# Sustainable clay/polymer nanocomposites

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# SUSTAINABLE CLAY/ POLYMER NANOCOMPOSITES

BY
BJARKE HØGSAA

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AALBORG UNIVERSITY
DENMARK

# Sustainable clay/polymer nanocomposites

AALBORG UNIVERSITY
DENMARK

by

**Bjarke Høgsaa**

**Ph.D. Dissertation**

**January 2020**

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## Preface

This Ph.D. thesis has been submitted to the Faculty of Engineering and Science at Aalborg University, Denmark, as part of the requirements for obtaining a Ph.D. degree within Materials Science, Mechanical and Manufacturing Engineering.

The project period was from October 2016 to January 2020 and the work was carried out at two locations; Department of Materials and Production at Aalborg University, in Aalborg, Denmark and the Joint School of Nanoscience and Nanoengineering (JSNN) at North Carolina Agricultural and Technical State University, Greensboro, North Carolina.

I want to thank and express my sincere gratitude to my main advisor Jesper de Claville Christiansen and my co-advisor Elham Fini for their guidance and patience in supervising my work. They presented me with this amazing research topic to explore and gain more knowledge on how to understand and create more sustainable alternatives to advanced polymeric and asphalt systems.

I would also like to express my immense gratitude to all my colleagues and coauthors at the different departments at Aalborg University and North Carolina Agricultural and Technical State University. Their mentorship, collaboration, and teamwork have been essential for me to investigate and explore the obtained results in the produced publications.

A special thanks and acknowledgment to my girlfriend Lisbeth for standing by me on this rocky road to get my degree. Without her love and patience, especially after the birth of our baby girl Gry, this thesis work would never have been published.

A final thanks to my remaining family and friends for putting up with me in this period.

January 31, Denmark

Bjarke Høgsaa

## Abstract

The main objective of this Ph.D. project was to investigate the potential of new materials produced from bio-renewable resources, in this case from plant and animal waste, as surface modifiers and powerful compatibilizers for clay/polymeric nanocomposites.

With the new trend of recyclability and sustainability, focus has shifted towards producing safer and more eco-friendly alternatives to surface modifiers.

These new materials, produced from thermochemical conversion of bio-renewable resources, were chosen based on their chemical composition where selected compounds in a pig manure derived bio-residue (BR) and in a wood-derived bio-crude (WB) could act as surface modifiers. The BR was used to organically modify sodium montmorillonite (MMT), a 2:1 single sheet smectite, and the WB were used to modify Halloysite nanotubes (HNT), a 1:1 single sheet rolled-up tube, which is part of the kaolin group.

The two organoclays were investigated to determine the degree of intercalation and potential interactions with the respective modifiers for the determination of successful organic surface modification.

Based on the identified interactions in the produced organoclays, it was chosen to investigate if Hansen Solubility Parameters (HSP) could be used as an identification tool to determine which of the remaining compounds in the BR and WB could facilitate potential interactions with linear low-density polyethylene (LLDPE) and high impact polystyrene (HiPS), as compatibilizers.

The organoclays were mixed and embedded into their respective polymers, using a series of compounding, extrusion and injection molding. The obtained nanocomposite samples were experimentally characterized for the obtained properties, and interactions of each material system were investigated and reported. Selected computational molecular modelling simulations and analyses of the interactions between the nanoclays and modifiers, and between the modifiers and polymers, were used to support the experimental results and the HSP analyses.

In Paper A, it was demonstrated that BR successfully intercalated the MMT with verified interactions and changed morphology of the organoclay. These findings were confirmed by selected experimental and computational analyses.

In Paper B, three grades BR-modified organoclay were embedded into the LLDPE matrix to investigate the interactions between the organoclays and the matrix. Hansen solubility parameters indicated that almost all the identified compounds in the BR are compatible with the LLDPE. This was supported with the experimental and computational results.

In Paper C and D, it was experimentally and computationally demonstrated that compounds of WB interacted with the surfaces of HNT with the polystyrene phases of the HiPS. However, in Paper C, it was shown that the LLDPE was not compatible with WB-modified HNT, which resulted in decreased material properties.

It was revealed in this work, that Hansen solubility parameters can be used as an early tool for identification of compatibility between the constituents in nanocomposites.

These results support that BR functions as good intercalants and compatibilizers for MMT in LLDPE and WB is a suitable compatibilizer for HNT in HiPS.

Both BR and WB could potentially become reliable, ecofriendly and sustainable alternatives to conventional surface modifiers for greener and more sustainable clay/polymeric nanocomposites.

## Resumé (Danish abstract)

Hovedformålet med denne Ph.d.-afhandling var at undersøge potentialet i nye materialer fremstillet af biologisk genanvendelige ressourcer, i dette tilfælde fra plante-og animalsk affald, som potentielle overflade modifikatorer til nanoler- og polymer-baseret nanokompositter.

På grund af nye tendenser imod genanvendelighed og bæredygtighed, er der behov for et nyt fokus på at producere mere sikre og miljøvenlige alternativer til konventionelle overflade modifikatorer.

Disse nye materialer, fremstillet ved hjælp af en thermokemisk processering of bæredygtige ressourcer, blev valgt på grundlag af deres kemiske sammensætning, hvor udvalgte forbindelser i den animalske biorest (BR) og den træ-afledt bio-råolie (WB) kunne fungere som overflade modifikatorer. BR blev brugt til organisk modificerer natrium montmorillonite (MMT), en 2:1 enkelt plade smectite, og WB blev brugt til at modificere halloysite nanorør (HNT), et 1:1 enkelt ark oprullet nanorør, som er en del af kaolingruppen.

De to modificerede lertyper blev undersøgt for at bestemme graden af dispergering og de potentielle interaktioner med de respektive modifikatorer til en endelig bestemmelse af en potentiel vellykket organisk overflade modifikation.

Baseret på de identificerede interaktioner i de producerede organo-ler, blev det valgt at undersøge om Hansens opløseligheds parametre (HSP) kunne bruges som et identifikationsværktøj til at bestemme, hvilke af de resterende kemiske stoffer i BR og WB kunne lave potentielle interaktioner med de valgte polymerer, lineær low-densitet polyethylene (LLDPE) og slagfast polystyren (HiPS), som en potentiel compatibilizer.

De modificerede ler blev mikset ind i deres respektive polymerer med en række sammenblandinger, ekstruderinger og sprøjtestøbninger. De fremstillede nanokomposit prøver blev eksperimentelt karakteriseret for de opnåede egenskaber, og samspillet mellem hver materiale system blev undersøgt og rapporteret. Der blev udført udvalgte simuleringer og analyser af samspillet mellem nanolererne og modifikatorerne, samt mellem modifikatorerne og polymererne til at understøtte de eksperimentelle resultater og HSP-analyserne.

Det blev bevist i artikel A, at BR havde penetreret MMT med en høj succes rate med verificerede interaktioner og ændre morfologi af de organisk modificerede nanoler. Disse resulter blev verificeret af udvalgte eksperimentelle, samt simulering analyser.

I artikel B blev tre udgaver af BR-modificerede organo-ler indlejret i LLDPE-matrixen for at undersøge interaktionerne mellem leren og polymeren. Resultaterne af Hansen opløselighedsparametrene indikerede at næsten alle de identificerede

forbindelser i BR er kompatible med LLDPE. Dette blev understøttet med de eksperimentelle og beregningsmæssige resultater.

I artiklerne C og D, blev det eksperimentelt bevist at udvalgte komponenter af WB interagerede med overflader af HNT, samt ligeledes med polytyrene faserne af HiPS. Men i artikel C blev det imidlertid påvist, at LLDPE ikke var kompatibel med det WB-modificeret HNT, hvilket resulterede i reducerede materialeegenskaber.

I dette arbejde blev det vist at Hansen opløselighedsparametre kan anvende som et tidligt værktøj til identifikation af kompatibiliteten mellem bestanddelene i nanokompositter.

Både BR og WB er blevet bevist som kraftfulde intercalants og compatibilizers for MMT i LLDPE og HNT i HiPS. De kunne potentielt blive pålidelige, miljøvenlige og bæredygtige alternativer til konventionelle overflade modifikatorer.

## Table of content

## Nomenclature

In the following are a list of the abbreviations used in this Ph.D. thesis are listed.

### Abbreviations

| **Abbreviations** | | |
|---|---|---|
| BR | | Bio-residue |
| DSC | | Differential scanning calorimetry |
| FTIR | | Fourier-transform infrared spectroscopy |
| GC-MS | | Gas chromatography–mass spectrometry |
| HiPS | | High Impact Polystyrene |
| HNT | | Halloysite nanotubes |
| HSP | | Hansen Solubility Parameters |
| HSPiP | | Commercial software to determine HSP |
| LDPE | | Low-density Polyethylene |
| LLDPE | | Linear Low-density Polyethylene |
| MMT | | Montmorillonite |
| MSDS | | Material safety data sheet |
| Na-MMT | | Sodium montmorillonite |
| OHNT | | Organically modified halloysite nanotubes |
| OMMT | | Organically modified montmorillonite |
| PBD | | Polybutadiene |
| PE | | Polyethylene |
| PHA | | Poly (hydroxyalkanoate) |

| | | |
|---|---|---|
| PLA | | Poly (lactic acid) |
| PP | | Polypropylene |
| PS | | Polystyrene |
| TEM | | Transmission electron microscopy |
| TGA | | Thermogravimetric analysis |
| WB | | Wood-derived bio-crude |
| XRD | | X-ray diffraction |

# Part 1: Introduction

## Chapter 1: Project background

***In this chapter, a brief background review of clay/polymeric nanocomposites is given to give the reader an insight into the research area.***

Polymeric materials have been fundamental components for technological advancements achieved in the last century. The ease of processing and properties of these materials have been key to meet the complex demands of reliable products. The option to add fibers and fillers into polymers can change properties (e.g. thermal, mechanical, and barrier) of the base polymer significantly. That is why composite materials have become an important expansion of the polymeric materials due to improved properties with additions ranging from 1-80 volume %, of filler (Ray, Okamoto 2003).

A newer type of composite materials are the nanocomposites, where one of the dimensions of the filler materials is measured in nanometer. These solid fillers can be inorganic minerals, organic materials, or pure plant-based (e.g. clays, ceramic, carbon fillers, natural fibers, etc.), where the filler material differ from the polymer matrix in composition or structure (Paul, D. R., Robeson 2008).

One of the most known nanocomposite material systems are the clay/polymeric nanocomposites which have been implemented with successful commercial usage since the Toyota group in 1985 demonstrated improved mechanical and thermal properties of polyamide/montmorillonite clay-based composite system with a small amount of clay present (Kojima, Usuki et al. 1993). After this success, a great deal of research in the last 30 years has gone into the clay/polymeric nanocomposites field with many publications of altered and tailored material properties with different polymers and clay systems. Successful translations and implementations of these scientific findings have found their way into various industries (e.g. Automotive, Aerospace, Medico and Food packing) as new advanced materials for extreme applications and products.

### How to produce a clay/polymeric nanocomposite

The process of designing and producing an clay/polymeric nanocomposite is not a trivial matter, due to different chemical structures and morphologies of the constituents of the clay/polymeric nanocomposites, as well as the different processing procedures. The three most common techniques to produce a clay/polymeric nanocomposite are:

- In-situ polymerization
- Melt blending
- Solution blending

These procedures either polymerize the matrix around the nanoclay, mixes the nanoclay with a melted polymer or a solvent to dissolve the polymer to mix it with the nanoclay (Ray, Okamoto 2003, Sikdar, Katti et al. 2006, Hussain, Hojjati et al. 2006, Hotta, Paul 2004, Paul, D. R., Robeson 2008).

The different techniques have advantages and disadvantages depending on the material system in question.

In this thesis, it was chosen to use melt blending with the addition of dried nanoclay powder. However, a straight physical mixture of a polymer and nanoclay is not always sufficient to produce a clay/polymeric nanocomposite (Pavlidou, Papaspyrides 2008).

Two issues must be addressed to obtain a clay/polymeric nanocomposite with enhanced properties:

- Matrix - filler compatibility in the interphase between the constituents of the clay/polymeric nanocomposite
- Dispersion of the nanoclay in the polymer matrix

However, with the right considerations, all classes of polymeric materials (e.g. thermoplastics, thermosets, and elastomers) can be used as matrices for new and powerful clay/polymeric nanocomposites with favorable and tailored properties (Pavlidou, Papaspyrides 2008, Fukushima, Tabuani et al. 2009).

### Matrix – filler interphase compatibility and filler dispersion

The structure, dimensions and chemical composition of the nanoclay determine if the nanoclay is compatible with a selected polymer matrix material. If there is an incompatibility in the interphase between the nanoclay and the polymer (e.g. between a hydrophobic/non-polar polymer and the hydrophilic/polar nanoclay), the material properties of the clay/polymeric nanocomposite will be affected. Often this leads to an agglomerated state, and thus poor dispersion of the clay particles (Paul, Robeson 2008). The process of dispersing the layered nanoclays into a polymer matrix can be complex, due to the nanoclays initial stacking of the clay platelets in tactoids.

The solution is the introduction of a new constituent, which is a compatibilizer or organic surface modifier, that can alter the surface of one of the other constituents for increased compatibility (Uddin 2008). The compatibilizers act as bridges, by facilitating chemical or physical interaction between the nano-clay and the polymer matrix which disperses the clay particles in the polymer matrix and lead to increased material properties. Many different types of organically modified nanoclays, or organoclays, have been produced to be compatible with different polymers (De Paiva, Morales et al. 2008). The different properties of each organoclay depend on the type, structure, and geometries of nanoclay (e.g. montmorillonite (MMT), kaolinite, and halloysite nanotubes (HNT)) and the organically surface modifier used, as well as the established interactions between them.

More details on the potential structures and interactions with the modifiers and the polymer matrices will be described in Part 2. An overview of the thesis is listed on page 23.

## The environmental drawback of clay/polymeric nano composites

The implementation and production of composite, polymeric materials and clay/polymeric nanocomposites have been extremely successful; however, the disposal of the produced products after usage is a worldwide problem, which is gaining more and more attention, especially in the case of fossil fuel-based polymers (Zini, Scandola 2011). Therefore is research in how to safely dispose these materials among some of the most investigated areas of this present time, but a straightforward strategy of universal disposal is still not determined.

One of the accepted strategies is to replace the conventional and known materials with bio-based alternatives, preferably from bio-renewable resources, to reduce the accumulation of unwanted fossil derived materials in the ecosystems around the world. This trend can be seen in similar studies for clay/polymeric nanocomposite systems, where the aim of producing greener alternatives is increasing every year (Zini, Scandola 2011).

## Green and tailored surface modifiers

A lot of research has been conducted focusing more on conventional clay/polymeric nanocomposite systems with nonpolar polypropylene (PP), Polyethylene (PE) or Polystyrene (PS) as matrix material with organically modified organoclays for increased material properties, due to the large global consumption of these materials. Based on this consumption, several surface modifiers and compatibilizers have been developed to alter the natural incompatibility between the filler and matrices to ensure the desired properties. Surface modifiers are complex molecules that must be compatible or increase compatibility between the nanoclay and the selected matrix.

An example of one of these surface modifiers is the methyl tallow bis-2-hydroxyethyl ammonium cations, a quaternary ammonium salt which can be cation exchanged with the sodium ions in sodium MMT to yield an intercalated and organically modified O-MMT. A commercial version of this O-MMT is Cloisite 30B from BYK Additives, the old Southern Clay products (Saad, Dimitry 2012).

## Project focus

In this Ph.D. project, it was chosen to investigate if two new materials from bio-renewable resources could act as potential sustainable surface modifiers for increased matrix – filler compatibility and filler dispersion for constituents in newer versions of conventional clay/polymeric nanocomposites.

The first material is a bio-residue (BR) which was produced at North Carolina Agricultural and Technical State University (NC A&T State) as part of a new group of bio-adhesives. The original feedstock for these new materials was based on animal waste (e.g. chicken feces or swine manure).

The second material is a wood-derived bio-crude (WB), produced at the Energy Technology group at Aalborg University (AAU). The material was produced as a new sustainable source of chemicals and fuels, produced from waste plant materials.

More details on these two materials and the other constituents (e.g. the nanoclays and the selected polymers) of new clay/polymeric nanocomposite systems are listed in Part 2.

## Chapter 2: Project scope and approach

***In this chapter, the scope and the work methodology are presented. A thesis overview is also presented to give the reader a more in-depth insight into this thesis.***

### Scope of the Ph.D. thesis

The scope of this thesis is to get a scientific understanding of the potential of bio-residue and wood-derived bio-crude to acts as new bio-renewable replacements for conventional surface modifiers and compatibilizers, and their effects on the interphases and properties of conventional clay/polymer nanocomposites.

Similar research has been performed with related systems (Durmus, Kasgoz et al. 2007, Rawtani, Agrawal 2012, As' habi, Jafari et al. 2013, Lin, Ng et al. 2011).

(Durmus, Kasgoz et al. 2007) demonstrated that a commercial organically modified MMT, mixed with two different compatibilizer in LLDPE, could produce enhanced material properties and interactions between the OMMT and LLDPE. Similar work were done by (As' habi, Jafari et al. 2013) with PLA/LLDPE blends and two commercial OMMTs. (Rawtani, Agrawal 2012) described how LLPDE could be compatible with HNT with a Ethylene graft as a surface modifier. (Lin, Ng et al. 2011) successfully produced HNT/HiPS nanocomposites with increased impact strength with by emulsion polymerization and a compatibilizer.

However, the novel organic products used in this thesis were produced as byproducts in a conversion process of wasted materials for other applications as a series of new materials or new sources of chemicals, and never been tested before as intercalants or modifiers within this area.

This has led to the following research question:

**Which compounds present in the compositions of the BR or WB can potentially act as surface modifiers for selected nano-clays and polymers in proposed thermoplastic nanocomposite systems?**

To assess the potential and effectiveness of the modifiers the first step is to perform full characterizations of the chemical compounds present in the BR and WB. Based on the identified compounds, selected nanoclays and polymers for each modifier will be chosen and new clay/polymeric nanocomposites will be produced. The new clay/polymeric nanocomposites and their respective constituents will be investigated to assess the potential of each modifier. The results of experimental analyses of the chosen constituents of each of the produced clay/polymeric nanocomposites will be compared with literature studies of similar clay/polymeric nanocomposites and computational molecular analyses, as wells as solubility studies.

Due to the time frame of this Ph.D. project, the primary focus has been on the scientific problems related to the compatibility and potential interaction with the modifiers with the selected nanoclay and the polymers, and how to identify and potentially verify the active modifying compounds present in the BR and WB, using solubility as assessments tools for compatibility.

## Project approach

The project approach utilized in this thesis is based on literature studies on the current state of clay/polymeric nanocomposites, both conventional synthetic and green alternatives, to gain an understanding of the potential usage of designated bio-oils and -crudes as new and more environmentally friendly replacements constituent in clay/polymeric nanocomposites. Based on these studies several hypotheses are formed and experimental testing, analyses, and computational results will be compared with the current state of the art within the field of clay/polymeric nanocomposites to confirm or disprove the hypotheses.

## Thesis overview

The format of this Ph.D. thesis is a collection of publications, where the main findings and results are shown.  To present the background, hypotheses, and results to the reader, this thesis is divided into six parts and eight chapters. The outline of the Ph.D. thesis is illustrated in the following pages.

## Part 1: Introduction

Chapter 1: **Project background**

In this chapter, a brief background review of clay/polymeric nanocomposites is given to give the reader an insight into the research area.

Chapter 2: **Project scope and approach**

In this chapter, the scope and the work approach are presented. A thesis overview is also presented to give the reader a more in-depth insight into this thesis.

## Part 2: Examination of the constituents of new clay/polymeric nanocomposites

Chapter 3: **Chemical composition of the bio-renewable materials**

In this chapter, the chemical compositions of the BR and WB based on existing literature and results of experimental analyses are detailed. The results are discussed and compared with the state of the art of organic compatibilizers for clay/polymeric nanocomposites to determine suited other constituents of the new clay/polymeric nanocomposites.

Chapter 4: **The other constituents of the clay/polymeric nanocomposites**

In this chapter, the chemical structure and morphologies of the selected constituents of new clay/polymeric nanocomposites, based on the results of the finding of Chapter 3, are described to give the reader an insight into the choices for each composite system in the articles of this thesis.

## Part 3: Hypotheses

Chapter 5: **Presentation of hypotheses**

It was shown with literature studies, that BR and WB could potentially compatible with selected nano-clays and polymers in the two first parts of this thesis. Based on this, three hypotheses were formed to investigate the potential and these hypotheses are the basis for the produced articles, presented in Part 4.

## Part 4: Results and discussion

Paper A: **Multiscale Investigation of a Bioresidue as a Novel Intercalant for Sodium Montmorillonite**

In this journal paper, it was demonstrated a novel bio-residue (BR) could be used as a new powerful intercalant for sodium montmorillonite (MMT) and produce an intercalated state.

Paper B: **A Novel Bioresidue to Compatibilize Sodium Montmorillonite and Linear Low-Density Polyethylene**

In this journal paper, the organically modified BR-MMT nano-clay from Paper A was successfully embedded as a strong compatibilizer for LLDPE with proven interactions and improved thermal properties.

Paper C: **Intermolecular interactions of bio-modified halloysite nanotube within high impact polystyrene and linear low-density polyethylene**

In this journal paper, it was shown that WB can organically modify HNT to be compatible with HiPS, it remains incompatible with LLDPE, regardless of the modification process.

Paper D: **Multi-scale Characterization of Wood-Based Bio-Crude as a Sustainable Modifier for Nanocomposites Containing Halloysite Clay**

In this journal paper, HNT was organically modified with WB and embedded into a HiPS matrix. Interactions between the HNT, WB, and HiPS were proven with increased thermal properties.

Chapter 6: **Extended summary**

This chapter is to summarize the findings and outcomes of Papers A-D, and discuss if the presented hypotheses are proved or disproved.

## Part 5: Concluding remarks

Chapter 7: **Conclusions**

In this chapter, a summarization of the conclusions from Papers A-D obtained in this project are presented.

Chapter 8: **Future works**

In this chapter, the future challenges and potential extensions of this project are presented.

## Part 6: Additional publications

Paper E: **Examining the Implications of Wax-Based Additives on the Sustainability of Construction Practices: Multiscale Characterization of Wax-Doped Aged Asphalt Binder**

In this journal paper, the effect of incorporating paraffin wax in aged asphalt and the potential effect as an rejuvenator is investigated.

## Part 2: Examination of the constituents of new clay/polymeric nanocomposites

## Chapter 3: Chemical composition of the bio-renewable materials

**In this chapter, the chemical compositions of the BR and WB based on existing literature and of the results of experimental analyses are detailed. The results are discussed and compared with the state of the art of organic compatibilizers for clay/polymeric nanocomposites to determine suited other constituents of the nanocomposites.**

The processes of converting wasted biomass into sustainable materials and energy has gained a lot of attention in the last couple of decades.

One of these conversions is the conversion from mass to into biofuels, bio-oils, other oil-related byproducts, and chemicals. The bio renewable feedstock for these materials could be from many different sources (e.g. algae, rice straws, coconut peals and manure from different life stock) (Fini, Elham H., Kalberer et al. 2011, Hosseinnezhad, Fini et al. 2015).

The biggest benefits from these conversions of wasted materials is the reduction of CO2 emissions and greenhouse gases, and the converted materials could be a new source of income for the farming and production industries for a more circular economy.

The BR and WB are potential examples of wasted products for new applications for a more circular economy.

### Bio-residue (BR)

The BR was developed as one of many byproducts by the conversion of organic waste materials by a patented thermal liquefaction process. The schematic of the conversion process is shown in Figure 1.

The raw material in this project, is liquefied swine manure, which is processed by thermal liquefaction with specific heat and pressure settings (Fini, Elham H. 2017). One of these products is the sticky and thick bio-residue (BR), which was originally used as a bio-adhesive for asphalt systems.

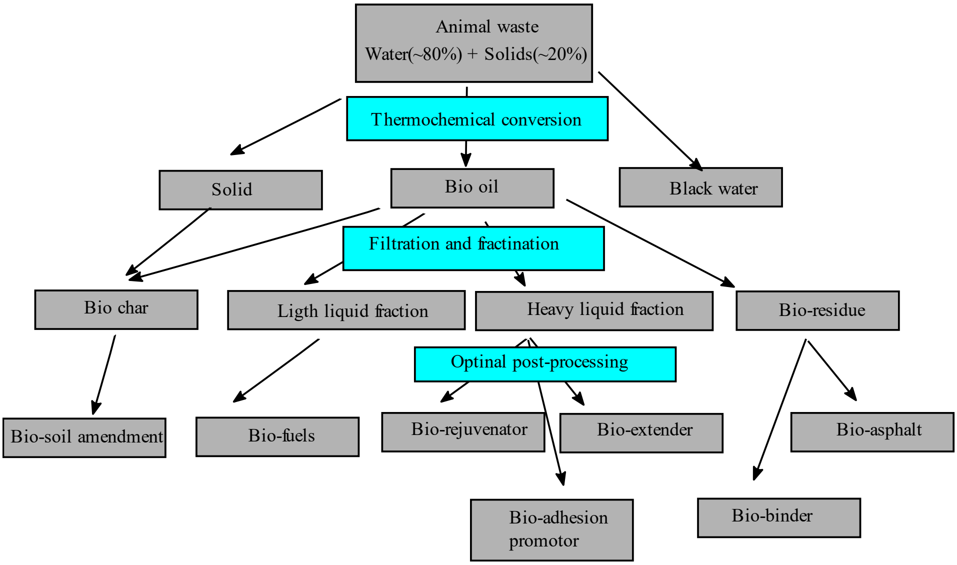


**Figure 1**: Schematic of the conversion process from liquid swine manure into bio-adhesives (Fini, Elham H. 2017).

However upon chemical examination of the BR with selected GC-MS and FTIR analyses and some of the other products (e.g. bio-oil and bio-binder) of the conversion process, the potential broadened (Fini, Elham H., Kalberer et al. 2011, Fini, Elham H., Al-Qadi et al. 2012, Mills-Beale, You et al. 2014).

The compounds were highly nitrogen-rich and oxygenated species (e.g. amides, amines, and long fatty acids). The registered oxygen and nitrogen levels of the bio-binder, the postproduction product of the BR,  are 13.19 wt. % and 4.47 wt. %, which is much higher than crude oil or crude oil, bituminous binders with levels around 1.0 wt.% and 0.8 wt.%. (Hosseinnezhad, Fini et al. 2015).

It was demonstrated by (Rooj, Das et al. 2012), that long fatty acids can act as compatibilizers between the hydrophilic nano-clays and nonpolar polymers( e.g. polyolefins). The amides and amines could be used with cation-ion exchange to intercalate and organically modify the nano-clays as well.

The potential compatibility between pure MMT and BR was indirectly established by the work of (Walters, Fini et al. 2014), where the bio-binder were mixed with an organically modified MMT, Cloisite 30B. The results showed that the bio-binder increased the basal distance of the OMMT. However, it was unclear if it was the tallow-based modifier of Cloisite 30B or the MMT, that were compatible with the bio-binder.

More information on how to produce the bio-residue can be found in the following works (Fini, Elham H., Kalberer et al. 2011, Hosseinnezhad, Fini et al. 2015).

### Wood-derived bio-crude (WB)

The wood-derived bio-crude (WB) was obtained through glycerol-assisted aspen wood thermal liquefaction, which was similar to process of obtaining the BR. More information on the process to produce the WB can be found in (Pedersen, Thomas H., Jasiūnas et al. 2015, Pedersen, Thomas Helmer, Grigoras et al. 2016, Pedersen, Thomas Helmer, Jensen et al. 2017).

(Pedersen, Thomas Helmer, Jensen et al. 2017) performed a full chemical identification of the compounds in WB with selected GC-MS analyses on the volatile fractions and the heavier, non-volatile fraction. The identified compounds were divided into four groups: hydrocarbons, ketones, aromatic oxygenates, and other non-aromatic oxygenates.

The oxygenated species comes from the high oxygen levels of around 16 wt.% present in the bio-crude (Pedersen, Thomas Helmer, Jensen et al. 2017). The oxygenated species and the ketones could be used to organically surface modify hydrophilic surfaces of nano-clays.

The hydrocarbon and phenolic compounds could potentially be compatible with nonpolar polyolefins or polystyrene polymers.

Both materials have unique compounds present in their chemical compositions, based on the earlier and current GC-MS studies of the materials or byproducts. These identified compounds will be the focus for the potential applications as intercalants or compatibilizers for clay/polyethylene and clay/polystyrene.

## Chapter 4: The other constituents of the clay/polymeric nanocomposites

***In this chapter, the chemical structure and morphologies of the selected constituents of new clay/polymeric nanocomposites, based on the results of the finding of Chapter 3, are described to give the reader an insight into the choices for each composite system in the articles of this thesis.***

### Nanoclays

A group of nanofillers, that have proven their potential to enhance material properties of composite materials, is the sheet nanoclays or phyllosilicates. Due to the sheet structure, one of the dimensions, are measured in nanometers. These types of minerals can have the ability to enhance the properties of nanocomposites( e.g. mechanical, thermal and barrier properties) at very low additions of 1-4 % clay addition.(Hotta, Paul 2004) It was chosen to introduce two different nanoclays in this Ph.D. project. The reason was too potentially determining the potential chemical or physical interactions, due to the different chemical structures, shapes, and morphologies of the nanoclays. However, both clay types belonged to the phyllosilicate family.

### Montmorillonite (MMT)

The best-known member of the phyllosilicate group is MMT, which is a 2:1 layered clay mineral. MMT has been investigated extensively, due to its ability to have different degrees of dispersion, due to its layered structure. The layered structure, or clay platelets, are held together by Van der Waals forces, electrostatic forces, and hydrogen bonding. (Cowan, White 1958, McAtee Jr, Concilio 1959, Yariv, Cross 2001, Heinz, Vaia et al. 2006, Heinz, Vaia et al. 2007, Heinz 2012). Each platelet consists of a aluminum oxide sheet sandwiched between two silicon oxides sheets. (Paul, D. R., Robeson 2008). The negative charges of the clay platelets are counterbalanced by positive counterion, see the schematic in Figure 2.

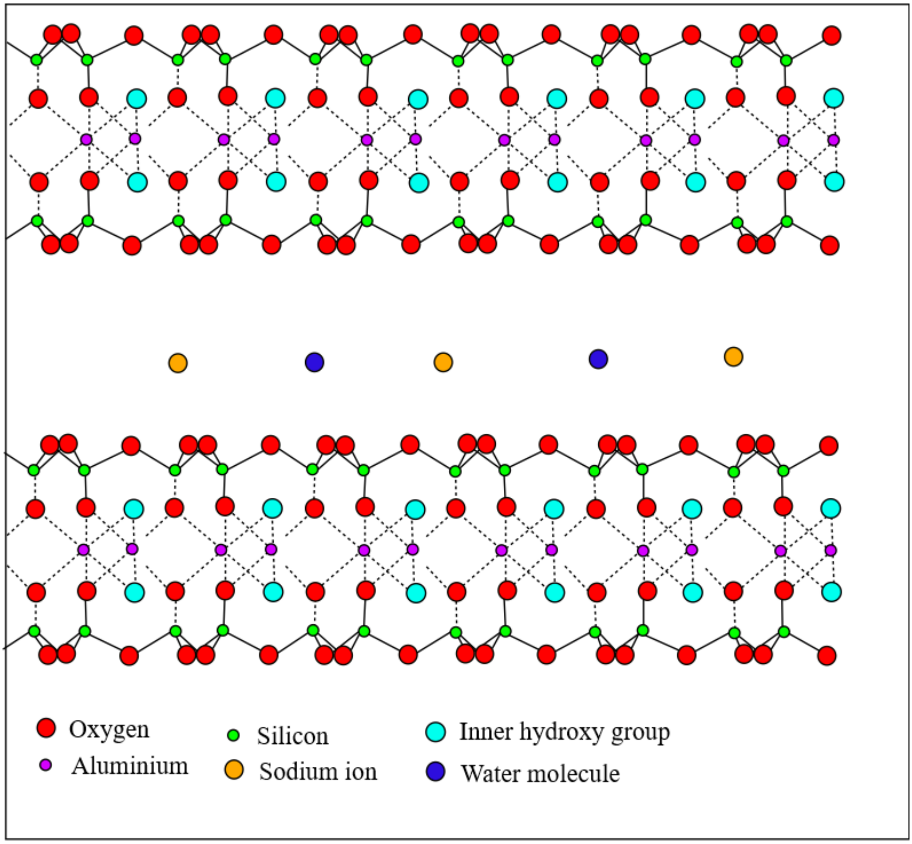


**Figure 2**: Modified schematic based on a DFT-based molecular model of Na-MMT with sodium counterion in the interior galleries of the MMT platelets (Høgsaa, Fini et al. 2018).

All types of MMT have specific interlayer spacings between the clay platelets, based on the counter ions (Önal and Sarkaya, 2008). The organic modification processes can alter this distance of the interlayer spacing to three different stages:

- Immiscible, where the clay particle has agglomerated in the polymer matrix
- Intercalated structure, where there are isolated stacks of clay platelets with an intercalant in the interior galleries of the clays
- Exfoliated structure, where individual clay platelets are dispersed uniformly in the polymer matrix
  (Alexandre, Dubois 2000)

All three stages are illustrated in Figure 3.

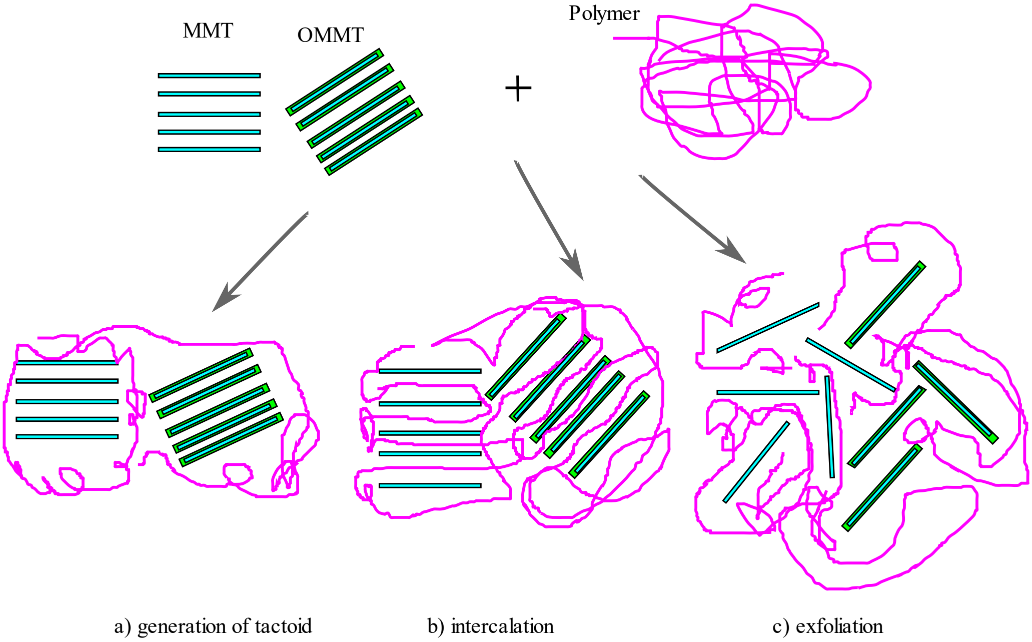


**Figure 3**: Modified schematic of the degrees of dispersion of MMT and OMMT in polymer (Alexandre, Dubois 2000).

Two known intercalation mechanisms are cation exchange and dipole-dipole interaction.

The first mechanism is dipole-dipole attraction, which is a physical attraction between the polar groups (e.g. -OH or -COOH) of the surfactant and the oxygen groups of MMT (Potarniche, Vuluga et al. 2013). These attractions can increase the state of dispersion. In this process the counter ions are still present in the MMT after modification.

The second is cation exchange, the clay is submerged into water and the charges between the platelets and ions are reduced and the interlayer distance increased which causes the clay to swell. Due to the swelling, the ions in the interior layer can then be replaced with similarly positively charged cation ions. The most common organically modified MMTs are based on the process of cation exchange of positive cations in the interlayer spacing of the MMT with ammonium-based cations to an intercalated state with increased spacing (e.g. the Cloisite series with the hydrogenated tallow tails) (Saad, Dimitry 2012). These larger amphiphilic cations can be attracted to the natural hydrophilic surfaces of the MMT, and the hydrophobic parts are attracted to hydrophobic surface of a polymer matrix. These types of molecules can be used as bridges, or compatibilizers, between the polymer and the clay (Paul and Robeson, 2008). These bridges, if implemented successfully, can transfer loads, adds stiffness and barrier properties for reduced diffusion and increased thermal resistance.

In the papers of this thesis Cloisite® Na+ from Southern Clay Products (Now part of BYK Group), which is a single sheet MMT nano-clay, enriched with additional Na+ ions, was used.

### Halloysite nanotubes (HNT)

HNT is the second member of the phyllosilicate group. Unlike MMT, HNT is a single layer sheet rolled into a hollow tube. The external surfaces of the HNTS are comprised of siloxane (-Si-O-Si-) and the internal surfaces are aluminol (-Al-OH), see the schematic in Figure 4 (Yuan, Tan et al. 2015). The rolled-up layers are separated by a single layer of H2O molecules.

HNT can be easily dispersed into polar polymers due to OH groups on the external surfaces of HNT (Gorrasi 2015, Pedrazzoli, Pegoretti et al. 2015). However, in nonpolymeric matrices, the HNT will agglomerate due to incompatibility issue(Yuan, Tan et al. 2015). The polar and compatibility discrepancy can be reduced and fixed with proper modification processes, which can expand the basal spacing of halloysite nanotubes (HNT) through intercalation of inorganic and organic compounds in their interior lumens or grafting on the external surfaces (Yuan, Tan et al. 2015).

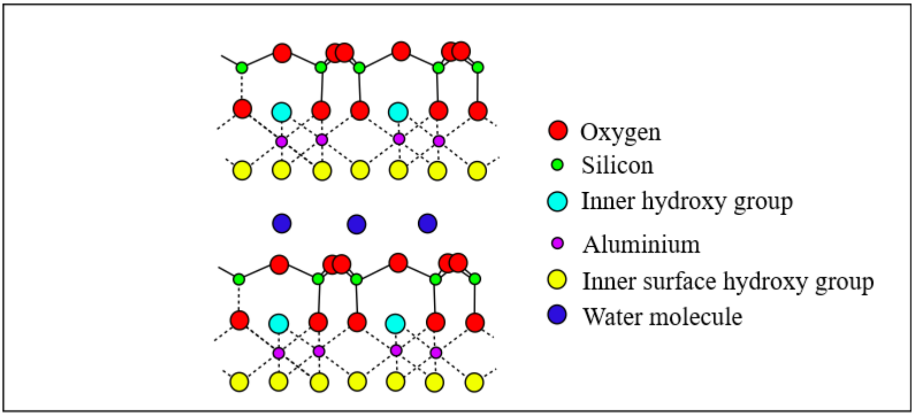


**Figure 4**: Modified schematic based on a DFT-based molecular model of rolled-out single sheet HNT (Høgsaa, Pedersen et al. 2019).

Due to reactive aluminols, located on the inner side or at the ends of the tubes, the HNT can be chemically surface modified with covalent bonds(Liu, Guo et al. 2007).

Another way to modify HNT is with physical modifications, where a modifier is attracted onto the clay surface by van der Waals forces, hydrogen bonding, and electrostatic attraction. (Yuan, Tan et al. 2015).

In the papers of this thesis it was chosen to use HNT® from Naturalnano, which is a single sheet, rolled nano-clay.

## Polymers

Two different types of non-polar thermoplastic polymers, high impact polystyrene (HiPS) and linear low-density polyethylene (LLDPE), were chosen and used in this work. The two polymers have different properties (e.g. thermal, mechanical and morphologies) to accommodate the needs of different products and applications. Both polymers are highly used in various industries. Understanding the chemical structures of the two polymers is key to determining if potential interactions between the modified organoclays and polymers can be established.

### High impact Polystyrene (HiPS)

HiPS is an important thermoplastic polymer that is extensively used in products and fields including transportation, electronic packaging, automobile, and household appliances (Zhang, Wang et al. 2003, Arráez, Arnal et al. 2019). HiPS is an immiscible, phase-separated, polymer blend with major polystyrene (PS) and minor Poly(butadiene)(PBD) phases. The molecular formula for PBD is (C2H4)n and PS (C8H8)n. The two phases are non-polar and with double bonds and benzene rings. As evident based on the chemical structures of HiPS, illustrated in Figure 5, PS and PBD are hydrophobic. Most commercial HIPS can have about 88-96% PS and the rest is PBR primarily (Carraher Jr 2017). The PS is grafted and polymerized onto small particles of PBR, which are dispersed in the PS solution, which in turn ensures compatibility between the phases. The PBD gives flexibility to the more stiff and brittle PS, which makes the polymer more impact resistant without losing the other properties of the PS, which is the reasoning behind the naming of this polymer grade. The hydrocarbon structures and the phenolic compounds are believed to be compatible with selected compounds of the WB and serve as sites for physical or chemical interactions.

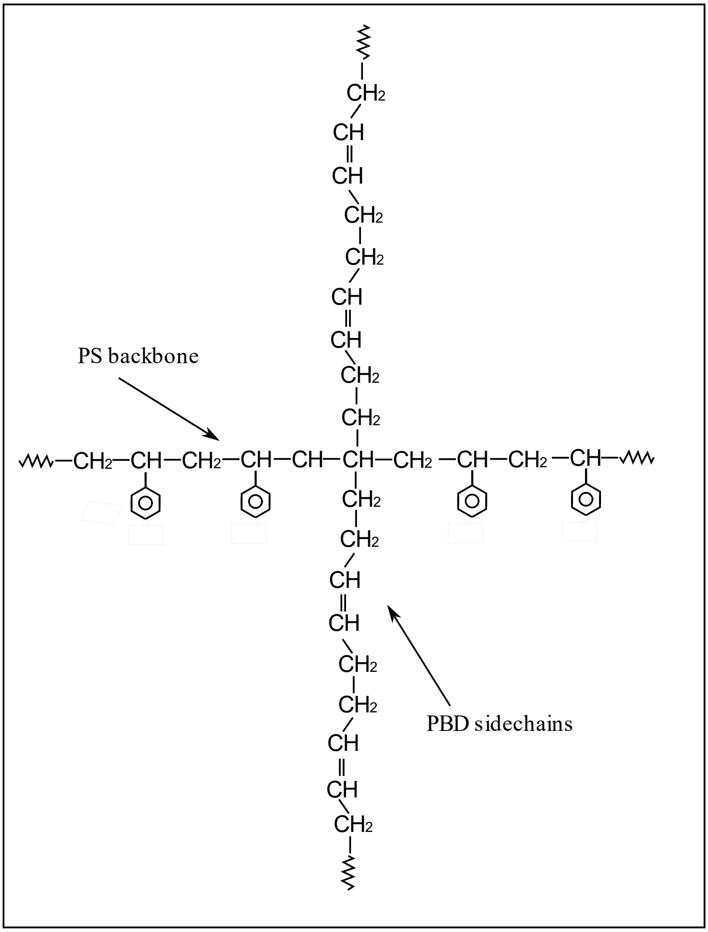
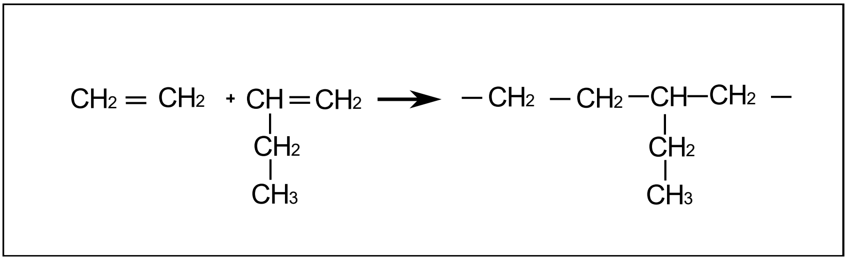


**Figure 5**: Schematic of chemical structure of HiPS.

In the papers of this thesis it was chosen to use Polystyrene impact 6541from Total petrochemicals, as a high impact polystyrene to investigate with.

## Linear Low-Density Polyethylene (LLDPE)

LLDPE is one of the most widely used polyolefins in many fields and products. (e.g. film, injection molding, blow molding, rotational molding, tubing, and wire and cable coating applications). However compared to other polyolefins, LLDPE has a lower thermal resistance and weaker mechanical properties (Simpson, Vaughan 2002). This polymer will have a lot of advantages by the addition of nanoclay to improve the reduced properties (Jin, Seol et al. 2009). This single monomer-based group is hydrophobic and non-polar polymer. The molecular formula and repeating unit for PE is $(C2H4)n$. The non-polarity is due to a polymer backbone comprised of carbon (C) with side groups of hydrogen (H). The number and size of the side groups can vary which alters the properties of the polymer. The chemical structure of LLDPE is illustrated in Figure 6.



$$CH_2=CH_2 + \underset{\substack{|\\ CH_2\\ |\\ CH_3}}{CH}=CH_2 \longrightarrow -CH_2-CH_2-\underset{\substack{|\\ CH_2\\ |\\ CH_3}}{CH}-CH_2-$$

**Figure 6**: Schematic of the formation and chemical structure of LLDPE.

The short branch structure of LLDPE is obtained due to a co-polymerization, where low-density polyethylene (LDPE) is mixed with a small amount of another monomer (e.g. but-1-ene, hex-1-ene or oct-1-ene) to produce C4, C6 and C8 LLDPE grades respectively. The Cx stands for the number of carbon atoms of the original comonomer. It is the short hydrocarbon branches, which are believed to be compatible and sites for interaction with some of the compounds present in the BR and WB.

In the papers of this thesis it was chosen to use Flexirene® MS20 from Polymeri Europa, which is a C4-LLDPE, as one of the polymer matrices.

# Part 3: Hypotheses

## Chapter 5: Presentation of hypotheses

***It was found through literature studies and preliminary analyses, that due to their chemical compositions, BR and WB could potentially be compatible with selected nano-clays and polymers in the two first parts of this thesis. Based on this, three hypotheses were formed to investigate the potential and these hypotheses are the basis for the produced articles, presented in Part 4.***

### Hypothesis 1: The potential as an intercalant/surface modifier

Based on the identified compounds of the BR and WB in Chapter 2 it was chosen to design and investigate two new organoclays, a OMMT and a OHNT, with a focus on the changes of properties and morphologies. The first was a BR-modified MMT and the second was a WB-modified HNT. These choices were made due to the potential intercalation and interaction options stated in Chapter 3.

These choices and observations lead to the following hypothesis:

**BR and WB can be used as new sustainable intercalant/surface modifier for selected nanoclays to produce new grafted or intercalated/exfoliated organoclays**

Selected experimental, such as XRD, TEM, FTIR and TGA, supported with computational test and analyses, were used to investigate and potentially verify this hypothesis with a focus on the obtained interactions and intercalation mechanisms. Especially the works of (Xi, Frost et al. 2005, Mallakpour, Dinari 2012a, Mallakpour, Dinari 2012b) demonstrated that the placement and interaction of organic surfactants with nanoclays can be determined with regards to the decomposition temperature of the modified nanoclays. Paired with the works of (IJdo, Kemnetz et al. 2006, Cole 2008), which showed that the MMT has four distinct peaks, which corresponds to four Si-O stretching modes, that are affected with regards to the state of intercalation/exfoliation of the clay particles. For OHNT, there are peaks associated with the inner surface OH groups and the inner Al-OH groups, as wells as peaks, that are characteristic of opening and modification of the HNT lumen. The results of these test are supported by the conventional TEM and XRD, which is commonly used to determine the degree of exfoliation and interaction in nanoclay.

The organic surface modification of the nanoclays was conducted with a solution-intercalation process tailored for the selected processes and based on known practices of clay surface modification from the literature study.

## Hypothesis 2: Hansen solubility parameters as an identification tool to identify potential compounds

Based on determined interactions between the nanoclays and the BR and WB, investigating the first hypothesis, it was chosen to investigate if it is possible to identify which of compounds of the BR and WB, described in Chapter 2, are compatible with the selected nonpolar polymers: HiPS and LLDPE, described in Chapter 3. This could potentially identify which of the compounds could act as compatibilizers. Another newer way to assess compatibility is usage of solubility parameters.

In 1967, Charles Hansen developed and demonstrated in his thesis work the future power of the Hansen Solubility Parameters (HSP) (Hansen 2007, Abbott, Hansen 2008). These solubility parameters describe the cohesive forces of a given material from three different contributions: dispersive (δD), polar (δP) and hydrogen bond cohesive forces (δH).

Dr. Hansen introduced the polar component, to extend on the known Hildebrand solubility parameters, which did not consider the effects of the polar components of the materials. This division of parameters has become a powerful tool to investigate and quantify the solubility of various materials (e.g. polymers, solvents, nanoparticles and pigments) (Hansen 2007).

Based on the principle of like dissolves like, the original HSP was based on experimental solvolysis with a finite amount of solvents, which was time-consuming and extensive (Abbott, Hansen 2008). However, the HSP has been extended to include a database of previously recorded analyses of various materials, and a molecular simulation method known as  the Yamamoto-Molecular Break (Y-MB) method, which can generate initial estimations of selected materials solubility. All these features are part of the commercial software, HSPiP. The assessment of the solubility is determined based on a relative distance between two materials solubility parameters, where a reduced distance determines if the materials are soluble or not. However, if two materials are soluble then be extension the materials are compatible (Hansen 2007).

This is a key factor to potentially use the Hansen solubility parameters as a potential identification tool, when investigating a mixed substance like the BR or the WB, to determine the chemical species that could act as potential intercalants or compatibilizers without intensive experimental work.

This led to the following hypothesis:

**HSP can be used to determine which compounds of the BR and WB are compatible with the selected nonpolar polymers HiPS and LLDPE**

The identified compounds were analyzed with the commercial software HSPiP to determine the solubility parameters of each compound present in the BR and WB. The interaction radiuses for the polymers were defined with data from other works (Abbott, Hansen 2008).

### Hypothesis 3: The potential as n compatibilizer

The investigated organically modified grades of nanoclays, produced to investigate the 1st hypothesis were melt blended into the designated polymer, LLDPE and HiPS to further determine the potential of the produced organoclays.

A good compatibility in the nanoclay- polymer matrix interphase and good dispersion of the nanoclay in the nanocomposite give improved thermal and mechanical properties. Reduced compatibility would result in agglomerated state and reduced dispersion, which will lead to reduced material properties.

This led to the following hypothesis:

**The BR-modified MMT and WB-modified HNT can be used as new sustainable compatibilizers in new clay/polymeric nanocomposites with nonpolar HiPS and LLDPE respectively**

The produced organoclays were melt blended into the designated matrices and the resulting clay/polymeric nanocomposites were tested with selected experimental and computational tests and compared with the results obtained in the 2nd hypothesis with focus on potential compatibility and dispersion for improved rheological and thermal properties.

Especially the works of (Lertwimolnun, Wiboon, Vergnes 2005, Lertwimolnun, W., Vergnes 2007, Klitkou, Jensen et al. 2012) have demonstrated that an increase in the complex viscosity can be indications of the state of dispersion and exfoliation, as well as interactions between the nanoclay and the polymer matrix.

However in the works of (Mackay, Dao et al. 2003, Dörr, Sadiki et al. 2013), it was demonstrated that a decrease in the complex viscosity is an indication of a particle-induced viscosity reduction, due to a clay agglomeration. This agglomerated state and poor dispersion is due to reduced compatibility in the interphase between the nanoclay and the polymer matrix. Reduced dispersion will lead to reduced material properties of the resulting nanocomposites.

# Part 4: Results and discussion

## Paper A

**Title:**

Multiscale Investigation of a Bioresidue as a Novel Intercalant for Sodium Montmorillonite

**Authors:**

Ellie H. Fini, Bjarke Høgsaa, Jesper de Claville Christiansen, Catalina-Gabriela Sanporean, Erik Appel Jensen, Masoumeh Mousavi and Farideh Pahlavan

**Journal and publisher:**

The Journal of Physical Chemistry C, at ACS publications

**Background:**

This article is based on the 1st hypothesis in Chapter 5

**DOI:** 10.1021/acs.jpcc.6b11966

**Status and date:** Published on January 2, 2017

**No. of pages:** 9

**Volume and pages:** 121 (3), 1794-1802

## Paper B

**Title:**

A Novel Bioresidue to Compatibilize Sodium Montmorillonite and Linear Low-Density Polyethylene

**Authors:**

Bjarke Høgsaa, Ellie H. Fini, Jesper de Claville Christiansen, Albert Hung, Masoumeh Mousavi, Erik Appel Jensen, Farideh Pahlavan, Thomas H. Pedersen and Catalina-Gabriela Sanporean

**Journal and publisher:**

Industrial & Engineering Chemistry Research, at ACS publications

**Background:**

This article is based on the 2nd and 3rd hypotheses in Chapter 5

**DOI:** 10.1021/acs.iecr.7b04178

**Status and date:** Published on January 5, 2018

**No. of pages:** 12

**Volume and pages:** 57 (4), 1213-1224

## Paper C

**Title:**

Intermolecular interactions of bio-modified halloysite nanotube within high impact polystyrene and linear low-density polyethylene

**Authors:**

Masoumeh Mousavi, Bjarke Høgsaa and Ellie H. Fini

**Journal and publisher:**

Applied Surface Science, at Elsevier

**Background:**

This article is based on the 1st and 3rd hypotheses in Chapter 5

**DOI:** 10.1016/j.apsusc.2018.12.151

**Status and date:** Published on December 21, 2018

**No. of pages:** 11

**Volume and pages:** 473, 750-760

## Paper D

**Title:**

Multi-scale Characterization of Wood-Based Bio-Crude as a Sustainable Modifier for Nanocomposites Containing Halloysite Clay

**Authors:**

Bjarke Høgsaa, Thomas H. Pedersen, Masoumeh Mousavi, Albert M. Hung, Erik Appel Jensen, Donghong Yu, Jesper de Claville Christiansen, Catalina-Gabriela Sanporean and Ellie H. Fini

**Journal and publisher:**

ACS Omega, at ACS publications

**Background:**

This article is based on the 1st, 2nd, and 3rd hypotheses in Chapter 5

**DOI:** 10.1021/acsomega.9b02871

**Status and date:** Published on November 14, 2019

**No. of pages:** 10

**Volume and pages:** 4 (22), 19934-19943

## Chapter 6: Extended summary

***This chapter is to summarize the findings and outcomes of Papers A-D, and discuss if the presented hypotheses are proved or disproved.***

In the following chapter, the main outcomes and findings from these publications, Papers A-D (Fini, Ellie H., Høgsaa et al. 2017, Høgsaa, Fini et al. 2018, Mousavi, Høgsaa et al. 2019, Høgsaa, Pedersen et al. 2019), are discussed with respect to hypotheses 1-3 from Chapter 5.

### Discussion of papers A, B, and D with regards to Hypothesis 1

Based on the obtained results in papers A, B and D, the first hypothesis was confirmed, with BR and WB intercalated and surface modified MMT and HNT respectively.

The produced BR-modified MMT and WB-HNT were experimentally and computational investigated with a focus on the intercalation/grafting process and potential mechanisms, cation exchange and dipole-dipole interactions, with the identified compounds (e.g. in the BR, with the outer surfaces and interior galleries of the MMTs, and in the WB, with the outer surfaces and the interior lumens of the HNTs).

Several grades of OMMT and OHNT (33, 50 and 66% loading of modifier) were produced to determine what mechanisms were potentially obtained. The identified mechanism was determined to be ion-dipole and dipole-dipole interactions between the oxygenated species in BR and WB with the MMT and HNT respectively.

The different feedstocks for the BR and WB have produced unique compounds in both materials. The BR is rich in nitrogen and the WB has questionably small amount, however, both materials have many oxygenated species (Fini, Elham H., Kalberer et al. 2011, Pedersen, Thomas Helmer, Jensen et al. 2017). It is these oxygenated species which can facilitate the ion-dipole and dipole-dipole interactions with the HNT and MMT.

In Paper A it was found that:

BR had intercalated the MMT with a around 10% addition of BR, which was affirmed with the results of the XRD, FTIR, and thermal analyses. The rheological properties confirmed interaction between the MMT and BR with transitions in the complex viscosity, associated with filler-matrix network interactions. Based on the results of the computational analyses it was shown that it was the carboxyl groups of the long fatty acids which best facilitated the intercalation, follow by the least effective amide groups of the BR.

In Paper B, it was found that:

with increasing dosage of BR, the basal distance increased and toward a more exfoliated state, compared to pure MMT.  The results are proof that some of the compounds present in BR can intercalate/exfoliate the MMT, however the most stabile grade of organoclay is the 50% BR-modified version, according to the results of the zeta potential. A potential confirmation that it is the long fatty acids that have intercalated the MMT could be seen in the thermal results of the 50% BR version. This grade has the lowest thermal stability, which could be a high presence of long fatty acids. In the studies of (Rooj, Das et al. 2012), it was demonstrated that long fatty acids thermally degrade faster when mixed with a clay catalyst. The highest mass of trapped surfactant molecules between the MMT and BR were reported for the 50% grade and the TEM imaging of this grade showed intercalated/exfoliated results.

In paper D, it was found that:

WB had grafted the outer surfaces and a small amount had entered the lumens of the HNTs. However, only one of the OHNT had signs of chemical interactions with the HNT. This was the most stable grade, with 33% WB modifier, which had the lowest average zeta potential This was confirmed by the FTIR analysis with  a missing peak, compared to the other grades of OHNTs, which indicate an interaction between the HNT and WB. The other analyses supported that WB had successfully organically modified the surfaces of the HNT.

The results of both types of organoclays showed that the right dosage and further processing( e.g. a washing procedure to remove unbound excess modifier) is needed to get more precise results. However, these results are still valid to show the potential of the BR and WB as powerful surface modifiers and intercalants for MMT and HNT respectively.

### Discussion of papers B and D with regards to Hypothesis 2

Based on the obtained results in papers B and D, the second hypothesis was confirmed. HSP was successfully used to identify and determine which compounds of the BR and WB were compatible with HiPS and LLDPE.

Based on the obtained results of the successfully intercalated and organically surface modified/grafted MMT and HNT, the proposed HSP analyses were performed for the BR and WB. The analyses were set up for two systems, BR with LDPE in Paper B and WB with HiPS in Paper D. Interactions radii for LDPE and PS were used as closest polymer analogous for LLDPE and HiPS respectively.

In both systems, there were identified compatible compounds with the chosen analogous; with BR, it was the free fatty acids and amides, and with WB, it was the ketone and other oxygenated species, that were soluble or compatible. These results are good indicators that some compounds in the BR and WB could be good compatibilizing agents for the polymer analogues.

However, due to use of analogues and molecular simulation, and not extensive laboratory solvolysis tests, the results could be more accurate. But the extensive laboratory work was deemed out of scope for this project.

Based on the identified interactions in the OHNTs and OMMT in the work of 1st hypotheses, the oxygenated groups of the FFA and amides of the BR would be bound to the MMT. The hydrocarbon tails of FFA and amide compounds are compatible with the LDPE.

In the case of WB and PS, it is the aromatics compounds of WB that are compatible with the PS and the oxygenated species with the HNT.

The HSP analyses helped with an initial identification of if the chosen matrices would be compatible with BR and WB. The analyses also confirmed that it is only a few selected compounds in the BR and WB, that are compatible with the matrices. BR and WB have very mixed types of compounds present in their chemical compositions and a tailoring extraction process could be suitable for the future, however these preliminary results are promising.

## Discussion of papers B, C, and D with regards to Hypothesis 3

Based on the obtained results in papers B,C and D, the third hypothesis was confirmed, with the BR-modified MMT and WB-modified HNT were used as new compatibilizers HiPS and LLDPE respectively.

To investigate the 3rd hypothesis, three nanocomposite systems were made, based on the results of the two first hypotheses. The produced organoclays were meltblended into their designated polymers with a 2% clay concentration for OMMT and 5% clay concentration for OHNT systems respectively.

In Paper B, it was shown by:

the rheological results that only the LLDPE with the BR-modified with 50% dosage formed a yield stress, that is associated with proper dispersion, compatibility in the filler-matrix interphase, and intercalation/exfoliation. The results showed inhomogeneity of the samples, which were supported by the TEM analyses, where larger aggregates were detected, as well as exfoliated clay platelets. The results are also supported by the thermal results, where the onset of the 50% BR OMMT grade had a lower onset than the pure LLDPE. This is associated with high agglomeration. The two other grades showed no yields stress. The XRD results showed 31-34% increases the basal distances and intercalated structures of the OMMTs. These results demonstrate that some of the compounds in the BR are powerful compatibilizing agents for MMT/LLDPE systems. However, the issues with processing and homogeneity of the obtained results, indicate that further improvement are needed in these areas.

In Paper C:

The thermal and rheological results of HiPS/WB/HNT and LLDPE/WB/HNT with 33% WB modified HNT were analyzed. The results of the computational analyses of the two systems, showed that the HIPS/WB/HNT would yield a compatible system with improved materials properties. However, the LLDPE and WB should be incompatible. These results were confirmed by the experimental results, where the thermal resistance of the HIPS/WB/HNT system where increased and the LLDPE/HNT and LLDPE/WB/HNT had lower thermal resistance than the pure LLDPE. This is the same for the rheological results where no soft solid formations were detected for the LLDPE system, but present in the HIPS/WB/HNT.

In Paper D:

The results of the rheological analyses showed that only the 33% OHNT produced a soft solid formation, which is supported by that only the 33% OHNT had signs of chemical interactions and bonding with the HiPS. The increasing layer of WB reduced the compatibility between the OHNT and HiPS, by reducing the electrostatic charges of the OHNT. The pure HNT in HIPS produced highly agglomerated structures in the nanocomposites, so WB had a compatibilizing effect, but the dosage of WB had to be correct. This was supported by results of the TEM where the 33% showed no larger aggregates unlike the two other grades of OHNTs. The thermal results showed improved thermal resistance with the incorporation of WB.

The results of both nanocomposite systems showed that BR and WB could be good compatibilizing agents. However, processing issues on how to produce more well dispersed and intercalated organoclays and the nanocomposites must be addressed in the future.

# Part 5: Concluding remarks

## Chapter 7: Conclusions

***In this chapter, a summarization of the conclusions from Papers A-D obtained in this project are presented.***

The objective of the Ph.D. project was to investigate the potential of two materials from wasted, sustainable resources could be used as alternative intercalants and compatibilizers for greener clay/polymeric nanocomposites. Based on the state-of-the-art literature review and the chemical characterizations of the BR and WB, three hypotheses were formulated which formed the basis for four publications.

In the following chapter, the main contributions and findings from these publications, Papers A-D (Fini, Ellie H., Høgsaa et al. 2017, Høgsaa, Fini et al. 2018, Mousavi, Høgsaa et al. 2019, Høgsaa, Pedersen et al. 2019), are listed.

Two different nanocomposite systems were designed and investigated with the two materials from bio-renewable resources, BR and WB. The difference in the original feedstocks of BR and WB, swine manure and aspen wood respectively, resulted in different compounds presented in the two oil-like substances.

### 1st and 2nd publications (Papers A and B)

The first type of system was a MMT/LLDPE nanocomposite, which was compatibilized with BR. The results of the experimental and computational analyses of three different grades of BR-MMT organoclays with increasing dosage of BR, and their respective LLDPE nanocomposites showed that BR could be used as a new and powerful compatibilizer, that could be a replacement for conventional surface modifiers and compatibilizers for MMT/LLDPE-based nanocomposites. The carboxylic and amide groups of the BR was identified as the intercalating compounds, which entered the interior galleries of the MMT to yield partly intercalated and partly exfoliated O-MMT in its raw form or embedded in the LLDPE.

The interaction and intercalation mechanisms were identified as ion-dipole or dipole-dipole between the polar compounds in the BR and silica oxide groups of the MMT. Based on the computational results the carboxylic groups were better than the amides to intercalate the MMT, however, with the addition of the LLDPE, some of the basal distance could decrease.

The results of the rheological analyses showed a transition from pure Newtonian responses of the LLDPE and BR to pseudo solid responses in the BR-MMT and the LLDPE/BR-MMT nanocomposites. These transitions are indications of interaction between the constituents of the nanocomposites. However, there was an optimal amount of BR needed to get the transition with a 50% loading with clear signs of interactions between all the constituents of the nanocomposites. So, more research into processing , purification of the OMMTs, and processing of the nanocomposites are needed to find more improved thermal and mechanical properties.

### 3rd and 4th publications (Papers C and D)

The second set of systems were HNT/LLDPE and HNT/HiPS, where both systems were compatibilized with WB. Like the 1st system with BR, three grades organoclays were produced with a solution intercalation process. The results of the experimental characterization of the three grades of OHNT, modified with WB, showed that WB had entered the lumen of the HNT and signs of grafting on the outer surfaces of the HNT. Computational and experimental analyses showed that the WB molecules' active functional groups (e.g., carbonyl, hydroxyl, and carboxylic) interact with the HNT surface while their aromatic tails interact with the phenyl groups of the polystyrene.

Furthermore, the studies reveal how WB molecules act as a bridge between the hydrophobic polymer and the hydrophilic clay, improving the compatibility in the interphase. The latter is evidenced by Hansen solubility parameters and reflected by improved dispersion of clay within the polystyrene matrix. Laboratory examination through rheometry, morphological and thermal tests, showed improved dispersion, leading to improved thermal resistance and rheological properties in the nanocomposite.

However, the nanocomposites with LLDPE was not compatible with new OHNTs and the experimental results showed a reduction in the thermal resistance and no formation of soft solid in the complex viscosity of the nanocomposites. The computational results supported the incompatibility between selected compounds of WB with LLDPE.

### Overall conclusions

The results of the examinations of all the new organoclay and respective nanocomposites, it was evident that the WB and BR could both be powerful intercalants and compatibilizers for nonpolar-based clay nanocomposites.

Use of HSP to determine compatibility proved a convenient way to identify which of the compounds present in the BR and WB were compatible with the selected polymers. The interactions within the produced organoclays were identified by the experimental analyses and the confirmed with selected computational results. This strategy proved to be a powerful way to tailor and produce new clay/polymeric nanocomposites.

However, the processing of the organoclay and the nanocomposites with melt blending must be optimized to gain a deeper understanding of the intercalation and compatibilizing mechanisms

The common denominator for the potential of the all the compounds present in the BR and WB are as building blocks as new constituents or other usages. These wasted materials have a lot of hidden potentials that hopefully will be research more and the results used to help make a more sustainable future for composite and other industries. The processing issues must be addressed but the results obtained in this project shows the potential of these two materials to the fullest.

# Chapter 8: Future works

***In this chapter, the future challenges and potential extensions of this project are presented.***

The current Ph.D. project has been the initial work towards greener clay/polymeric nanocomposites from bio-renewable and sustainable resources. The future challenges are considered in this chapter.

## Optimization of processing of the organoclays

The solution-intercalation process successfully produced organically modified and grafted MMT and HNT. However, based on the experimental results there were signs of the excess surface modifier. The XRD of the OMMT showed results from intercalated to exfoliated structures depending on the dosage of BR. The three OMMT will be melt blended and an appropriate washing procedure to remove the excess compatibilizer or unbound compounds will help to standardize the results of intercalated or exfoliated OMMT's or OHNT's.

## Tailor ability of the compatibilizers

The BR and WB are mixtures of many different compounds as evident by the chemical characterizations by GC-MS for the HSP analyses, see supporting information of Papers A and D for BR and WB respectively. The experimental and computational results on this Ph.D. project showed that it is selected compounds in the WB and BR, that potentially facilitated the organic modification. If these compounds could be extracted from wasted materials and become eco-friendly and sustainable intercalants and compatibilizers and tailored to selected nanofillers and polymers, the potential is limitless. The process of extracting the intercalating compounds can be expensive, but if the traditional fractionation process is used and the right temperature and pressure setting with the right feedstock are found to produce the right fraction of compounds then the tailorability of clay/polymeric nanocomposites is a massive advancement.

## Green clay/polymeric nanocomposites

Sustainable materials and bio-renewable solutions have attracted tremendous attention from research and manufacturing industries due to their potential to replace conventional crude oil/petroleum based-polymers (Nampoothiri, Nair et al. 2010, Reddy, Vivekanandhan et al. 2013). The future shortage of fossilized fuels and oils will be a potential problem for industries and the world population in general if more sustainable solutions are not developed to meet the upcoming demands (Goda, Cao 2007). Two bio-friendly alternatives to conventional fossil fuel based polymers are Poly (lactic acid) (PLA) and poly (hydroxyalkanoate)(PHA). Both biopolymers are bioactive thermoplastic aliphatic polyesters, but PLA is produced from agricultural farming and PHB is naturally produced from microbial production (Lim, Auras et al. 2008). PLA can be produced by condensation polymerization of lactic acid monomers produced from renewable resources via a fermentation process. Commercial PLA versions are used in several industries (e.g. 3d printing and packing industries) (Harris, Lee 2008). PHA is still considered too expensive to be a standalone polymer for commercial usage, but recent advances in research in alternative sources of food for the bacteria and polymer blends with other bio-based and conventional polymers are clearing the way for this new polymer type to become a viable alternative to current options (Luzier 1992, Avella, Martuscelli et al. 2000). Both PLA and PHA are highly desired due to their nontoxicity, biocompatibility, and biodegradability (Reddy, Vivekanandhan et al. 2013). Several studies have been conducted on PLA/MMT and PHVB/MMT nanocomposites with pure enriched sodium montmorillonite (e.g. Cloisite Na+) and organically modified commercial nano-clays (e.g. Cloisite 30B, Cloisite 15A). These studies showed reduced and enhanced material properties depending on the interactions with these commercial organically modified nano-clays, which are based on quaternary ammonium salts and tallow-based intercalants (Zhao, Cui et al. 2013, Zhao, Zhao et al. 2015, Carli, Crespo et al. 2011, Paul, M., Alexandre et al. 2003, Cabedo, Plackett et al. 2009, Ahmed, Varshney et al. 2010). Based on these studies and the results obtained in this Ph.D. thesis BR could potentially be a replacement for the surface modifiers and a complete green clay/polymeric nanocomposites can be made.

### Producing nanofillers and biopolymers form the BR and WB

The identified compounds in the BR or WB could potentially be synthesized into new polymers from bio-renewable materials, especially the amine or amides present in the BR could be used. All alternative resources to conventional fossil-fuel sources for produce new polymers are key for further development.

The same extraction could be used for the carbon nanoparticles, which are present in both the BR and WB due to the thermal liquefaction process used to make the two materials. These new nanoparticles could be made with additional carbonization, vacuum drying, and freeze-drying. A great deal of research has been conducted for the various carbon nanostructure (e.g. nanotubes, nanofibers, graphene, fullerene, etc.) and both BR and WB could be good sources for producing these particles.

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# Part 6: Additional publications

## Paper E

**Title:**

Examining the Implications of Wax-Based Additives on the Sustainability of Construction Practices: Multiscale Characterization of Wax-Doped Aged Asphalt Binder

**Authors:**

Alireza Samieadel, Bjarke Høgsaa and Elham H. Fini

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