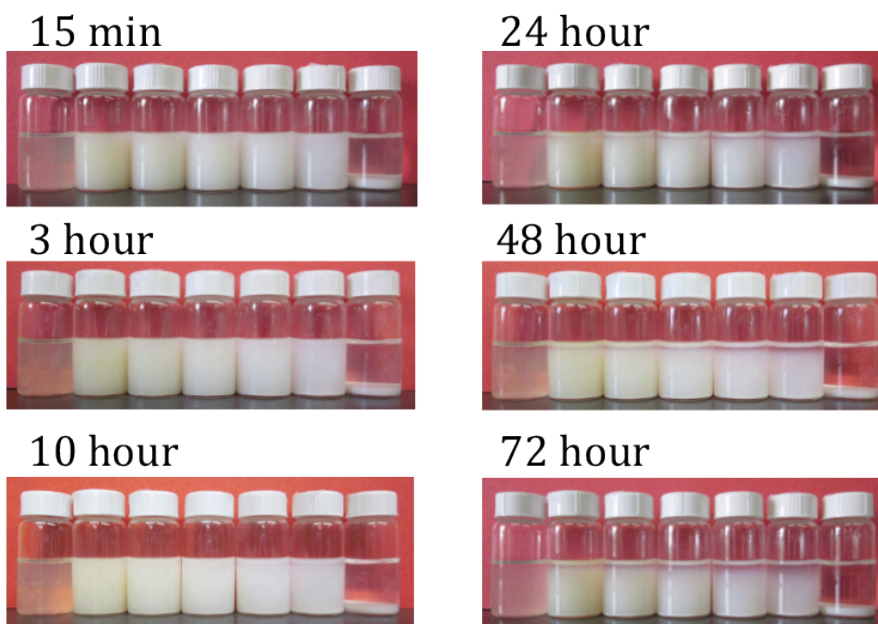


Figure 47. HNT as received 0.5 wt.% in water. In order from right to left, the ratios of HNT:MMT are: 0:1; 1:2; 1:1; 1:0.5; 1:0.25; 1:0.1; 1:0.

Even at the lowest loadings, MMT showed profound stabilization of the HNT in solution (Figure 47). All of the solutions containing both the HNT and MMT showed increased stability over that of the pure HNT only solutions.

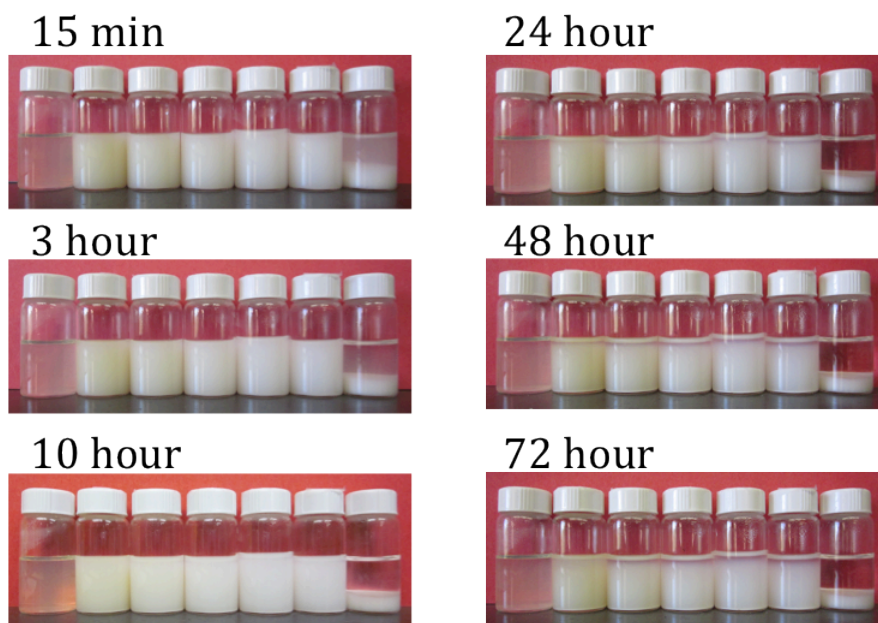


Figure 48. Washed HNT at 0.5 wt.% in water. In order from right to left, the ratios of HNT:MMT are: 0:1; 1:2; 1:1; 1:0.5; 1:0.25; 1:0.1; 1:0.

The 0.5 wt.% of washed HNT series showed similar behavior to that of the raw HNT series, showing that the H_2O_2 treatment did not greatly alter the surface chemistry of the HNT (Figure 48, previous page).

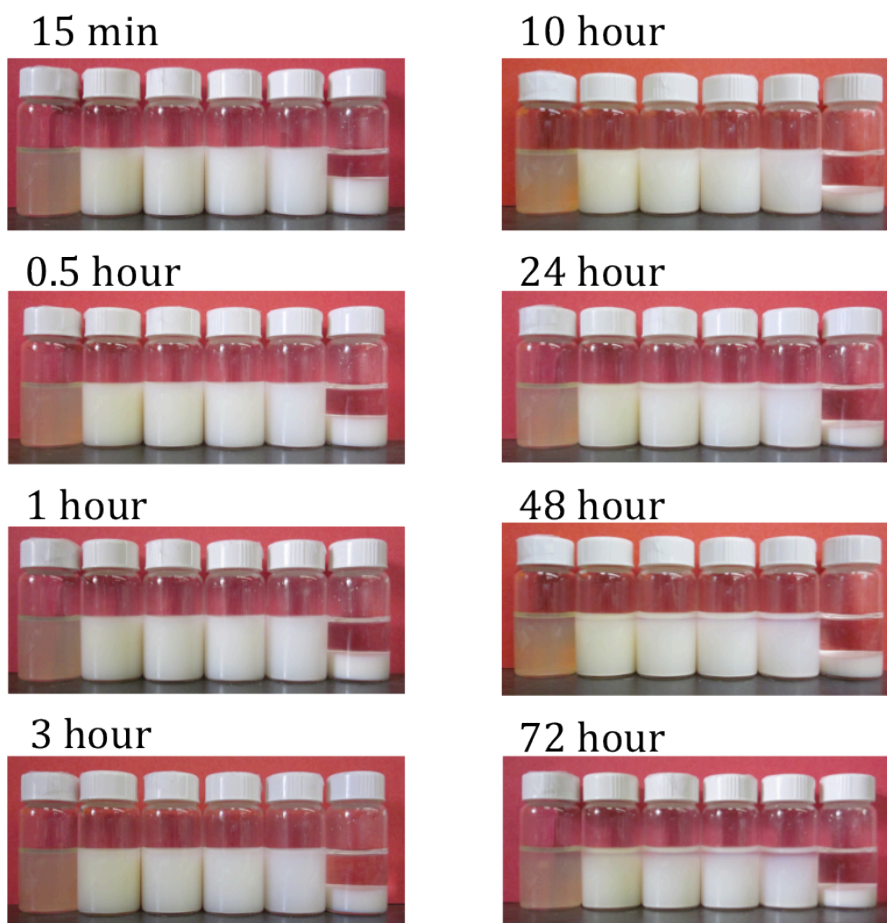


Figure 49. HNT as received 1.0 wt.% in water. In order from right to left, the ratios of HNT:MMT are: 0:1; 1:1; 1:0.5; 1:0.25; 1:0.1; 1:0.

Similar behavior was observed in the 1.0 wt.% raw HNT and washed HNTs, with increased stability up to 72 hours for all of the HNT/MMT dispersions when compared to the HNT-only dispersion (Figure 49, this page, and Figure 50, next page). However, it is much more apparent that the HNT-only dispersion began settling as soon as it was removed from the ultrasonicator, and began to settle before the samples could be moved to the bench for photography.



Figure 50. Washed HNT at 1.0 wt.% in water. In order from right to left, the ratios of HNT:MMT are: 0:1; 1:1; 1:0.5; 1:0.25; 1:0.1; 1:0.

3.3.2 Thin Film Casting

Transparent thin nanocomposite films were cast containing only PVOH, HNT, and MMT (Figure 51). The maximum loadings were 10.0 wt.% clay, with 9.0 wt.% being HNT and the other 1.0 wt.% being MMT. Due to good dispersion and nanoscale filler size, all films were transparent. Once the films were cast and dried, samples were cut for thermal and mechanical testing.

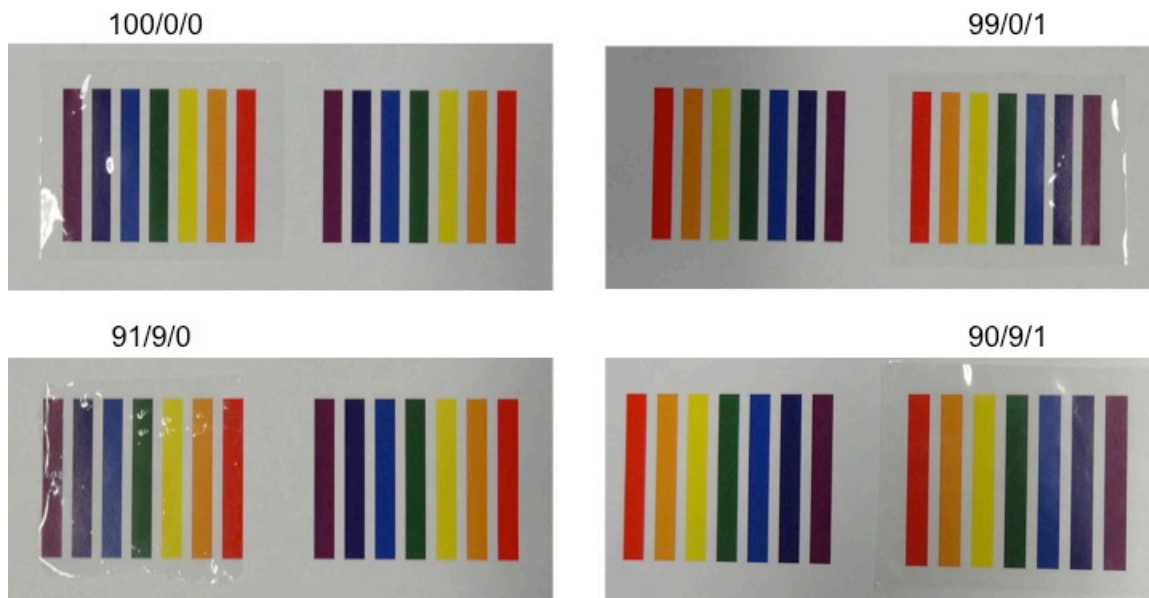


Figure 51. Transparent neat PVOH and PVOH/HNT/MMT nanocomposite films produced by casting aqueous solutions on glass plates.

3.3.3 Thermal Analysis Results

The addition of HNT and MMT clays did not alter the initial decomposition of the PVOH (Figure 52, next page). In all cases, the residual weights are close to that of the nominal loadings. The thermogram shows that the addition of even up to 9.0% HNT shows no major signs of delayed thermal degradation. The two nanocomposites with 1% MMT do show slightly delayed decomposition near 300 °C over the neat PVOH and the PVOH/HNT 91/9/0 nanocomposite.

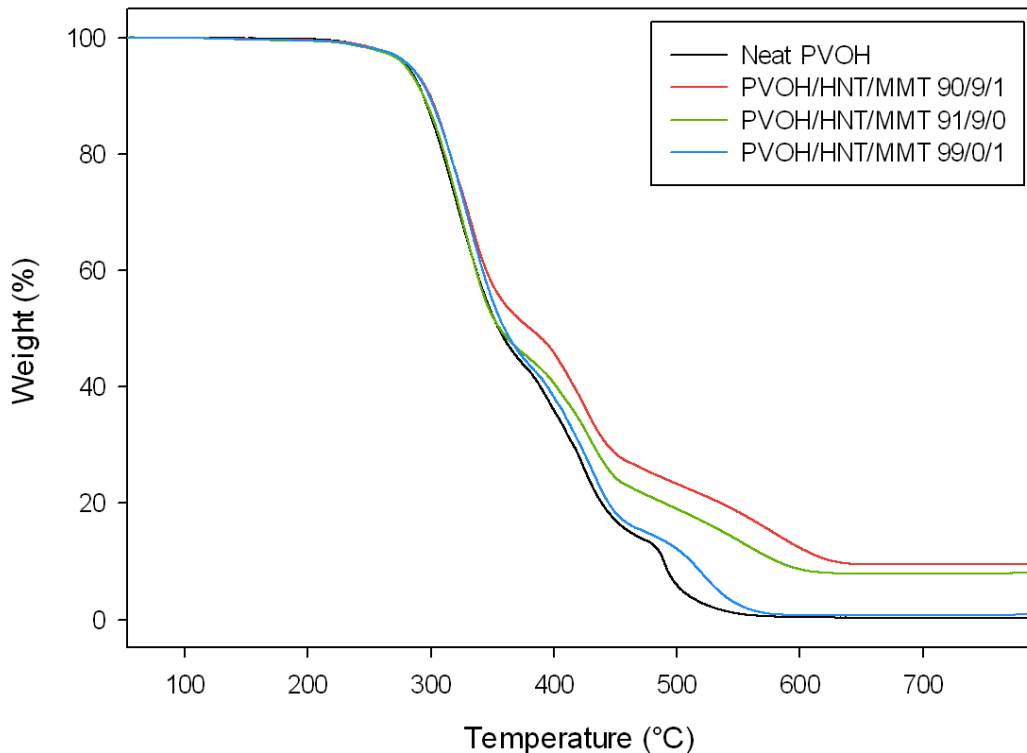


Figure 52. TGA thermograms of PVOH/HNT/MMT nanocomposites.

3.3.4 Mechanical Properties

The mechanical properties of the PVOH/HNT/MMT thin films were improved with the loading of a stiff nanotube into a ductile material. The Young's Modulus and stress at break increased with increased nano-clay loading, but decreased the elongation at break (Figure 53, next page).⁵⁰ As the films were between 0.032 and 0.057 mm thick, a large amount of variation was expected, especially when considering the plasticizing effect humidity has on PVOH. The Young's Modulus results can be found in Table 5, next page, along with the average maximum stress at break and average strain at break values.

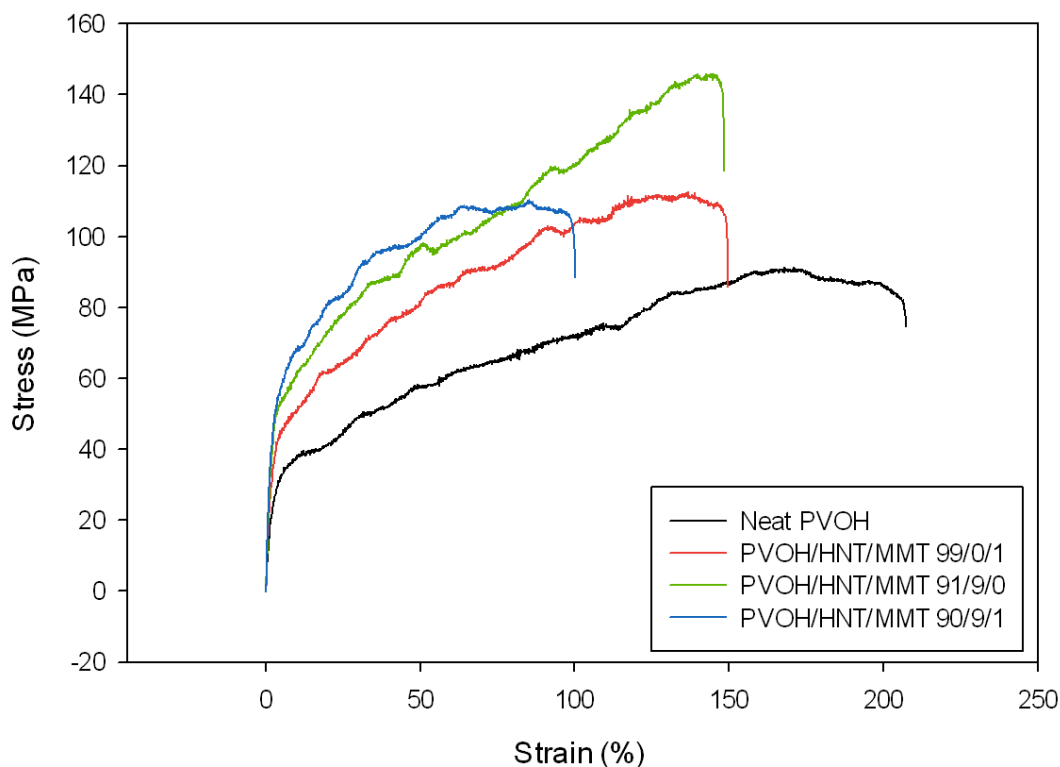


Figure 53. Stress strain curves of PVOH/HNT/MMT nanocomposite. The graph is not an average, but the run that best represented the average values in Table 5.

Table 5. Mechanical data of PVOH nanocomposites.

Sample Name	Young's Modulus (MPa)	Maximum Tensile Stress at Break (MPa)	Maximum Tensile Strain at Break (%)
Neat PVOH	1219±573	93±6	154±34
99/0/1	1750±302	113±8	137±11
91/9/0	1965±559	131±19	138±21
90/9/1	2079±380	137±19	93±17

3.4. Conclusions

Halloysite has been suspended in water for up to 72 hours with as little as 10 wt.% addition of MMT to HNT. Peroxide treatment of the HNT had little effect on the suspension of HNTs in water. The stable suspension was used to prevent agglomerations of the HNTs during the drying of PVOH thin film nanocomposites.

PVOH has been cast into transparent, thin films and the addition of inorganic clays has improved the mechanical properties without severely altering the thermal and optical properties. The PVOH/HNT/MMT 90/9/1 film showed a 71% increase in the Young's Modulus over neat PVOH, while the strain at break decreased by 40%. The decreased strain was not unexpected, as both the HNT and MMT are very rigid nanofillers, and the PVOH is a very ductile polymer. The addition of nanoclays did not delay the thermal degradation of the nanocomposites.

The mechanical improvements observed will make PVOH more useful in new applications, especially when high mechanical performance is required.

CHAPTER IV

SUMMARY AND FUTURE WORK

The use of HNTs as a nanoscale reinforcement to polymers has been explored in both a very rigid polymer (PLA) and a very ductile polymer (PVOH). The PLA/HNT nanocomposites were processed with a twin-screw extruder and injection molded into final products, while the PVOH/HNT/MMT nanocomposites were cast into thin films. In all cases, simple processing and increased Young's Modulus was observed. The Young's Modulus was improved by 35% in the 10.0 wt.% PLA/HNT nanocomposite, 47% increase in the 5.0 wt.% PLA/HNT-SDS nanocomposite, and a 71% improvement was observed PVOH/HNT/MMT 90/9/1 films.

Even with the addition of HNTs to PLA and PVOH, the thermal decomposition of the neat polymer was not greatly affected. This was not entirely unexpected, as the long, narrow HNT particle will only minimally affect the heat transfer thru the bulk polymer.

Halloysite has been suspended in water for up to 72 hours with as little as 10 wt.% addition of MMT to HNT. Peroxide treatment of the HNT to remove organic contaminants had little effect on the suspension of HNTs in water. The stable suspensions with the addition of MMT were used to prevent the agglomeration of the HNTs during the drying of PVOH thin film nanocomposites. PVOH/HNT/MMT nanocomposites have been cast into transparent, thin films with excellent optical clarity.

The use of halloysite as rigid nanofiller can be utilized in many different polymer systems, from very ductile materials to brittle materials, to increase the strength of the

resulting nanocomposites with minimal change to overall processing. This adds value to the material, expanding its possible uses, even to the point of competing with engineering plastics. One major benefit of halloysite over other nanotubes is that it is environmentally benign, and when incorporated into a biodegradable polymer, the result after biodecomposition is not harmful to the environment. Halloysite is also very easy to disperse, although proper alignment is a bit more difficult. The mechanical improvements observed in both PLA and PVOH will allow the use of both polymers in new applications, especially where high mechanical performance and biodegradability are both required.

Further research should be performed to examine the barrier properties of each polymer/nanocomposite system. In the future, other polymer/nanocomposite systems should be explored, such as high performance epoxies and elastomers. The increased Young's Modulus will increase the value of the nanocomposites and expand the use of most polymers, especially where minimal environmental impact is desired

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VITA

Matthew Charles Hartline was born in Pensacola, Florida, on October 26, 1986, the son Vanessa Guillot Hartline and Charles Ray Hartline. After completing his work at Stony Poing High School, Round Rock, Texas, in 2005, he entered Texas State University-San Marcos. During the fall of 2007, he attended Auburn University. He received the degree of Bachelor of Science from Texas State in May 2011. In August, 2011, he entered the Graduate College of Texas State.

Permanent Address: 5584 Sapelo Trail

Norcross, Georgia 30096

This thesis was typed by Matthew C. Hartline