SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
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EFFECTS OF SODIUM DODECYL SULFATE TREATED HALLOYSITE NANOTUBE ON THE PROPERTIES OF POLY(LACTIC ACID) NANOCOMPOSITES FILM

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled: **“Effects of sodium dodecyl sulfate treated halloysite nanotube on the properties of poly(lactic acid) nanocomposites film”**. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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LIST OF ABBREVIATIONS

$CaCO_3$	Calcium carbonate
CSP	Coconut shell powder
DSC	Differential Scanning Calorimeter
FTIR	Fourier Transform Infrared Spectroscope
ΔH_f^o	Endothermic enthalpy of the 100% crystallized PLA
ΔH_c	Cold crystallization enthalpy
ΔH_m	Endothermic enthalpy of the samples
HNT	Halloysite nanotube
LA	Lactic acid
PA	Polyamide
PE	Polyethylene
PET	Polyethylene terephthalate
PLA	Poly (lactic acid)
PP	Polypropylene
RH	Relative humidity
SDS	Sodium dodecyl sulfate
T	Transmittance
T_1	Transmittance of PLA/HNT nanocomposite films
T_o	Transmittance of neat PLA nanocomposite films
T_c	Crystallization temperature
T_{cc}	Cold crystallization temperature
T_g	Glass transition temperature
TiO_2	Titanium dioxide

T_m	Melting temperature
T_{m1}	First melting temperature
T_{m2}	Second melting temperature
USA	United States of America
UV	Ultraviolet
UVr	Ultraviolet radiation
UVR	UV-blocking ratio
VR	Visible-shielding ratio
w	PLA weight percentage
X_C	Degree of crystallinity
ZnO	Zinc oxide

LIST OF SYMBOLS

%	Percent
°C	Degree Celsius
°C /min	Degree Celsius per minute
cm^{-1}	Per centimetre
g	Gram
J/g	Joule per gram
m %	Mass percentage
min	Minute
mL min^{-1}	Millilitre per minute
nm	Nanometre
ppm	Parts per million
rpm	Revolutions per minute
w/w	Mass fraction
wt %	Weight percentage

KESAN TIUB NANO HALLOISIT DIRAWAT NATRIUM DODESIL SULFAT KE ATAS SIFAT FILEM KOMPOSIT NANO POLI(ASID LAKTIK)

ABSTRAK

Natrium dodesil sulfat (SDS; muatan daripada 0.6 g kepada 4.8 g) telah digunakan untuk merawat tiub nano halloisit (HNT) untuk meningkatkan keserasian antara poli(asid laktik) (PLA) dan HNT. Daripada analisis Spektrometer Infra-Merah (FTIR) pada HNT dirawat SDS, didapati Indeks Si-O telah meningkat sehingga 1.8 g SDS dan menurun selepas muatan ini. Hal ini menandakan muatan optimum SDS dan memberi nisbah bagi HNT kepada SDS adalah 1:0.36. Saput komposit nano PLA/HNT (ketebalan dalam lingkungan 0.13 mm hingga 0.15 mm) telah disediakan dengan menggunakan pengadun dalaman diikuti oleh pengacuanan mampatan. Keupayaan saput komposit nano PLA/HNT menyekat UV telah ditentukan dengan menggunakan spektrofotometer UV-Vis. Keupayaan saput komposit nano PLA/HNT menyekat UV telah meningkat dengan pengingkatan muatan HNT (dari 1% berat ke 8% berat). Saput komposit nano PLA/HNT dirawat SDS-3% menunjukkan keupayaan penyekatan UV yang lebih tinggi daripada PLA/HNT-3%, dengan ketelusan yang bersesuaian. Kelakuan penghabluran komposit nano PLA/HNT telah dikaji dengan menggunakan kalorimeter imbasan pembezaan (DSC). Komposit nano PLA/HNT dirawat SDS-3% menunjukkan darjah penghabluran (X_C) yang lebih tinggi daripada PLA/HNT-3%. Selain itu, kesan kadar penyejukan (5, 10, 20, dan 30°C/min) pada kelakuan penghabluran PLA/HNT dirawat SDS-3% telah dikaji. Adalah didapati kadar penyejukan yang perlahan (iaitu, 5°C/min) dapat meningkatkan lagi X_C bagi komposit nano PLA/ HNT dirawat SDS-3%.

EFFECTS OF SODIUM DODECYL SULFATE TREATED HALLOYSITE NANOTUBE ON THE PROPERTIES OF POLY(LACTIC ACID) NANOCOMPOSITES FILM

ABSTRACT

Sodium dodecyl sulfate (SDS; loading from 0.6 g to 4.8 g) was used to treat the halloysite nanotube (HNT) in order to increase the compatibility between poly(lactic acid) (PLA) and HNT. From the Fourier Transform Infrared Spectroscopy (FTIR) analysis on the SDS treated HNT, it was found the Si-O Index increased up to 1.8 g SDS and then decreased beyond this loading. This marked the optimum loading of SDS and it gave the HNT to SDS ratio of 1 to 0.36. The PLA/HNT nanocomposite film (thickness in the range of 0.13 mm to 0.15 mm) was prepared using the internal mixer followed by compression molding. The UV blocking ability of the PLA/HNT nanocomposite film was determined using UV-Vis Spectrophotometer. The UV blocking ability of PLA/HNT nanocomposite film increased as the increasing loading of HNT (from 1 wt% to 8 wt%). The PLA/SDS treated HNT-3% nanocomposite film showed higher UV blocking ability than PLA/HNT-3%, with acceptable transparency. The crystallization behaviour of PLA/HNT nanocomposites was studied by using Differential Scanning Calorimeter (DSC). The PLA/SDS treated HNT-3% nanocomposite exhibited a higher degree of crystallinity (X_C) than the PLA/HNT-3%. Besides that, the effect of cooling rate (5, 10, 20 and 30°C/min) on the crystallization behaviour of PLA/SDS treated HNT-3% was studied. It was found that the slow cooling rate (i.e., 5^{o}C/min) further increased the X_C of the PLA/SDS treated HNT-3% nanocomposite.

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Nowadays, petrochemical-based plastics are broadly utilized in many industries. However, the interest in the use of biodegradable and bio-based alternatives in industries have raised, for example packaging applications due to the environmental concerns over these materials. The chemically synthesised biopolymers such as polyglycolic acid, polyvinyl alcohol, poly (lactic acid) (PLA) which are known as the renewable resource-based biodegradable plastics can be produce through various methods. One of the chemically synthesised biopolymers which often used as a replacement for conventional petrochemical-based packaging plastics is PLA due to its extraordinary properties (De Silva et al., 2014).

According to Tábi et al. (2010), there is a lot of research altered from the conventional petrol based polymers to biodegradable polymers. This situation may cause by the fact that some of these biodegradable polymers can be bio-based while the conventional plastics are petrol-based. Other than that, the degradation properties of these biodegradable polymers also give the great advantage in contrast with the low recycled ratio of the mass plastics such as polyethylene (PE) and polypropylene (PP). Products derived from biodegradable polymers able to fit in the natural recycling processes.

Based on the finding from Li & Dou (2014), PLA is a biodegradable and linear aliphatic thermoplastic polyester which can be obtained from renewable sources such as corn sugar, potato, and sugar cane. PLA is broadly utilized as a part of broad application including containers, textiles, surgical sutures, engineering materials and food packages.

The high modulus, high strength, good biocompatibility, and high optical transparency properties which exhibits in PLA make it become a promising biodegradable polymer material (Tham et al., 2016a). According to De Silva et al. (2014), PLA is mostly used in packaging, biological, automotive and textile applications as composite or coating materials. It has been classified under the generally recognized as safe (GRAS) category for the food packaging industry. During the early stages of application, PLA usage was limited to specific areas such as coated papers and high-valued films due to its high production cost. Currently, PLA is applied in various applications such as drinking cups (including high heat packaging), packaging polymer for containers and lamination films for short shelf-life products such as fruits and vegetables because the improvement in technology has made the PLA become a more cost effective polymer (costing around 2.2 USD/kg).

However, PLA still exists some disadvantages such as slow degradation rate, poor heat resistance and slow crystallization rate. According to Araújo et al.(2013), in spite of having a lot of good properties, PLA still has some limitations on the certain applications due to its weaknesses in some aspects, for example, low thermal stability, poor oxygen barrier and low heat distortion temperature. PLA exhibits poor barrier properties to oxygen in packaging films and low thermo-oxidative stability. One of the important considerations in the application of food packaging to preserve fresh food products is the oxygen barrier property. The shelf life of the product will extend when the oxygen permeation through the film was reduced because the oxygen permeability coefficient of the polymer film decreases. Hence, various types of nanofiller have been used on the preparation of PLA nanocomposites such as graphene, carbon nanotube and nanoclay to overcome the weakness of PLA (Tham et al., 2016b).

Adding halloysite nanotubes (HNT) into PLA is one of the strategy to improve the mechanical and thermal properties of the nanocomposites. According to the Liu et al. (2013), HNT modified polymer composites have raised researcher’s interest in the recent years due to their unique structures and properties. The main factors which able to improve the performances of the nanocomposites are the good dispersion of the HNT in polymer matrix and the strong interfacial interaction between two phases (Luo et al., 2016). According to De Silva et al. (2014), HNT known as a low cost and high performance fillers. It’s having the extraordinary properties such as tubular structure, biocompatibility, high surface area and large aspect ratio. Recently, HNT have been utilized effectively as nanofillers in many research in order to enhance the mechanical and thermal properties of various types of polymers due to its outstanding properties. The dispersion of HNT can be further improved by the addition of surfactant for example, sodium dodecyl sulfate (SDS) (Lun et al., 2013).

Recently, most of the research reported that the PLA/HNT composites fabricated by melt compounding showed the improvement in tensile, flexural, impact properties and thermal properties due to it the hydrogen bonding interaction between PLA and HNT (De Silva et al., 2014). According to Castro-Aguirre et al. (2016), PLA is exposed to sunlight during its lifetime for applications in packaging containers or films. The low wavelength and high energy UV radiation will cause the PLA undergoes plastic degradation. The photodegradation of PLA was increased due to the presence of carbonyl group in PLA chemical structure which absorbs UV radiation at about 280 nm via n- π^* electron transition. In this research, HNT was added into PLA to increase the UV blocking ability of the PLA. When PLA exposed to UV radiation for a longer time, the mechanical properties of PLA will be influenced. The PLA will become brittle due to the decrease in stress and strain at break. UV radiation can cause an increase in molecular weight distribution and decrease in molecular weight of PLA. According to Copinet et al. (2004), PLA has the ability to form highly crystalline structures which is more difficult to hydrolyse than amorphous parts of the polymer. The microbes and enzymes are often used to study the degradation mechanism of PLA and its copolymers. In addition, UV exposure occurred in market may be one of the possible factor for plastic degradation when PLA is used as packaging materials.

Kaygusuz & Kaynak (2016) reported that the cooling rate applied during injection moulding in many industrial products is too fast to allow crystallisation of PLA. There is a lot of research study using the organic or inorganic additives such as calcium carbonate ($CaCO_3$), montmorillonite, carbon nanotubes and talc to regulate the crystallisation of PLA. However, Battegazzore et al. (2011) claimed that PLA is a promising candidate for the fabrication of thermoformed containers, stretch-blown bottles and biaxially oriented films due to it highly transparent and rigid property with a relatively low crystallization rate.

1.2 Problem Statement

Based on the finding from Luo et al. (2016), due to the incompatibility between the hydrophilic HNT and hydrophobic PLA, the HNT with high surface energy are easy to agglomerate at high filler content, resulted in poor dispersion in PLA matrix. Therefore, it is necessary to modify the surface of HNT with organic group to improve the dispersion of HNT in PLA matrix. Adding the surfactant could be one of the possible strategy to improve the dispersion of HNT in the PLA matrix.

Besides that, Copinet et al. (2004) reported that in case of using PLA as packaging materials, UV exposure may be one of the possible reason for plastic degradation. The ultraviolet light (315 nm) had an enhancing effect on the degradation of PLA plastic films and it will accelerate the decrease of mechanical properties, glass transition temperature and molecular weight of PLA. Incorporation of UV stabilizer is a common method to improve the UV stability of polymer. Nevertheless, in this research, UV blocking ability of HNT will be explored.

The crystallization behaviour of PLA strongly affect both the processability and productivity. Thus, it is necessary to control the crystallization of PLA to adapt for various application. Adding HNT and SDS treated HNT might influence the thermal properties and crystallization behaviour of the PLA. Thus, the crystallization of the PLA/HNT should be studied in this project as well.

1.3 Research objectives

The research objectives of this project are:

(a) To investigate the effect of sodium dodecyl sulfate (SDS) treatment on the properties of PLA/HNT nanocomposites.

(b) To study the effect of HNT on the UV blocking ability and transparency of PLA.

(c) To investigate the crystallization behaviour of PLA/HNT nanocomposites.

1.4 Thesis Structure

Chapter 1: Introduce the PLA and HNT and the advantage of the PLA/HNT nanocomposites. Besides that, current problem for the PLA/HNT nanocomposites are discussed.

Chapter 2: Discusses in details of the literature review of PLA, HNT and SDS. The terminology of nanocomposites, dispersing agent, UV blocking ability and thermal properties of PLA are explained in this chapter.

Chapter 3: Provides the information about the materials and method used in this study which is suitable methodologies conducted base on certain standard for all conventional testing procedure with description of the sample characterization methods.

Chapter 4: Focuses on the experimental result obtained throughout the experiment and discussion as well as the further elaboration on the problems encountering during experiment.

Chapter 5 Summarizes the significant findings in this study. Suggestions for future studies are also recommended.

1.5 Scope of Study

In this research, SDS will act as a dispersing agent to treat the HNT through the chemical modification in order to improve the dispersion of HNT in PLA matrix. The SDS treated HNT was characterized by Fourier Transform Infrared Spectroscope (FTIR).

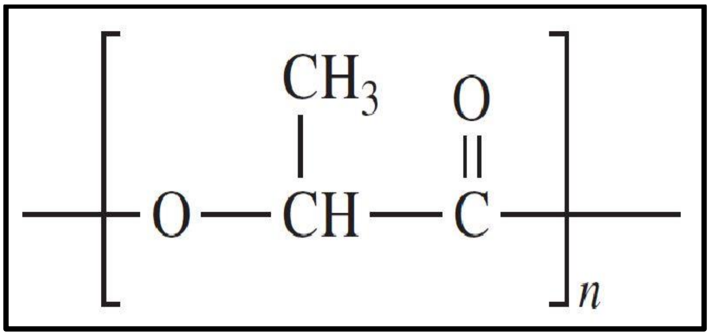
The effect of HNT on the transparency and UV blocking ability of the PLA was be studied through the UV-Vis Spectrophotometer. The crystallization behaviour of the PLA/HNT nanocomposites was characterized using Differential Scanning Calorimeter (DSC). In addition, the effect of cooling rate on the crystallization behaviour of the PLA nanocomposites was studied.

CHAPTER 2

LITERATURE REVIEW

2.1 Poly (lactic acid) (PLA)

PLA known as a green-biopolymer which is the best alternatives to replace petro-chemical based commodity plastics. This can diminish the carbon impression and waste transfer dangers to the earth. PLA is an aliphatic thermoplastic biopolymer produced from agricultural sugar feed stocks, for example, corn and beet. Chemical structure of monomer PLA showed in Figure 2.1(De Silva et al., 2015).



$$\left[-O-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\overset{\overset{\displaystyle O}{\|}}{C}- \right]_n$$

Figure 2.1: Chemical Structure of PLA (De Silva et al., 2015).

According to Arjmandi et al. (2016), many research have been done on PLA in both research and industrial aspects. The PLA is a semi-crystalline polymer with glass transition temperature (T_g) around 55 to 59°C and melting point 174-184°C. Based on the finding from Jamshidian et al. (2016), PLA facing some limitation when applied in thermally processed packages due to its low glass transition temperature property. The low melting temperature and deformation property which found in PLA make its more applicable in the thermoforming and heat sealing application.

Besides that, Lasprilla et al. (2011) reported that PLA exhibits a good process ability, high Young's modulus, good mechanical strength and thermal plasticity. Jamshidian et al. (2016) claimed that PLA having the higher tensile modulus and flexural modulus compare to PS, PP and HDPE. PLA also have an optical transparency which is comparable to petroleum-based polymer (Arjmandi et al., 2016). PLA known as a transparent plastic which has the similar characteristics compare to common petrochemical-based plastics, for example, polypropylene and polyethylene (Laxmana Reddy et al., 2013). Hence, conventional synthetic polymers in various applications can be replaced by the PLA. The good crease- retention, excellent aroma barrier, grease and oil resistance and high strength properties are exhibit in PLA (Giita Silverajah et al., 2012).

PLA derived from renewable resources with low cost and non-toxic to human body and environment has increased the interest of researcher. Besides that, PLA is recyclable to its monomers with a large production (Araújo et al., 2013). According to Hung et al. (2013), commercial PLA exhibits various good properties such as biocompatibility, great mechanical properties, mechanical property, biodegradability, low environmental impact and thermoplastic processibility. Jeon and Kim (2013) reported that the greenhouse gases produced during the production of PLA is much lower compare to the fossil resource-based plastics. Figure 2.2 showing the PLA life cycle starting with corn and sugar-beet and the biological systems use the solar energy by the process of photosynthesis (Murariu & Dubois, 2016).

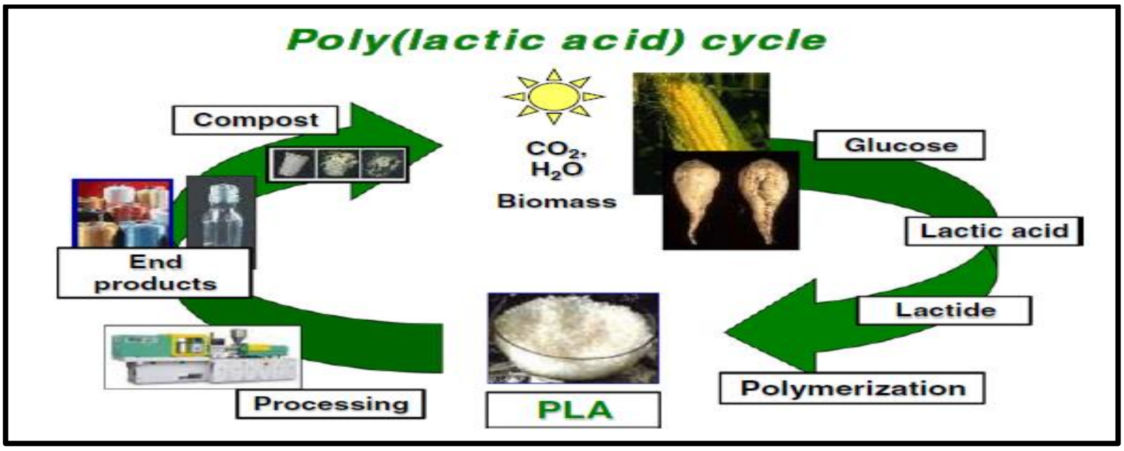


Figure 2.2: PLA life cycle starting with corn and sugar-beet and the biological systems use the solar energy by the process of photosynthesis.

According to Lasprilla et al. (2011), two important methods for PLA synthesis are ring opening polymerization of lactic acid cyclic dimer and direct polycondensation of lactic acid. Figure 2.3 shows the reaction mechanism for direct polycondensation of lactic acid and ring opening polymerization of lactic acid. The solvent is used and higher reaction times are required for the direct condensation. The polymer produce through this method will having the molecular weight between low to intermediate. Based on the finding from Raquez et al. (2013), lactic acid (LA) exist two optical isomer which is D,D-lactide (D-LA) and L,L-lactide (L-LA) due to presence of two chiral centers has showed in Figure 2.4.

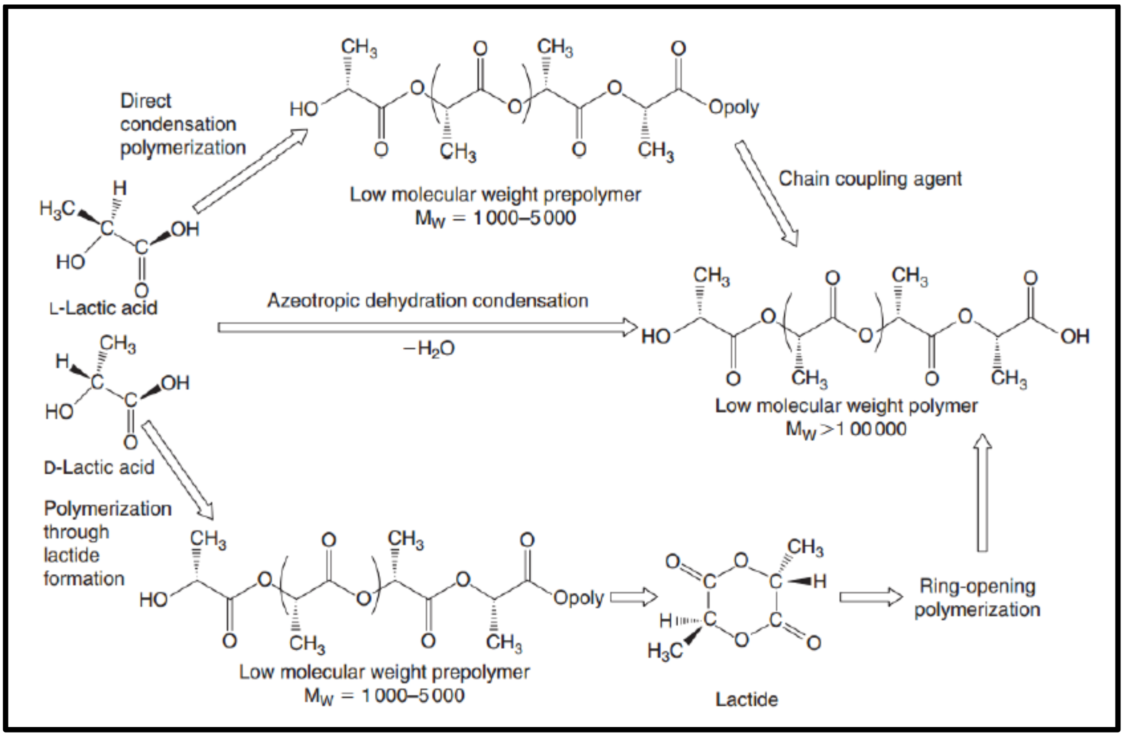


Figure 2.3: PLA synthesis methods (Lynch, 2014).

The molecular weight of PLA can be controlled in the ring-opening polymerization (ROP) of the lactide with the presence of the catalyst. Ratio and sequence of D and L-lactic acid units in the final polymer can be control by the monomer used and reactions conditions (Lasprilla et al., 2011).

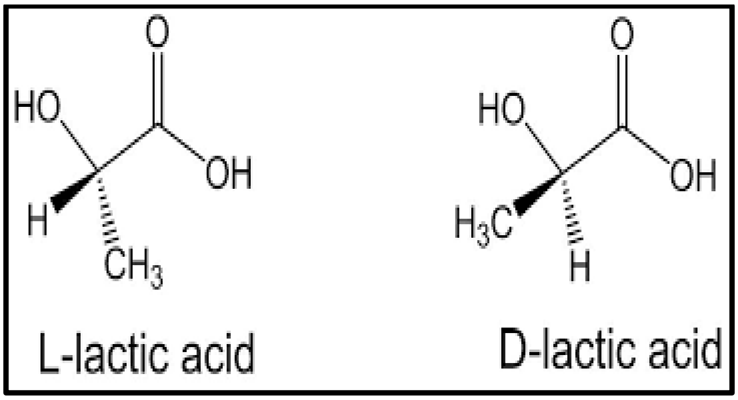


Figure 2.4: Optical isomer of lactic acid (LA) (Raquez et al., 2013).

According to Castro-Aguirre et al. (2016), both PLA and fossil based polymers exhibit the similar limitation on the processing which is poor homogeneity at lower limits of temperature and degradation at upper limits of temperature. Hence, the processing and components qualities can be optimize through the understanding of PLA's crystallinity and melt rheological properties. Before PLA undergoes the processing, PLA must be dried to water content less than 100 ppm (0.01%, w/w) to prevent hydrolysis which may cause the reduction of the molecular weight. The hygroscopic property of PLA make its very sensitive to temperature and high relative humidity (RH). PLA dried to values which less than 250 ppm water (0.025%, w/w) during industrial production. PLA resin should be dried below 50 ppm water (0.005% w/w) when PLA is readily processed at temperatures higher than 240°C or with longer residence times to prevent the reduction of the number average molecular weight. One of the important techniques for continuous melt processing of high molecular weight PLA is the melt extrusion after the PLA was properly dried.

According to Castro-Aguirre et al. (2016), the competitive cost and the high attention of public on the impact of polymer to the environment has largely increase the production of PLA for industrial applications. The two major groups of industrial applications for PLA are consumer non-durable goods and consumer durable goods. The consumer durable goods are commodity products with the minimum 3 year lifetime, for example, cars, medical products and appliances. While, the consumer non-durable goods are the product which has the lifetime less than 3 years, for example, short-term medical items, service ware and packaging. However, the product categories may be overlap which depend on the designation of PLA. Besides that, PLA has used in various application such as fibers and textiles, environmental remediation, packaging and service ware and medical.

PLA had been applied for medical application which is medical devices and implants since the early 1960s. The PLA will undergo the degradation after certain time make it become a suitable materials for medical implants. The wicking properties and ability to absorb organic compounds in PLA make its suitable for the fiber application. PLA suitable for wipes application due to it ability to absorb moisture and fairly polar properties. Besides that, the packaging and service ware make from PLA has increased a lot along the pass 5 years. A lot of the efforts have been done in both academia and industry research to strengthen the green-packaging market, in order to fulfil the customer requirements for packaging produced from renewable resources. There is some challenges for using the PLA as the commercial packaging applications which is the limitation on the barrier and mechanical properties. However, the performances of PLA in packaging application can be enhanced through the adjustment of polymer processing, blending with other polymers and adding some additives such as antioxidants, plasticizers and nucleating agents. In addition, PLA can used in the application for cigarette filters, paints and 3D printing (Castro-Aguirre et al., 2016).

According to Li et al. (2010), PLA had applied in the electric appliances and automotive parts in order to replace the petroleum-based polymers. One of the major consideration for electric and automotive applications is the heat resistance and the processability of PLA in the molding process. PLA is a semicrystalline polymer with a glass transition temperature (T_g) of around 60°C and melting temperature of around 170°C. The low T_g has limited the application of PLA in amorphous form. The crystalline form will giving the higher mechanical properties to PLA when the temperature higher than it T_g. The slow crystallization rate is one of the reason which make the PLA become poor processability and difficulty on demoulding. Hence, strategy to increase the crystallization rate of PLA is very important, so that the final product able to fulfil the requirements.

Besides that, PLA is brittle and presents low thermal stability, low impact resistance and moderate gas barrier properties, which are all important properties for packaging applications. Jamshidian et al. (2010) reported that PLA will experience rapid loss of molecular weight due to its thermally unstable. This will be the result of thermal treatment at processing temperatures. The degradation will happen on the ester linkage of PLA during the thermal processing. The thermal degradation of PLA usually happen at the temperature which below the melting point of PLA. When the temperature was higher than the melting point then the degradation rate will increase rapidly. The random main-chain scissions will happen during the thermal degradation of PLA. There is some reaction occur during the thermal treatment. The PLA will undergoes degradation process when depolymerisation, hydrolysis, oxidative degradation, inter and intramolecular trans-esterification reactions to monomer and oligomeric esters are happen. The temperature and humidity of environment, shape and particle size of polymer, % D-isomer and crystallinity in PLA, molecular weight and metal impurities from the catalyst and residual lactic acid concentration will influence the degradation rate of PLA. Hung et al. (2013) claimed that the thermal processing of PLA is much affected by its highly heat sensitively and the poor thermal stability properties. The mechanical properties of PLA will decrease a lot after few times injection and moulding recycles due to its poor thermal stability. The thermo-hydrolysis and transesterification or depolymerisation are the main problem of recycling process.

Arjmandi et al. (2016) reported that PLA exhibits a low crystallization rate and prone to aging at room temperature is one of the important aspect for the industry application. Based on the finding from Jamshidian et al. (2010), rate of crystallinity is an important property of polymer. Amount of crystalline region and amorphous content in the polymer is indicated by its crystallinity. Polymer crystallinity is one of the important consideration during the material selection for a required application because the properties of polymer such as hardness, modulus, tensile strength, stiffness and melting point are influence by crystallinity.

PLA crystals able grow in three structural positions which known as α, β, and γ forms. They are described by various helix conformations and cell symmetries, which create through various thermal and mechanical treatments. During the melt or cold crystallization, the α form will develop. The β form grow upon the mechanical stretching of the more stable α form. While the γ form will grow on hexamethylbenzene substrate only (Jamshidian et al., 2010).

PLA having some weakness which restrict its applied in the commercial application when compared to the conventional polymers. According to Foruzanmehr et al. (2016), the moisture sensitivity and poor impact resistance are the weaknesses which exhibits in PLA. Hence, a lot of research have been done to overcome the weaknesses of PLA such as adding the plasticizer or reinforcing agent to the PLA matrix.

Based on the finding from Mutsuga et al. (2008), packaging for fresh food and lunch boxes were made from PLA in Japan. This show that the PLA have the high probability to contact with various types of food. Conn et al. (1995) reported that PLA only contain lactic acid as monomer hence migrated agents for PLA are lactic acid monomers, dimmers and oligomers. There is very limited migration from PLA into food. The intake of lactic acid from PLA is approximately 700 times less than the estimated daily lactic acid intake of a breast-fed infant. Hence, the PLA is safe using in the food packaging industry.

2.2 Halloysite Nanotube (HNT)

Based on the finding from Luo et al. (2016), HNT is a naturally alumino silicate clay with a Si/Al ratio of 1:1 and a molecular formula of $Al_2Si_2O_5(OH)_4 \cdot nH_2O$ (Figure 5). HNT exhibits the one dimensional (1D) hollow nanotubular structure with a length of about 200–1500 nm and inner diameter of 15–100 nm. HNT contains some unique properties which are rich functionality, natural availability and good biocompatibility. Thus, adding the HNT into the polymer matrix able to enhance the performance of nanocomposites such as tensile, flexural, impact and thermal properties. Besides that, the HNT also used in the household products and medical applications due to its non-toxic and biocompatibility properties (Zhang et al., 2016). HNT unique crystal structure is similar to the structure of carbon nanotubes (CNT) in terms of aspect ratio. HNT also exhibits high temperature resistant properties, hydroxyl group density on their surface is relatively low and presence of the nanoscale lumens. Hence, HNT was known as the excellent one-dimensional reinforcement nanomaterials for various polymers (Fang, 2016).

According to Huang et al. (2016), HNT is a natural mineral nanotube which having an empty lumen and high aspect ratio. There is a lot of advantages to use HNT as nanofiller in polymer. Besides low toxicity, inexpensive and exhibits several active group on their surfaces, HNT also promotes good biocompatibility and good dispersion properties. HNT able easily dispersed well in various polymers and this show that it exhibits great reinforcing ability for the composites. Lately, there is a lot of research study on HNT as a novel biomaterials. The unique nanostructure of HNT make it able to be applied as drug delivery carriers.

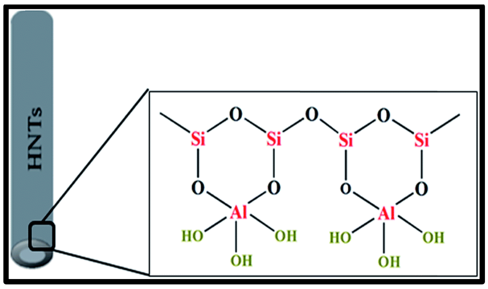


Figure 2.5: Chemical Structure of HNT (Hebbar et al., 2016).

According to Wang et al. (2014), HNT is a naturally occurred silicate with good chemical stability and large specific surface area which exhibits hollow structures with Si-OH groups on the external surface and Al-OH groups in the internal surface. HNT has selective functionalization because it contains a negative silica outer surface and positive alumina inner lumen (Biddeci et al., 2016). HNT become easier to functionalize and perfect to be used as substrates due to this characteristic. Wang et al. (2014) reported that HNT are chosen as dependable substrates in numerous field, for example, the association of honourable metal nanoparticles and numerous different materials with lower mechanical stability. Besides that, the dispersion of HNT in polymer matrix is easier compared to carbon nanotubes and graphene. This is due to the less π - π interaction between the tubulars of HNT and lesser functional groups on the outer surface (Wan et al., 2017). Zhong et al. (2016) claimed that one of the important properties of HNT compare to various clays, for example, kaolin, bentonite and montmorillonite is HNT no required exfoliation to smooth the surface of clay. Hence polymer nanocomposites with

HNT have attracted a lot of attention due to the significant reinforcing effect, decreased permeability, biocompatibility, tuneable barrier and delivery properties compared with those that have conventional spherical fillers.

There is silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3) in the HNT. The schematic diagrams of the crystalline structure of halloysite, and the structure of a halloysite nanotube showed in Figure 2.6. The The HNT unable to conduct the electricity because it possess a stable structural and chemical properties which lacks loosely held electrons. The conductivity properties can introduce to HNT through the doping process which produce few holes and defect on HNT. Natural HNT can conduct by a process known as ion exchange due to its clay characteristics. Besides that, the pores of HNT can contain water and the moisture ratio being in proportional to its porosity. The higher porosity in HNT absorbed more moisture hence the conductivity of HNT increased. HNT exhibits a low electron transfer ability when it was dehydrated after grinding and drying at 80°C for 12 hours (Zhang et al., 2016).

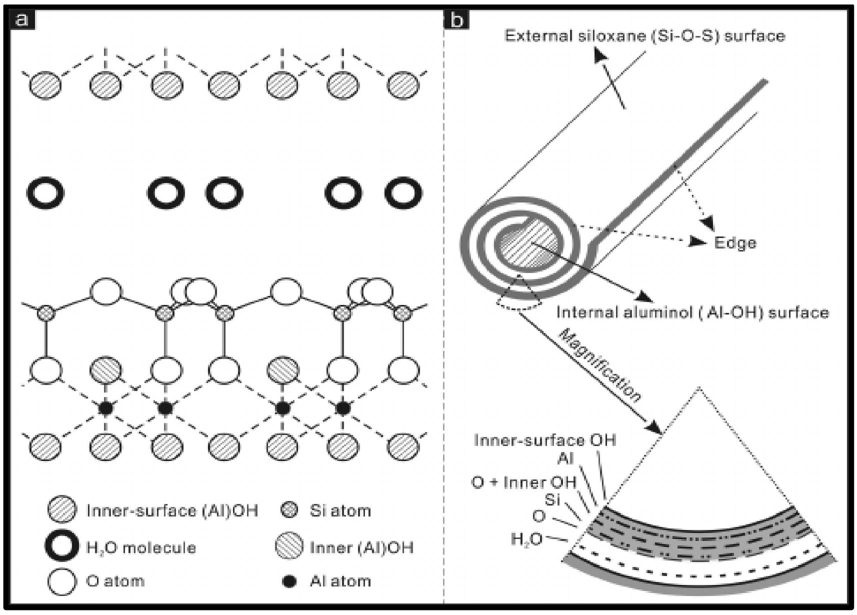


Figure 2.6: Schematic diagrams of the crystalline structure of halloysite, and the structure of a halloysite nanotube (Zhang et al. 2016).

According to Liu et al. (2013), HNT normally applied in various fields such as time-release capsule, bioreactor, catalysts of polymer degradation, template and high-tech ceramic applications. HNT is promptly dispersed in water because the excellent hydrophilicity and small dimension of HNT. Hence, solution mixing can be used to prepare the water soluble polymer-HNT nanocomposites. Besides that, applied shear forces on polymer melt able to separate the aggregates of HNT easily. Melt blending also one of the famous methods to mix the polymers with HNT. The mechanical and thermal properties of polymer nanocomposites was increased significantly after adding the HNT. The raw HNT exhibits high aspect ratio, uniform tubular morphology, high specific surface area and good dispersion ability in polymers. These characteristics make HNT become an ideal nanofillers for polymers.

Based on the finding from Liu et al. (2009), the rigid properties with high aspect ratio make the HNT become an ideal materials for preparing polymer composites. Besides that, the dispersion of HNT in polymer matrix by shearing is much easier compare to other nanoparticles is due to the geometrical and chemical properties of HNT. The rod-like geometry of HNT can disperse easily because the limited intertubular contact area. The hydroxyl density on the HNT outer surfaces is lesser than the fumed silica and other layered silicates, for examples, montmorillonite. HNT are inexpensive, biocompatible and plentifully available.

However, the absence of reactive groups on the surface of HNT was cause the poor interfacial interaction between the HNT and the polymer matrix. These problem highly affected the reinforcing efficiency of a typical polymer and cause the inadequate mechanical properties of the nanocomposites (Wan et al., 2017). According to Luo et al. (2016), the two major factors able to enhance the performances of the nanocomposites are the nanofillers able to disperse well in the polymer matrix and exhibits strong interfacial interaction between two phases. There is a natural incompatibility between the hydrophilic HNT and hydrophobic polymer matrix such as poly (l-lactide) (PLLA). Besides that, HNT with high surface energy are easy to agglomerate in polymer matrix at high filler content. This cause the nanofillers dispersed non-ideally in the polymer matrix poor interfacial interaction between the nanofillers and polymer matrix. Hence chemically modified HNT is required to improve the dispersion and interfacial adhesion with the polymer matrix.

2.3 Nanocomposites

Raquez et al. (2013) claimed that polymer nanocomposites are a multiphase materials which contain at least one of the constituent phases and nanofiller must has at least one dimension in the nanoscale range which is less than 100nm. Properties of the polymeric material will improve through a small amount loading of nanofiller. Multifunctional polymer composites which promotes better mechanical, electrical, optical, thermal or magnetic properties can be produced through adding the nanoscale fillers in polymers.

Nanocomposite materials are moulded by mixing no less than two distinct materials at the nanoscale. This technology can enhanced the structures and properties of materials as well as develop a new material. The morphology and interfacial qualities of the individual segments which used in the mixing will affect the properties of nanocomposites. There is a lot of research have been done on nanocomposite materials and coatings in order to develop a new material or new properties on the selective materials. Nanocomposite materials and coatings along these lines offer enormous potential for new applications such as aerospace, automotive, electronics, biomedical implants, non-linear optics, mechanically reinforced lightweight materials, sensors, nano-wires, batteries, bioceramics, energy conversion and many others (Öchsner et al., 2009).

Based on the finding from Raquez et al. (2013), nanofillers which existing in diverse sizes and shapes and can be grouped into three classifications upon the dimensionality of the nanosized particle which are plate-like nanofillers (1D), nanofibers or whiskers (2D) and nanoparticles (3D). The common filler geometries and their respective surface area-to-volume ratios has showed in Figure 2.7. Plate-like nanofillers (1D) having an aspect ratio at least 25 and show layer properties with thickness at 1nm. Nanofibers or whiskers (2D) having an aspect ratio at least 100 and diameter which is below 100nm such as carbon nanotubes and nanocellulose substrates. Nanoparticles (3D) showing a 3D dimensions below 100 nm such as silica particles and metal oxide.

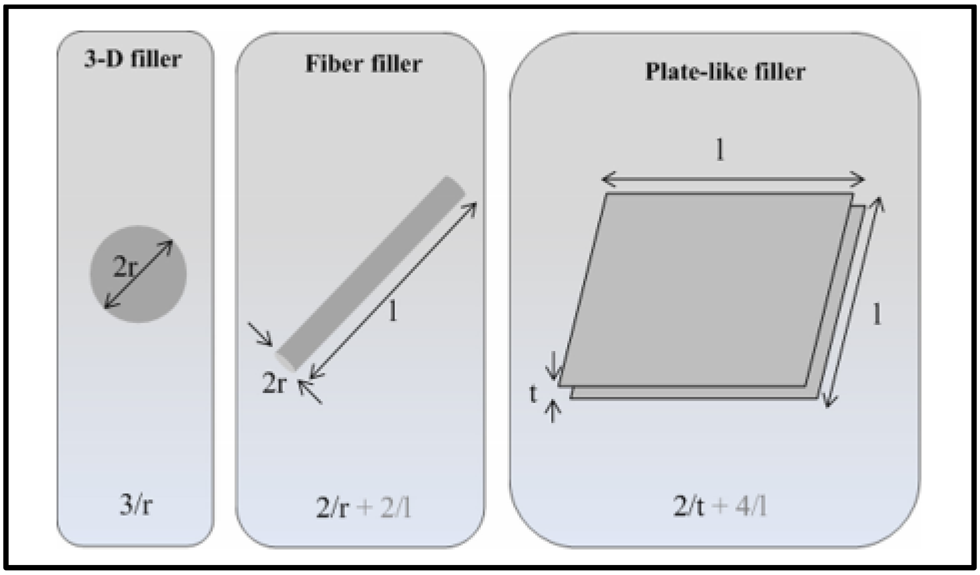


Figure 2.7: Common filler geometries and their respective surface area-to-volume ratios.

2.3.1 PLA nanocomposites

According to Liu et al. (2013), the high production cost of PLA is limited it in the biomedical applications. Currently, an innovation on the production process of PLA by

Natureworks LLC Company was significantly reduced the production price. This required further studies on PLA's properties and potential applications as bio-based and degradable plastic to replace the traditional oil-based non-degradable. The bionanocomposites can produced through the melt mixing by adding the natural HNT to PLA. The HNT dispersed well and having good interaction between PLA will promotes a polymer nanocomposites with higher mechanical and thermal properties. PLA/HNT nanocomposites are green materials because both PLA and HNT are produced from nature. Besides applied as degradable plastic, PLA/HNT nanocomposites have the potential in the medical application such as drug carrier. The HNT exhibits high loading efficiency and controlled release ability for drugs due to the unique lumen structures.

The elasticity is required for packaging application. Thus, the brittleness may restrain the utilization of PLA/HNT films in packaging industry. The 'post-drying' process during the films preparation will affect the stress-strain behaviours of PLA/HNT films. In addition, the biodegradation rate increased when the material is brittle. Hence, preparation of PLA/HNT composites are very useful in the packaging applications because biodegradability play a very important role (De Silva et al., 2014). According to Luo et al. (2016), due to the incompatibility between the hydrophilic HNT and hydrophobic PLA, the HNT with high surface energy are easy to agglomerate at high filler content, resulted in poor dispersion in PLA matrix.

2.4 Surfactants

Based on the finding from Romyen et al. (2009), surfactants are compounds which is able to reduce the surface tension of a liquid, the interfacial tension between two liquids or that between a liquid and a solid. Surfactants can also function as dispersants, wetting agents, emulsifiers, detergents and foaming agents. Besides that, surfactant can divide into four classes which is cationic, anionic, zwitterionic, and non-ionic. Surfactant promotes the amphiphilic properties which contain a hydrophilic group (heads) and hydrophobic group (tail) in the same molecules. The surfactant molecules combine together to form spherical aggregates which known as the micelle when the concentration of surfactant increases over the critical micelle concentration in a solution.

Romyen et al. (2009) claimed that surfactant molecule contains water insoluble, oil soluble component and water soluble component. Surfactant molecules will diffuse in water and adsorb at interfaces between air and water. The insoluble hydrophobic group may extend out of the bulk water phase either into the air or oil phase. The water soluble head group will always remain in the water phase.

According to Banat et al. (2000), micelles will form in the aqueous phase when the aggregation of the surfactants occurs. The hydrophobic tails will form the core of the aggregate and the hydrophilic heads are in contact with the surrounding liquid during the micelles formation. Besides that, spherical, cylindrical and bilayers micelles can be formed as well. Shape of aggregates was affected by the chemical structure of the surfactants. The shape of aggregates will affect by the balance of the sizes of the hydrophobic tail and hydrophilic head. Sample of aggregation of surfactant or micelle is shown in Figure 2.8.

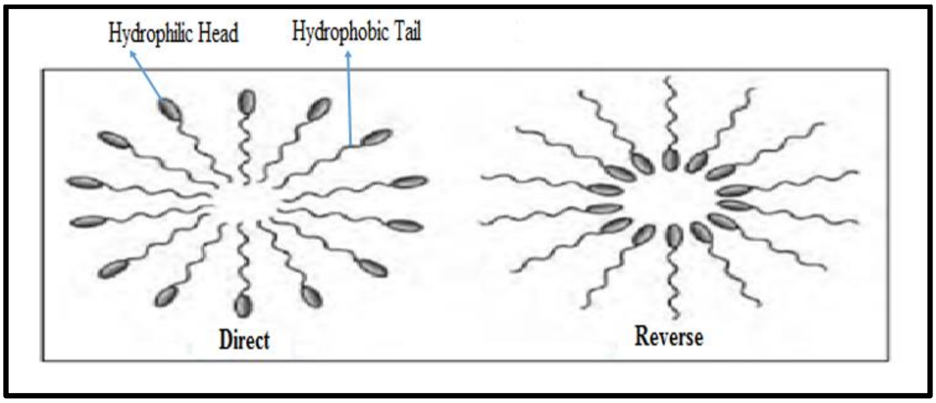


Figure 2.8: Micelle, hydrophilic type and hydrophobic type.

2.4.1 Dispersing Agent

According to Lei et al. (2016), dispersion methods can be characterized into two types which are physical and chemical methods. The ultrasonic dispersion, mechanical stirring dispersion, grinding and stirring dispersion in a high speed are known as the physical dispersion methods. While the incorporation of the various type of dispersing agents such as anionic superplasticizer, hydroxyl acids (salts), organic and inorganic phosphoric acid (salts) are known as chemical dispersion methods.

Dispersants have been broadly utilized in mineral processing, for example, anionic, cationic, polymeric and inorganic dispersants. The separation of agglomerates is the aim for the dispersing process. The dispersant able to deagglomerate the large agglomerates to smaller size. The excessive dispersing should be prevented at all the times in order to avoid the damage of after-treated pigment surfaces and loss of the application properties (Lun et al., 2014).

2.4.2 Sodium dodecyl sulfate (SDS)

SDS, ($C_{12}H_{25}SO_4Na$), is one type of anionic surfactants. The chemical structure of SDS has showed in Figure 2.9. SDS has a tail of 12 carbon atoms attached to a sulfate group. Hence, SDS exhibits amphiphilic properties. SDS has been used as the dispersant to disperse the $CaCO_3$ nanoparticles, calcium montmorillonite and silica nanoparticles. SDS has known as one of the efficient dispersants for dispersing the natural nanotube-like clays due to the ability to create a lather and its thickening effect (Lun et. al., 2014).

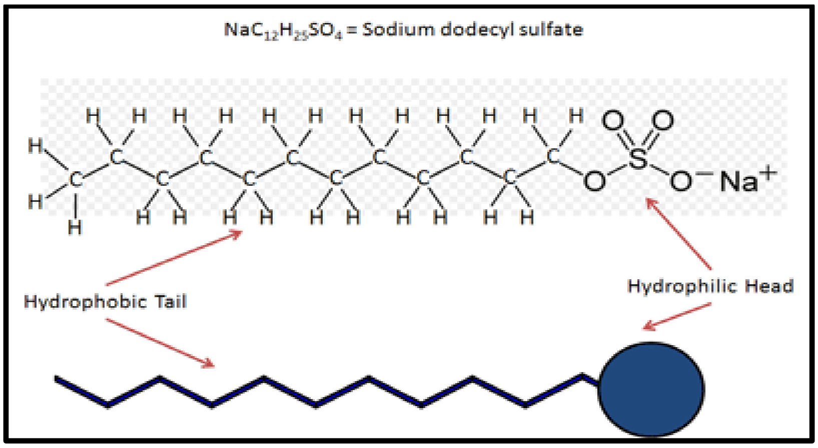


Figure 2.9: Chemical structure of Sodium Dodecyl Sulfate.

Based on the finding from Rosen and Kunjappu (2012), synthesis of SDS can be through the method by treating lauryl alcohol with sulphur trioxide gas, oleum, or cholorosulfuric acid to produce hydrogen laurylsulfate. Sulphur trioxide is one of the common gas which is normally applied in industry. After that, the resulting product will be added with sodium carbonate or sodium hydroxide and undergoes the neutralization process. Lauryl alcohol normally derived by hydrolysis from coconut oil or palm kernel oil, which liberates their fatty acids and undergoes hydrogenation. Commercially samples of SDS are usually a mixture between dodecyl sulfate and alkyl sulfates by using this synthesis process. Majority detergents for laundry in cleaning application is contained SDS. SDS act as a highly effective surfactant and applied in any task requiring the removal of residues and oily stains. For example, it was found in higher concentrations with industrial products including floor cleaners, engine degreasers and car wash soaps. It was found in shampoos, toothpastes, shaving foams and bubble bath formulations in part for thickening effect and ability to create lather.

2.4.3 SDS treatment for filler

Based on the finding from Chun & Husseinsyah (2016), poor interfacial compatibility between the hydrophobic polymer matrix and hydrophilic natural filler will produce a poor performance polymer composite. Amri et al. (2016) reported that filler chemical treatment is one of the method which commonly applied to increase the interfacial between filler and matrix in polymer composites. Filler chemical treatment able to reduce the hydrophilic character of natural filler efficiently. One of the chemical reagent is SDS which can use for the chemical treatment of chitosan fiber. Chitosan is a polysaccharide which contain higher amount of hydroxyl (–OH) and amine ($–NH_2$) groups along the chain. Adding SDS on chitosan chain decreased the hydrophilic properties of chitosan and bring the formation of chemical interaction between the polar groups of chitosan and polar head groups of SDS.

Chun et al. (2013) claimed that wettability, dispersion and filler-matrix interaction of natural filler based composites can be improved through the filler modification. Sodium dodecyl sulfate (SDS) was used as a coupling agent to treat the coconut shell powder (CSP) as to improve the properties PP/CSP composites. Lin et. al. (2011) reported that SDS is an anionic surfactant which can act as a good dispersing agent for HNT in aqueous solution. By adding the SDS, the HNT aqueous solution will become very uniform and stable.

2.5 UV blocking

There is only a very small portion of sunlight spectrum was constituted of ultra-violet rays. However, all the living things and their metabolisms are influenced by the ultraviolet radiation (UVr). There are a lot of research has been done on the effect of UVr to living things since 17th century. There is around 5–6% of total incident spectrum of radiations is UVr which having similar quantum energy as that of bond energies of organic molecules. Scientists have characterized the UVr into 3 categories which known