“Z”-ALIGNMENT OF HALLOYSITE NANOTUBES IN NORLAND 65

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Z-ALIGNMENT OF HALLOYSITE NANOTUBES IN NORLAND 65

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Thesis

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ABSTRACT

Halloysite nanotubes (HNTs) /polymer composites offer unlimited potential for new and unique properties at low nanoclay addition. Minimum success has been achieved in this field, although it has been heavily investigated for enhanced mechanical and diffusion properties. Due to their high isotropic properties, HNTs have a wide range of applications such as tensile and compressive strength enhancers and thermal, diffusive, and capacitance modifiers, etc. Particle alignment has been extensively explored in polymeric systems. However, most studies focus on the planar alignment, which do not take advantage of these anisotropy since the orientation in thickness direction (Z-direction) is not achieved. Hence, directed assembly techniques are introduced as a good assisted method to meet the requirement.

Field assisted assembly has already been broadly introduced, but there are still questions involving specific systems. One of them is how to form an ordered structure in “Z”- direction by utilizing these assembly techniques, in order to meet the “Z”-aligned structure requirement of most membranes and films for electronic devices. Therefore, the objective of this investigation is to utilize field assisted assembly to achieve “Z”- alignment of particle chain-like formations in polymeric matrices under electric field.
Traditional characterization techniques have been broadly used to investigate particle orientation in polymer nanocomposites such as scanning electron microscope (SEM), wide angle X-ray diffraction (WXRD). However, these techniques are unable to capture the real time molecular dynamics during alignment. As a result, a real time birefringence measurement system developed by our group was introduced to analyze the dynamics of HNT orientation in a Norland 65 (NOA65) polymer matrix during electric field assisted alignment.
ACKNOWLEDGEMENTS

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CHAPTER I
INTRODUCTION

The addition of nanoparticles to polymer matrices offers unique routes to enhance the properties of final products. There have been numerous studies focused on this field in academia and industry in the past two decades. Nanoclay added in polymer composites can have thicknesses ranging from a few nanometers to thousands of nanometers in length. Generally, nanoclay/polymer composites are formed by four experimental methods: solution intercalation, in situ intercalative polymerization, melt intercalation, and in-situ direct synthesis\textsuperscript{1-4}. Due to the unique nanostructure of nanoclay, with small addition of filler (<10%), uniformly dispersed nanoclay is believed to provide various advantages with the combination of mechanical, electrical, optical, thermal and other several properties towards to the polymer composites\textsuperscript{5-11}.

Nanoclays are nanoparticles of layered mineral silicates and they are categorized into five classes including montmorillonite, kaolinite, bentonite, halloysite and hectorite. Montmorillonite (MMT) is the most commonly used nanofiller in material applications. Plate-like montmorillonite is a hydrous aluminosilicate clay mineral with an average diameter around 1 um and thickness of $9.6\times10^{-9}m$\textsuperscript{12} as well as a $2:1$ expanding layered crystal structure. Clay layers are fully separated to form plate-like nanoparticles with high aspect ratio when
dispersed well in polymer matrix. The aspect ratio is around 10-1000 and the surface area is in the range of 750m²/g\(^1\). A 1:1 clay mineral is formed when an octahedral sheet is bonded to one tetrahedral sheet while two tetrahedral sheets bond with one octahedral sheet resulting in 2:1 clays\(^1\). During shear mixing, break up of clay platelets results in an aspect ratio of 30-300. Yalcin et al\(^1\) investigated that the presence of MMT in poly(vinyl chloride) (PVC) increased the orientation level for both amorphous and crystalline phases. Ergungor et al\(^1\) investigated that small amount of nanoclay enhanced the orientation level in Nylon 6 fibers at the different speeds of melt spining. Saha et al\(^1\) studied the influence of adding montmorillonite to a polymer matrix, obtaining enhanced mechanical, thermal and temperature dependence elastic modulus. However, it was observed that there is no much influence on optical clarity of the nanocomposites film with loading of MMT. Saurabh et al\(^1\) investigated the influence on ionic conductivity of the nanocomposite film after the alignment of MMT under electric field and resulted in enhanced ionic conductivity.

Halloysite nanotubes (HNTs) are another type of nanoclay used in absorbents, catalysts and polymer fillers. There were numerous studies focused on carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs) due to their high strength, large aspect ratio, and relatively low density of 1D tube-like nanofillers\(^1\),\(^2\). Compared with CNTs and BNNTs, halloysite nanotubes (HNTs) provide an inexpensive alternative with similar morphology and properties and BNNTs, halloysite nanotubes (HNTs) provide an inexpensive alternative with similar morphology and properties as CNTs. HNTs has a hollow tubular
nanostructure with a hydrated polymorph of the 1:1 phyllosilicate clay originated from kaolin group\textsuperscript{21}. High mechanical strength, good biocompatibility and large aspect ratio generate remarkable mechanical, thermal and biological properties in polymer nanocomposites\textsuperscript{22, 23}. HNTs are an excellent replacement for more expensive CNTs in some aspects of polymer nanocomposites.

Similar to Kaolinite, the molecular formula for halloysite is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\cdot\text{nH}_2\text{O}$. However, unlike the stacked-plate structure of kaolinite, halloysite has a hollow tubular as well as multi-walled structure. Due to its unique tubular nanostructure, the outer diameter of HNTs ranges from 40 to 70 nm while inner layer is from 10 to 40 nm, and its length is in the range of 0.2 to 2 \textmu m. The interior portions of HNTs are aluminols, while siloxanes and silanols/aluminols are exposed outside of the HNTs. Due to its relatively large surface area (specific area=$\approx$60 m$^2$/g)$^{24}$, it is easy for HNTs to agglomerate due to its large surface energy in polymer matrix. Hence, mechanical and surface modification methods were introduced to eliminate the particle agglomeration. For mechanical methods, ultrasonic vibration and ball mill may break up the clusters. For surface modification, potassium acetate\textsuperscript{25} and silane\textsuperscript{26} were proven to be effective surface treatments to decrease the size of HNTs clusters in different polymer matrix. There are numerous studies that show a small addition of halloysite improved the mechanical properties, thermal stability, dielectric properties, and wettability of the resulting nanocomposite\textsuperscript{27}. Handge et al\textsuperscript{28} demonstrated advanced tensile strength and Young’s modulus of HNTs/polyamide 6 (PA6) nanocomposites. Qiu et al\textsuperscript{29} found that HNTs can significantly increase the degradation temperature of
PVA. Prashantha et al\textsuperscript{30} found that the real permittivity ($\varepsilon$) of the PA-11/HNTs increased compared with the neat PA-11, and the real permittivity increased with the increasing of HNTs addition. It is also observed that the optical properties of PA-11/HNTs nanocomposites are rarely affected by the addition of HNTs.

However, there are very few studies focused on making full use of the anisotropy of HNTs by aligning the nanoparticles in polymer matrix under assistance field.

This investigation utilized Norland 65 (NOA65) as the polymer matrix. NOA65 is a liquid photopolymer that will cure when exposed to ultraviolet light. The application of NOA65 can be used as putting of lenses in metal mounts, binding plastic to glass and cold blocking\textsuperscript{31}.

For most applications of nanocomposites, with the orientation controlled self-assembly, ordered structures of nanocomposite film can be created\textsuperscript{32}. Directed field is another method to control the alignment and orientation of nanoparticles, such as electric field. By using an external field, directional anisotropy can be created to influence properties of the films in thickness direction. Electric field is widely used in potential application in flexible electronic\textsuperscript{33} and membranes\textsuperscript{34}.

In this investigation, the alignment of HNTs in NOA65 was achieved via an electric field. This was accomplished by utilizing an instrumented system that combines real time birefringence measurement with electric field application device that uses transparent conductive electrodes. With this measurement system, the kinetics of particle alignment can be observed as reflected in birefringence. Off line scanning electron microscope (SEM) used to characterize
orientation of nanoparticles in nanocomposite film. Wide angle X-ray diffraction (WAXD) is used as a solid method to investigate the ordered morphology.
CHAPTER II

BACKGROUND AND LITERATURE REVIEW

This section reviews the progress for application of halloysite nanotubes (HNTs) and discuss the electric field as an assembly assisted technique to orient particles in polymeric system to form ordered structures.

2.1 Halloysite Nanotubes (HNTs)

Halloysite, one of the most important mineral from kaolin group, was firstly named by Berthier in 1826\textsuperscript{35}. It has obtained increasing attentions in materials science and technology due to its tubular nanostructure. Raw halloysite is usually white shown in Figure 2. 1 (a) and Figure 1(b) shows the powder of raw halloysite. The molecular formula of halloysite is similar to kaolinite except that it contains additional water molecules between the layers. It is easy for halloysite to lose its interlayer water, so partly dehydrated halloysite is often observed. The molecular formula in its fully hydrated state is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\cdot2\text{H}_2\text{O}$\textsuperscript{36}. The hollow tubular nanostructure gives this material a high aspect ratio, like Figure 2. 1 (c) and (d) show. The d spacing of Halloysite is 10 Å in fully hydrated state while 7 Å in dehydrated state. The 10 Å fully hydrated state can convert quickly to the 7 Å dehydrated state on heating or even under ambient conditions. The inner and outer diameter of HNTs are in the range of 10-40nm and 40-70nm, respectively.
An ideal HNTs crystal is composed of a layered structure containing tetrahedrally coordinated $\text{Si}^{4+}$ and octahedrally coordinated $\text{Al}^{3+}$ in a 1:1 stoichiometric ratio (Figure 2.2a). It is reported$^{37}$ that halloysite has monoclinic unit cell ($\beta \neq 90^\circ$, $\alpha$, $\gamma=90^\circ$) (Figure 1), and the cell parameters are: $a=5.14\text{Å}$, $b=8.9\text{Å}$, $c=7.2\text{Å}$ and $\beta=99.7^\circ$. The surface chemistry of inner and outer surface are very different, the aluminols dominates the inner surface of HNTs, while the most portion of outer surface are siloxanes$^{38}$. Low content of hydroxyl groups on the surface results in a hydrophilic characteristic of HNTs (Figure 2.2). Therefore,
it is easy for halloysite to be dispersed in non-polar polymers via different mixing methods.

![Schematic diagrams of (a) the crystalline structure of halloysite-(10 Å), and (b) the structure of a halloysite nanotube (Reprinted with permission from Ref. 38.)](image)

Figure 2. 3 Unit cell of halloysite nanotubes

Halloysite tend to agglomerate in hydrophobic polymer system, because there are hydroxyl groups located on the halloysite surface resulting in HNTs are hydrophilic. It is reported that grafting silane coupling agent can increase the
interfacial adhesion of the HNTs/polymer nanocomposites by react with the hydroxyl groups on the surface of HNTs. For example, it is reported that the modification of silane coupling not only the graft the APTES directly onto the surface hydroxyl groups, but also oligomerization (Figure 2.4).

![Diagram of mechanism of the formation of cross-linked network](image)

Figure 2.4 Schematic of mechanism of the formation of cross-linked network (a), and of the grafting between bidentate bonded Si and AlOH groups (b). (Reprinted with the permission of Ref.38).

Potassium acetate (CH3COOK) can be also used as surface modifier to treat halloysite resulting in good compatibility in polymer system. K+ can be intercalated into the interlayers of HNTs, the distance between interlayers can be expanded39. After that polymer chains can be intercalated into the interlayer galleries resulting in a homogenous mixture of HNTs with polymers40.
HNTs are not hazardous and they are biocompatible as well as rich abundance in nature. The relative low price and high performance of this material make HNTs-polymer nanocomposites very competitive in industrial applications.

2.1.1 Methods for Fabricating HNTs-polymer Nanocomposites

Solution processing, in situ polymerization, melt processing and electrospinning are introduced as methods for fabrication of HNTs-polymer nanocomposites

2.1.1.1 Solution Processing

Solution processing is realized by dispersing HNTs and polymer firstly in a solvent with stirring or mixing treatment, and the nanocomposites are obtained as films or hydrogels after casting or precipitation then.
Chitosan\textsuperscript{41}, polyethylene glycol (PEG)\textsuperscript{42}, Latex rubber\textsuperscript{43} can be mixed with HNTs. Enhanced properties can be obtained after HNTs added in these materials. For example, HNTs/rubber nanocomposites can be obtained after the addition of HNTs in latex rubber, the modulus and hardness of the nanocomposite were significantly enhanced, because strong interfacial interactions were formed in the nanocomposites.

2.1.1.2 In Situ Polymerization

In situ polymerization can improve the dispersion of HNTs in firstly in the monomer, and then the nanocomposites. Covalent bonding can be generated by this method between HNTs and polymer matrix.

Vinyl-ester resins (VERs)\textsuperscript{44}, unsaturated polyester\textsuperscript{45} and epoxy resin\textsuperscript{46,47} can be used as polymer matrix to form HNTs/resin nanocomposites before the resin was cured. For instance, the glassy and rubbery moduli of the nanocomposite are higher than the neat epoxy resin.

2.1.1.3 Melt Processing

Various thermoplastics and rubbers have been mixed with HNTs via melt processing methods. For example, twin screw extruder can be used to mix HNTs with linear low-density polyethylene (LLDPE)\textsuperscript{48}, polypropylene (PP)\textsuperscript{49-51}, polyamide (PA6) via melt processing. Two-roll mill is a common instrument to mix HNTs with ethylene-propylene-diene monomer (EPDM)\textsuperscript{52}, butadiene-acrylonitrile rubber (NBR)\textsuperscript{53} via melt processing.
During the processing, interfacial compatibility can be obtained due to the strong shear force. The interfacial interaction can be improved during melt processing by surface treatment of HNTs.

2.1.1.4 Electrospinning

Electrospinning is a fiber synthesis method to draw charged streams of polymer solutions or polymer melts in a high voltage electric field to obtain continuous micro/nanofibers. Polyvinyl alcohol (PVA) and polylactic acid (PLA) have been used as polymer matrices for electrospinning with HNTs. Water was used to dissolve PVA. Dichloromethane (DCM) was used as a solvent for the PLA with dimethylformamide (DMF) to enhance the electric conductivity. The diameter of poly(lactic-co-glycolic acid) (PLGA)/HNTs composite fibers is larger than neat PLGA fibers, as Figure 2.6 shown. Compared with pure PLGA, mechanical strength of the PLGA/HNTs nanofibers was significantly enhanced, as Table 1 shown.
Figure 2. 6 SEM images of the electrospun of (a) PLGA and (b) PLGA/HNTs nanocomposites (Reprinted with permission from Ref.53)

Table 1 Tensile properties of electrospun PLGA and HNTs/PLGA nanofibrous mats (Reprinted with permission from Ref.53)

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<tr>
<th>Sample</th>
<th>Breaking strength (MPa)</th>
<th>Failure strain (%)</th>
<th>Young’s modulus (MPa)</th>
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<tr>
<td>PLGA</td>
<td>4.21 ± 0.35</td>
<td>76.15 ± 8.38</td>
<td>118.8 ± 10.5</td>
</tr>
<tr>
<td>HNTs/PLGA</td>
<td>6.61 ± 1.66</td>
<td>93.6 ± 21.0</td>
<td>141.8 ± 6.7</td>
</tr>
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2.1.2 Enhanced Properties of HNTs towards HNTs/polymer Nanocomposites

Due to their high aspect ratio, HNTs are universally used as a reinforced filler in polymer\(^{58}\). It is believed that the external load can be transferred from the polymer matrix to HNTs effectively resulting in mechanical reinforcement.

2.1.2.1 Mechanical Enhancement

For example, the Young's modulus and tensile strength of PA6 increased simultaneously with the addition of HNTs\(^{28}\), like Figure 2. 7 shows. As mentioned above, surface treatment can improve interfacial interactions between polymer and HNTs and lead significantly improvement in mechanical properties.
Figure 2. Mechanical properties of the B27/HA R and B40/HA R series of polyamide 6/halloysite nanocomposites at room temperature. (a) Representative curves of the tensile tests of the B27/HA R composites at room temperature (nominal stress vs. nominal strain). (b) Young’s modulus $E$. (c) Yield stress $\sigma_y$. (d) Reinforcement factor $E_{\text{composite}}/E_{\text{neat PA 6}}$ for the B27/HA R and the B40/HA R composites. (Reprinted with permission from Ref. 28)
Figure 2. 8 Theoretical and experimental relative Young's modulus versus nanotube concentration for PLA/HNT and PLA/m-HNT nanocomposites. (Reprinted with permission from Ref.55).

Quaternary ammonium salt was used as surface modifier to treat HNTs, and treated HNTs have a better enhanced effect on PLA than raw HNTs. The tensile strength and Young’s modulus both increased with the load of treated HNTs\(^5^9\) (Figure 2. 8).

2.1.2.2 Thermal Stability

Well dispersed HNTs exhibit a barrier effect on mass and heat transport. Because HNTs begin to degrade at about 400 °C, they have a much higher thermal stability than polymer. Thus, HNTs can effectively increase the thermal stability of polymers.

Thermal stability of PP/HNTs nanocomposites were studied\(^5^0\). As shown in Figure 2. 9, increasing thermal stability was observed with the loading of HNTs and surface treatment of HNTs have a better effect on the thermal stability of PP/HNTs nanocomposites.
Other studies report that HNTs can effectively increase the degradation temperature of PVA\textsuperscript{29}, PLA\textsuperscript{44}, chitosan\textsuperscript{60} and EPDM\textsuperscript{52}.

2.1.2.3 Dielectric Properties

The study of polyamide 11 (PA-11)/HNTs nanocomposite shows that higher real permittivity were obtained of the PA-11/HNTs nanocomposites than that of neat PA-11. The real permittivity increased with the increasing load of HNTs\textsuperscript{30}, as Figure 2. 10 shown.
2.1.2.4 Wettability Properties

Surface wettability is important in bonding of two materials in many applications. Contact angle can be used to determine the wettability and it is related to the chemical composition and surface roughness. Different changes in the surfaces wettability were investigated after adding HNTs in polymers. Giuseppe Cavallaro et al.\textsuperscript{61} found that the contact angle of HPC/HNTs nanocomposite increased with the increasing load of HNTs, while the contact angle of LM pectin/HNTs decreased with the increasing load of HNTs (Figure 2.11).
2.2 Electric Field Assisted Assembly Technique

Various forces on particle will be discussed below when a particle suspension is under the influence of uniform electric field.

2.2.1 Forces Acting on Particles in ER Suspension

A. Electrostatic Force

Electrostatic force can be observed between two neighboring particles as polarized particles can be regarded as dipoles. The dipole-dipole interaction can be attractive or repulsive, and it depends on the position of center line of particles in regarding to the direction electric field. These forces are attractive when the center line is parallel to electric field, while they are repulsive when the center
line is perpendicular to the direction of electric field. Figure 2. 12 shows the schematic of the two forces.

There is an alignment line in the direction of electric field due to the attraction between two particles, even the center line of two particles is not perfectly parallel to the electric filed (the angle between the center line and the electric field= 0~90 degrees).

The dipole-dipole force equation is given by:

\[ F = \frac{6m^2}{4\pi K_f \varepsilon_0 d^4} \]  

(2.1)
Where $d$ is the diameter of the particles, $m$ is the dipole moment, $k$ is the
dielectric constant of the suspending medium as well as $\varepsilon$ is the permittivity of
the free space.

B. Brownian Force

There are random forces called Brownian Force when particle size is very small. The
equation for Brownian Force as an isolated particle in a liquid medium is
given by:

$$\langle F_B(t)F_B(t + t') \rangle = 12\pi\eta \left(\frac{d^2}{2}\right)KT\delta(t')$$  \hspace{1cm} (2.2)

Where, $\eta$ is the viscosity of the medium, $d$ is the diameter of the particle, $k$ is the
Boltzmann’s constant, $T$ is the temperature and $\delta$ is the identity matrix and $\delta(t')$
is the Dirac delta function for a time scale $t'$.

C. Short-Range Repulsive Forces

Particles undergo repulsive forces when they are in the range of angstroms to
nanometers leading to lack of ability to aggregate spontaneously to form clusters.
These repulsive forces can be modeled as hard sphere interaction. The short-
range repulsive forces are given by:

$$F(R_{ij}) = -F_0 \exp[K(\frac{R_{ij}}{d} - 1)]e_r$$  \hspace{1cm} (2.3)

Where the factor $K$ is chosen to represent the range of repulsive force.

$$F(R_{ij}) = -F_0 \left(\frac{d}{R_{ij}}\right)^n e_r$$  \hspace{1cm} (2.4)
Equation 2.4 is chosen because it has same scale as the electrostatic force. It has been reported that Equation 2.3 gives increasing thick columns of particles while Equation 2.4 yields single particle chains\textsuperscript{64, 65}.

D. Stokes' Drag Force

The movement of particles in a fluid is only possible under electric field, when hydrodynamic force or drag force on particles is overcome. The equation for Stokes' Drag Force is given by

\[ F_D = -3\pi \eta d U_i \quad (2.5) \]

U is the velocity if the \(i\)th particle\textsuperscript{64}

E. Total Force Acting on a particle in ER fluid

The total force acting on the \(i\)th particle in ER fluid can be obtained by the sum of electrostatic, Brownian, short-range repulsive and Stoke's drag force:

\[ F_{TOTAL} = F_{ei} + F(R_{ij}) + F_D(X_i) + F_E(t) \quad (2.6) \]

The forces given by above are not at the same scale, the drag force can be negligible as compared to the electrostatic force for dilute suspension. However, when the suspension is a viscous polymer, there is a competition between the drag force and electrostatic force.
2.2.2 Particle Alignment with Electric field in polymer

Electric field alignment in polymer is widely studied and there are some important aspects are introduced below about the electric field alignment in polymer blend or nanocomposites.

Electric field is used to overcome the drag force of the viscous polymer matrix. However, most of the studies in the past were focused on the planar alignment with electric field rather than the cross section, which was easily observed by optical microscope.

Photo-curable and thermally-curable polymers are widely used as matrix to align particles under electric field. After electric field alignment, they are usually done either thermally for thermal-curable epoxies and polymer solutions or through UV irradiation for photo-curable resins, in order to immobilize the orientational microstructure after electric field alignment.

The most common setup for electric field is using two electrodes placed on the same plane and suspension is poured between the two electrodes. Thus alignment can be achieved in the in-plane direction. Figure 2. 13 shows a typical setup for particles in a photocurable resin under electric field and curing then\textsuperscript{66}.
Figure 2. 13: A typical assembly used for electric field assembly of polymer composites (Reprinted with permission from Ref.62)

Single walled carbon nanotubes (SWNTs) were aligned under DC and AC field\textsuperscript{67}. SWNTs tend to move to anode under DC fields, while higher density of alignment chains were found with AC field, as shown in Figure 2. 14. Alignment structure was dependent on frequency of the electric field, higher frequency resulted in a better alignment structure.
Figure 2. 14: SWNTs aligned in between electrodes by applying (a) DC voltage of 4 V and (b) AC voltage of 3V with a frequency of 6.5 kHz (Reprinted with permission from Ref.63).
Carbon nanofibers (CNFs) were used as alignment particles in polydimethylsiloxane (PDMS) under a DC electric field\textsuperscript{68}. Aligned network was found between the electrodes. From Figure 2. 15, longer duration time of electric field applied decided denser network formation. Different viscosities of the PDMS were studied to be found that alignment network was proportional to the viscosity of the polymer matrix.
Figure 2. 15: CNF network formation in PDMS using a DC electric field. (Reprinted with the permission form Ref.64)

Alignment of carbon nanofibers (CNFs) in epoxy under AC and DC fields were studied\textsuperscript{69}. A network formation was found by using AC of 400V/cm at 1KHz in Fig 2.5, while CNFs were attracted by the anode under DC field shown in Figure 2.
16 and Figure 2. 17. Alignment structure was frozen by curing the epoxy thermally. The anisotropic network structure was observed by electrical measurement, higher dielectric constant was measured after the alignment with electric field.

Figure 2. 16: 0.2% CNF dispersed in the amine curing agent, before (a) and 17 min after (b) the application of a DC electric field of 800V/m. (Reprinted with the permission of Ref.65)
Figure 2. 17: Network formation of 0.2% CNF dispersed in amine curing agent in an AC electric field of 400V/cm (a) before, (b) 1 min, (c) 30 min. (Reprinted with the permission of Ref.65).
CHAPTER III

“Z”-ALIGNMENT HALLOYSITE NANOTUBES IN NORLAND 65 FOR ENHANCED IONIC CONDUCTIVITY

3.1 Introduction

The addition of nanoparticles in polymer matrix can introduce unique properties at low concentration (<10%), such as thermal stability, diffusion and mechanical property. Many of these nanoparticles exhibit high anisotropy in properties such as optical, thermal conductivity, diffusivity. Nevertheless, these anisotropies can’t be made full use of by traditional processing methods, because they are unable to align the particles in the thickness “Z” direction.

For many fields, however, properties can be improved by aligning particles in the thickness “Z” direction, like membranes, flexible electronics, fuel cells, photovoltaics, supercapacitors etc. “Z”-alignment can be achieved by directed field assisted method, such as electric field. In this paper, we describe a study of “Z” direction alignment of halloysite nanotubes in Norland 65 by utilizing directed electric field, where the kinetics of clay alignment was investigated and UV curing was used to immobilize halloysite nanotubes after alignment.
Halloysite (Al$_2$Si$_2$O$_5$(OH)$_4$·2H$_2$O) nanotubes (HNTs) are novel one dimensional (1D) natural nanomaterials and aluminosilicate clay with high aspect ratios and hollow tubular nanostructures. Due to its high mechanical strength, biocompatibility, abundant natural resource and thermal stability, HNTs have been massively studied in the field of polymer nanocomposite. However, HNTs tend to agglomerate under the influence of the van der Waals force due to its relatively large surface energy$^{23}$. The shear stress provided by mechanical blending method, such as ball mill, mixer and ultrasonic vibration, can possibly disperse HNTs uniformly in polymer matrix and effectively break up the clusters. Meanwhile, surface modification can provide HNTs with expanding basal spacing between the interlayers of organic and inorganic compounds and good compatibility, therefore, result in a homogeneous mixture of HNTs with polymers during blending$^{23}$. In this study, surface treatment with two chemical solutions were introduced to improve the homogeneity of HNTs in the NOA65 matrix.

There are other applications including ionic conductivity, optical and dielectric properties on clay nanocomposites when clay particles are oriented in the thickness “Z” direction. Traditional processes do not provide particle orientation in polymer system, thus assisted field, such as electric-field$^{86,18}$, was introduced. When exposed to electric field, dielectric particles are charged and polarized. The torque they experience induces both rotational and translational motions in the matrix that leads to orientation$^{87}$. Because of the different dielectric constants between NOA65 ($\varepsilon$≈4) and halloysite ($\varepsilon$=7.9)$^{25}$, electric field induced dipolar interactions can be achieved$^{88}$. 

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The anisotropic property of the nanocomposites created by the orientation of particle can lead to changes in optical parameters including birefringence, transmission and scattering\textsuperscript{89,90}. In this paper, a powerful instrument will be introduced to observe the real-time birefringence development of the nanocomposites under external electric field, and to determine the orientation of the anisotropic particles.

3.2 Experimental Section

In this section, polymer matrix and nanofiller used in this project and experiment procedures are introduced.

3.2.1 Materials

For surface modification: Potassium acetate (PA) (≥99.0%, 1.57 g/cm\textdegree{} at 25 °C, SIGMA-ALDRICH), Toluene (anhydrous, 99.8%, SIGMA-ALDRICH), [3-(2 Aminoethylamino) propyl] trimethoxysilane (AEAPTMS) (≥80%, SIGMA-ALDRICH), Hydrochloric acid (HCl) (37%, SIGMA-ALDRICH).

For nanoparticle: Halloysite nanotube (HNTs) (diam. × L: 30-70 nm × 1-3 \textmu{}m, SIGMA-ALDRICH).

For matrix: Norland 65 (NOA65) (Norland Products)

3.2.2 Experiment Procedures

This section is divided as two parts, first part is to introduce how to prepare surface modified HNTs, and the other part is how to fabricate nanocomposites.
3.2.2.1 Preparation of Surface Modified HNTs

HNTs was chemically treated by potassium acetate (PA) and the applying procedures are as follow: 4 g of PA (Sigma–Aldrich) and 4 ml of hydrochloric acid (12 mol/L) were mixed together, and 1000 ml distilled water was added in a glass beaker placed on a hotplate stirrer to form a PA solution. Then 36 g of halloysite particles were added into the PA solution gradually and stirred for 5 h at 60 °C. Then, treated HNTs were washed by distilled water and collected by centrifugation. After drying in vacuum oven for 24h, the particles were grounded and filtered with a fine metal sieve (100 µm).

The procedures using AEAPTMS to treat HNTs surface are as follow: 2g of AEAPTMS was dissolved in 250ml toluene first, and 2g of pristine HNTs were added in the solution then. The mixture was stirred using magnetic bar at 80 °C for 24h. The slurry was cooled down to room temperature and washed with THF. And the HNTs particles were collected by centrifugation and dried at 80 °C. Then, the procedures to crush and sieve dried HNTs particles are the same as those for PA-treated HNTs.

3.2.2.2 Preparation of HNTs-NOA65 Membrane

Modified halloysite nanotubes were used as filler and Norland 65, a photocurable adhesive, was used as matrix.

Norland 65 is clear and colorless, so it is possible for birefringence measurement. It is reported that NOA65 was made of constituents as follow: 5 wt% photoinitiator benzophenone, trimethylolpropane diallyl ether, isophorone di-isocyanate ester and trimethylolpropane tris thiol. Ultraviolet can be used to
cure NOA65 epoxy and its curing time is remarkably fast, thus the fast curing can freeze HNTs after particles are aligned under electric field. There is no solvent evaporation involved in this photo curable resin system, therefore the thickness of membrane kept constant during the alignment.

Different concentrations of modified HNTs (2%, 4%, 6% by weight of NOA65) were prepared.

The modified halloysite nanotubes were dispersed in NOA65 using planetary centrifugal mixer (Thinky Mixer) at 2000 rpm for 30min and then sonicated by Hielscher UP400S ultrasonic processor at 50Hz for 40 seconds. The procedures above were repeated for 3 times to achieve well-dispersed suspensions.

The suspension was cured by ultraviolet light (OmniCure 2000 UV lamp) with the UV light source 10 cm away from the suspensions for 8 minutes.

3.2.3 Characterization


3.2.3.1 Real Time Birefringence Measurement

A real time measurement\(^{91-93}\) system was developed recently in our group to track fast temporal changes of in- and out-of-plane birefringence, thickness and weight during drying of solution cast films (Figure 3. 1). In this study, this measurement focuses on the changes of in- and out- of- plane birefringence during electric alignment. Two ITO coated transparent glasses with 1mm spacers
were used to load the suspensions. The ITO coated glass holder with suspension was placed in the light path of the optical system (Figure 3. 2). Different voltages at 100 Hz were applied between top and bottom conductive ITO coated glasses and the temporal changes of birefringence were recorded.

Figure 3. 1 Real time solution drying platform which measures changes in out-of-plane and in-plane retardation along with thickness, weight and temperature measurements
Figure 3.2 Modified setup to measure electric birefringence in both in-pane and out-of-plane direction.

There are two linearly polarized light beams in this optical system to measure the temporal birefringence. One passes normal to the film plane (parallel to the direction of electric field) to measure 0° retardation (birefringence can be calculated by retardation). The other one passes through the film at 45° to the film normal direction to measure the 45° retardation.

Real time birefringence can be calculated by retardation as shown in Equation 3.1 and Equation 3.2.

$$\Delta n_{12} = \frac{R_0}{d_t}$$  \hspace{1cm} (3.1)
\[ \Delta n_{23} = \frac{1}{d_t} \left[ \frac{R_0 - R_{\theta}}{\sin^2 \theta} \right] \]

(3.2)

where \( \Delta n_{12} \) is the in-plane birefringence and \( \Delta n_{23} \) is the out-of-plane birefringence, \( d_t \) is the thickness of film, \( R_0 \) is the retardation at 0°, \( R_{\theta} \) is the retardation at \( \theta \) degrees (where \( \theta \) is 45° in our experiment), and \( \bar{n} \) is the average refractive index of our material, which is 1.56.

For this measuring system, 0° retardation is positive, if the refractive index of polymer chain or particle in the machine direction is higher than transverse direction. The 0° retardation is negative if the refractive index in the transverse direction of the instrument is higher than machine direction. For 45° retardation, similarly, a positive retardation can be obtained for higher refractive index in the film plane while a negative retardation indicates that higher refractive index is in the thickness direction of the film.

3.2.3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM, JSM7401) was used at 5kv and 20mA to investigate the morphology of nanocomposite membrane with different concentrations of pure HNTs and modified HNTs under varying voltages of electric field. All samples were sputter-coated with silver by K575× coater before SEM observation.

3.2.3.3 Optical Microscope

Optical microscope (Leitz Laborlux 12 Pol S microscope) with a first order \( \lambda \) plate inserted was used to study the particle orientation under electric field, and
the first order λ plate was inserted with its slow axis oriented at 45° to the crossed polarizers. The sample birefringence response image was taken by a DC 290 Kodak Zoom digital camera connected to the optical microscope.

3.2.3.4 Wide Angle X-Ray Diffraction (WAXD)

Wide angle X-ray was used to characterize HNTs orientation in NOA65. It is a Rigaku RAPID II XRD system with a sealed-tube X-ray source (copper Kα = 1.5418 Å) operating at 40 kV and 30 mA, a spot focus collimator of 0.3 mm diameter, and a cylindrical image plate detector.

3.3 Results and Discussions

The results and discussions will unfold from six parts: Characteristics of Untreated HNTs, Effect of Chemical Treatments for HNTs Dispersion in NOA65, Morphology of PA Treated HNTs in NOA65 under Electric Field, Real Time Electric-Birefringence Measurement, Kinetics and Orientation of Alignment as well as XRD of Aligned Nanocomposite.

3.3.1 Characteristics of Untreated HNTs

The halloysite nanotubes used in this study had tubular shape with diameters in the range of 30-70 nm and lengths of 1-3 um, as shown in Figure 3. Figure 3. 4 (a) shows the length distribution of halloysite in the range of 0.3-1.2 um, and Figure 3. 4 (b) demonstrates that the diameter distribution of halloysite in the range of 70-90 nm.
Figure 3. 3 SEM image for halloysite powder dispersed in DI water

Figure 3. 4 (a) Diameter of halloysite nanotube; (b) Length of halloysite nanotube
3.3.2 Effect of Chemical Treatments for HNTs Dispersion in NOA65

Pristine HNTs agglomerate easily in NOA65, so silane and potassium acetate (PA) were used to treat HNTs for surface modification. SEM images of 4% HNTs-NOA65 films under electric field of 700V show different results between raw HNTs and surface modified HNTs in Figure 3.5. Figure 3.5 (a) is the SEM image of raw HNTs in NOA65, and raw HNTs have bad agglomeration in NOA65 under electric field. It is believed that HNTs' have a large specific surface area (≈60 m²/g) due to their nanoscale size resulting in particle agglomeration. Thus HNTs are easy to agglomerate under the influence of van der waals forces. Figure 3.5 (b) is the SEM image of silane treated HNTs in NOA65 under electric field, although the size of HNTs agglomeration was reduced, there are still many HNTs clusters observed in NOA65. Figure 3.5 (c) is the SEM image of PA treated HNTs in NOA65 under electric field. Obviously, HNTs are well dispersed and single HNTs can be observed aligned in NOA 65. Thus chemical treatment using silane doesn’t improve the dispersion of HNTs in NOA65, while chemical treatment of PA method can reduce agglomeration of HNTs effectively.
Figure 3. 5 SEM image for (a) raw, (b) silane modified HNTs and (c) PA-treated HNTs dispersed in NOA65.
3.3.3 Morphology of PA Treated HNTs in NOA65 under Electric Field

Different concentrations of PA treated HNTs in NOA65 matrix under 700V at 100HZ were prepared.

The morphology of NOA65/HNTs composites with 2 wt.%, 4wt.% and 6 wt.% PA HNTs prepared under electric field is investigated by SEM showing in Figure 3. 6, Figure 3. 7 and Figure 3. 8, respectively.

Figure 3. 6 2%HNTs aligned in NOA65 under electric field of 700V at 100Hz

Rotational and translational motions are caused by dielectrophoretic force due to the non-uniform field. Dipole-dipole interaction occurs to cause dielectrophoresis even in uniform field. The polarization field of one inclusion caused influence on neighboring ones resulting in attractive and repulsive forces between those inclusions. The attractive and repulsive forces cause the
formation of head-to-tail at low concentration and the formation of chains at high concentration.

Figure 3.6 shows the cross sectional morphology of 2% PA treated HNTs aligned in NOA65 under electric field, which shows good dispersion of HNTs alignment. Single halloysite nanotubes were found head-to-tail aligned in electric field direction (thickness direction). With concentration of HNTs increasing, alignment of HNTs in electric field direction was more obvious as shown in Figure 3.7 and Figure 3.8.

Figure 3.7 4%HNTs aligned in NOA65 under electric field of 700V at 100Hz

Figure 3.8 shows the SEM image of 6% PA treated HNTs aligned in NOA65 under electric field, and a good dispersion of HNTs still can be observed in
NOA65. The cross section of film demonstrated that when concentration of HNTs increasing to 6%, clay nanotubes were chained in the direction of the electric field.

![Image of cross section](image)

Figure 3. 8 6%HNTs aligned in NOA65 under electric field of 700V at 100Hz

3.3.4 Real Time Electric-Birefringence Measurement

HNTs undergo induced polarization when electric field is applied to the dielectric matrix with inorganic particle and the extent of polarization depends on the field variables. The field gradients experienced by these polarized particles lead to their rotational and translational motion within the matrix. Using the instrument described above, the rapidly preferential orientation direction can be tracked by obtaining the real time optically anisotropic behavior.
When an AC (100Hz) electric field were applied on the matrix with HNTs through the film thickness direction, the 45° retardation decreased immediately to a negative value while the 0° retardation remained constant at zero value as Figure 3. 9 (a) shown. In order to prove that the decrease of 45° retardation was only contributed from HNTs rather than polymer matrix, the same test was repeated without any filler. Figure 3. 9 (b) shows that there was no obvious change in both 0° and 45° retardation observed with the electric field applied suggesting that the resin has no contribution on the retardation decreasing at 45°. Since the decrease of retardation was only contributed by the orientation of HNTs, the effective thickness of HNTs in the film was used to calculate the in-plane and out-of-plane birefringence by using Equation 3.1 and 3.2, respectively.
Figure 3. 9 Response of in-plane and out-of-plane retardation under the electric field of 700V at 100Hz on (a) 4 wt% HNTs filled and (b) pure NOA65.

Halloysite is biaxial mineral and has three principal indices of refraction. The values of refractive index are respectively \( N_z = 1.565 \), \( N_y = 1.564 \) and \( N_x = 1.559 \) at dehydrated state (7Å), while \( N_y = 1.490 \) at fully hydrated state (~10Å)\(^{94,95}\). The
crystalline structures of halloysite nanotubes was examined by WAXD technique. The peak of pure HNTs and modified HNTs are respectively at $2\theta = 11.61^\circ$ and $11.75^\circ$ basal spacing for the (001) plane, as shown in Figure 3. 10. Bragg equation (3.3) was used to calculate the d spacing of the modified HNTs in this experiment, which is 7.523 Å closed to dehydrated state (7Å).

$$2d \sin \theta = \lambda \quad (3.3)$$

Since the refractive index of three principal axes depend on the hydration state of halloysite nanotubes, which is the content of water in halloysite more accurately, the specific refractive index along three axes are hardly obtained as it depends on the environment of halloysite processing. Thus equations (3.4) were developed to analyze the refractive index of halloysite along three principal axes. Since the form of sample is between fully hydrated ($N_Y = 1.490$) and dehydrated ($N_Y = 1.564$), we can assume that:

$$\begin{align*}
7\text{Å} \times x + 10\text{Å} \times y &= 7.523\text{Å} \\
x + y &= 1
\end{align*} \quad (3.4)$$

$$\begin{align*}
x &= 0.8257 \\
y &= 0.1743
\end{align*}$$

Where x is the portion of dehydrated state and y is the portion of fully hydrated state.

Thus the value of refractive index at y axis: $N_Y = 1.564x + 1.490y = 1.551$. Thus
Figure 3. 10 WAXD spectra of (a) pure HNTs and (b) modified HNTs.

the refractive index along X and Y axis were averaged to $N_{XY}=(N_X+N_Y)/2=1.555$
as the in-plane refractive index and $N_z=1.565$ is the out-of-plane refractive index.
Thus the intrinsic birefringence is $\Delta n_{\text{HNTs}} = N_{\text{XY}} - N_z = -0.01$, and Figure 3. 11 shows the schematic of refractive index for halloysite. This showed that the longitude plane of HNTs oriented along the electric field or thickness direction when the electric filed was applied. Simultaneously, $0^\circ$ retardation remained constantly at 0 nm as HNTs exhibit rotational randomness in the planar view direction since the $N_z$ and $N_{\text{XY}}$ values average to 0 for in-plane retardation and thus birefringence.

![Figure 3. 11 Schematic showing in-plane and out-of-plane refractive index of HNTs](image)

**Figure 3. 11** Schematic showing in-plane and out-of-plane refractive index of HNTs

### 3.3.5 Kinetics and Orientation of Alignment

In order to study the HNTs orientation kinetics, birefringence was studied at different applied voltages and particle concentrations. A constant frequency of 100Hz was used during E-field alignment.
(a)
Figure 3. Kinetics of HNTs orientation as detected by birefringence response at a series of voltages and clay concentration of (a) 2 wt%, (b) 4 wt% and (c) 6 wt%.

When low voltage was applied, the birefringence increased slowly and the final plateau value is relatively low. With higher applied voltage, the rate of increasing of birefringence and the final plateau value immediately increased, as Figure 3.12 shows.
Figure 3. 13 shows that the final plateau value was appreciably decreased with increasing concentration of HNTs, when the applied voltage kept constant at 700V. It is the viscosity that plays a very important role in reorientation kinetics of clay particles. Particles orient and rotate due to the torque from dielectrophoretic force which is proportional to the applied voltage and induced dipole, and the torque has to be greater than drag forces due to viscosity to induce particles orientation. As Figure 3. 14 shows, with increasing clay concentration, the viscosity of clay suspension directly increased. There were larger size of clay tactoids at higher clay concentration since exfoliation is more difficult compared
to lower clay concentration. Hence, the viscosity of clay suspension has a great influence on the kinetics of particle orientation.

![Graph showing change in viscosity with different clay concentration](image)

**Figure 3.14** Change with viscosity with different clay concentration

The parameter of orientation order can be calculated from birefringence can be calculated by using:

\[
\text{Orientation} = \frac{n_{\text{final}}}{\Delta n} \quad (3.5)
\]
Where, $\Delta n_{\text{final}}$ is the value of final plateau for birefringence, $\Delta n$ is the intrinsic birefringence of halloysite nanotubes since the polymer matrix doesn’t contribute to the orientation as mentioned above.

With the increasing addition of nanoclay in matrix resin, the value of orientation decreased (Figure 3.15). The value of orientation is 0.6 at 2% clay addition through the thickness direction. However, with the loading of clay particle increasing at 6%, the value of orientation decreased to 0.37 due to higher clay concentration resulting in larger interparticle interaction leading to frustration among particles.

![Figure 3.15](image)

Figure 3.15 Effect of clay concentration on change in orientation calculated through birefringence
Polarized light microscopy can be used to observe the orientation of clay particle when they exhibit optical anisotropy under E-field. Optical system is as Figure 3. 16 shows to take optical micrographs, the first order lambda plate was inserted along the gamma direction at 45° to the crossed polarized and analyzer. When clay particles oriented with its higher refractive index axis parallel to the slow axis (gamma direction), clay particles appeared blue since high refractive index of particle oriented in the same direction as the high refractive index axis of the lambda plate, and higher refractive index of particles normal to the gamma direction appeared yellow.

Figure 3. 16  Birefringence response of halloysite nanotubes oriented under electric field observed with polarized optical microscope with first order red wave plate.
Using polarized microscope with first order lambda plate, the alignment of HNTs in NOA65 can be observed. All observable colors can be observed in the in-plane micrograph including yellow and blue since the clay particles were randomly dispersed under the cross polarized and the first order lambda plate. When the direction of E-field is parallel to the slow axis, clay particles turned blue under E-field applied, since HNTs aligned with the direction of E-field. Similarly, if the direction of E-field is normal to the slow axis, clay particles appeared yellow when E-field was applied. Since the refractive index of polymer matrix was same in all direction, thus the background appeared red.

In our experiment, the direction of E-field was set parallel to the slow axis. The images at different times showed the alignment of the clay particles, as Figure 3.17 shows. At the very beginning, background was red and yellow and blue colors can be observed in different parts of the images. It is important to note that it is difficult to observe single HNTs under microscope due to their small dimension, so the particles with different color were clusters of HNTs. When E-field was applied at 100s, the background color turned from red to dark purple because those well-dispersed HNTs were aligned along the E-field (slow axis). The higher refractive index of single HNTs was along the slow axis resulting in blue, thus the addition of blue and red turned to dark purple. With the time of E-field applied increasing, chaining of HNTs can be observed in the time sequence images. The texture of clay chains becomes clearer and thick chains can be obtained at 900s. It is believed that a polarization field on one inclusion disturbs the electric field on the neighboring inclusion producing attractive and repulsive forces
between inclusions, and these attractive and repulsive forces cause the formation of clay chains of the inclusions in the polymer matrix.

![Time sequence images showing alignment of HNTs in the electric field](image)

**Figure 3.** Time sequence images showing alignment of HNTs in the electric field (700V/mm, 100Hz) with electric field parallel to the slow axis of the red wave λ plate.

### 3.3.6 XRD of Aligned Nanocomposite

WXRD is a characterization to study the orientation of HNTs in NOA65 after curing. Three X-ray patterns were obtained with X-rays along x, y and z axes of
NOA65/HNTs films. With electric field applied, HNTs were orientated in the Z-direction or the thickness direction of the nanocomposite film, which is parallel to the direction of applied electric field. When X-rays pass through the thickness direction of the film, there was no anisotropy observed as shown in (Figure 3. 18).

Figure 3. 18  WAXD patterns of 6 wt% HNTs/NOA65 film with X-rays taken in thickness direction under electric field of 700V at 100Hz.
However, when X-rays pass through x and y axis, which is perpendicular to the thickness direction, narrow azimuthal breadth of diffraction peak can be observed from the X-ray patterns signifying the orientation of clay particles along “Z”-direction, as Figure 3. 19, Figure 3. 20 and Figure 3. 21 show.

![Figure 3.19: WAXD patterns of 2 wt% HNTs/NOA65 film with X-rays taken in (a) x axis and (b) y axis under electric field of 700V at 100Hz.](image)
Figure 3. 20 WAXD patterns of 4 wt% HNTs/NOA65 film with X-rays taken in (a) x axis and (b) y axis under electric field of 700V at 100Hz.
As we mentioned before, the first peak (2θ=11.75°) is attributed to the (001) plane from crystal lattice of modified halloysite nanotubes, and the 2θ of the (001) plane for nanofilm after alignment matches to particle’s. When clay particles oriented by electric field, the (001) plane rotated correspondingly (Figure 3. 22).
By plotting the intensity as a function of the azimuthal angle (Figure 3. 23), the orientation factor can be obtained and was given by:

\[ f = \frac{1}{2} (3 \cos^2 \theta - 1) \]  \hspace{1cm} (3.3)

Where \( F \) is the parameter of orientation order and \( \theta \) is the angle the halloysite nanotube and the normal director.

Figure 3. 22 (001) plane oriented with the orientation of HNTs
As a perfectly oriented system, \( f = -0.5 \). The orientation factors of different concentrations are very close to the perfectly orientation factor of -0.5 as Figure 3.24 shows that there was a very good orientation of HNTs in the thickness direction under the electric field. Orientation factor calculated from birefringence and XRD analysis were similar as the value of orientation factor decreased with clay addition increasing at 700V/mm. As a solid observation technique, WAXD
again proves that larger tactoids due to higher clay concentration cause lower orientation of clay nanotubes as larger interparticle interaction.

Figure 3.24 Orientation factors calculated from XRD for different clay concentration.
CHAPTER IV
CONCLUSION

Potassium acetate (CH₃COOK) treatment of halloysite nanotubes was successfully used in this study as a method of surface modification to effectively decrease HNT’s clusters in Norland 65 epoxy. It was shown that modified halloysite nanotubes can be well dispersed via centrifugal and ultrasonic mixing.

“Z” (thickness direction)-alignment and clay orientation was achieved with the electric field assisted resulting in optimized properties in thickness direction, such as dielectric properties, thermal conductivity, barrier properties, ion exchange. This study analyzed the Z-alignment orientation of HNTs under an applied electric field. A birefringence measurement system was developed to study the dynamics of HNTs orientation during their electric field alignment. By using this tool, the change of HNTs orientation with different HNT concentrations was investigated. The increasing rate and final plateau value of birefringence increased with voltage, which signified that HNTs oriented faster and more oriented HNTs observed with voltage increased at constant clay concentration. Viscosity is a crucial part in clay orientation under electric field. Increasing viscosity hindered clay orientation, where higher clay concentrations increased the viscosity due to larger interparticle interactions. Thus the properties of
nanocomposite can be tailored by changing the clay concentration and voltage of the electric field to obtain the required microstructures.
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