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Bio-Based Roofing Membrane

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Abstract

This project aims to develop and research a polymer composition and manufacturing process to develop a bio-based roofing membrane as part of the *Engineering Design 2* class (BREE 490) and *Engineering Design 3* class (BREE 495). The purpose of the project is to reduce our dependence on fossil fuels as well as the quantity of wastes generated in the construction and agriculture industries by implementing the concept of passive design. This concept relies on natural breathable materials that reduce the impact on the environment and that promote a circular life cycle. The report summarizes the information and research conducted on 3 main bio-materials (lignin, castor oil and hemp) with the goal of identifying the best alternative from our design constraints and criteria. The main material under investigation is the hemp filled polylactic acid (PLA) bioplastic reinforced with a biochar coating because of its economic advantages, its ease of manufacturing, its accessibility and its compatibility with current membrane installation methods. Furthermore, the incorporation of plasticizers and compatibilizers such as polypropylene glycol diglycidyl ether and polybutylene adipate-co-terephthalate are promising biodegradable additives that can be used to improve the material's mechanical properties. The bio-based roofing membrane can be manufactured from a continuous extrusion process using a flat sheet die. The raw material for the processing consists of a composite matrix made of standardized bioplastic pellets and natural fibers.

Table of Contents

Introduction.....	1
1. Our client’s company: Soprema.....	2
2. Design Approach.....	3
3. Occupational Health and Safety and Assessment of Alternatives.....	4
4.0 Environmental, Social and Economic Considerations.....	6
4.1 Kraft lignin.....	7
4.2 Castor oil.....	9
4.3 Hemp.....	11
4.4 Conclusive Assessment of Alternatives.....	13
5. Bio-Based Membrane Material Composition.....	15
6.0 Processing Guide of a Hemp Filled Polylactic Acid Roofing Membrane.....	19
6.1 Pre-Drying Methods.....	19
6.2 Cleaning and Purging.....	22
6.3 Twin-Screw Extrusion Compounding	24
6.4 Standardized Quality Assurance Tests.....	30
Conclusion.....	34
Appendix A: Hemp PLA Technical and Safety Data Sheets.....	35
References.....	38

List of Figures

Figure 1: *Polylactide Homopolymer Moisture Take-Up Curve*

Figure 2: *Commercial twin-screw extruder modes*

Figure 3: *Screw layout of a twin-screw compounding extruder*

Figure 4: *Effect of CNC content on the Water Vapor Permeability and Oxygen Permeability of PLA films*

Figure 5: *Manufacturing process diagram of a CNC reinforced H-PLA waterproofing roofing system*

List of Tables

Table 1: *Pugh matrix of the researched bio-materials in comparison with SBS-modified bitumen*

Table 2: *Tensile Test performed on dog bone samples following ASTM D638 procedures*

Table 3: *Typical Polylactide Homopolymer Drying Conditions*

Table 4: *Temperature Ranges of Purging Compounds at ASAClean*

Table 5: *Extrusion Temperature Profile for Hemp Filled Polylactic Acid (H-PLA)*

Table 6: *Extrusion Parameters for Hemp Filled Polylactic Acid*

List of Acronyms

ASTM: American Standard Test Method

CBD: Cannabidiol

CNC: Cellulose Nanocrystals

CRD: Construction, Renovation, Demolition

EJ400: Polypropylene glycol diglycidyl ether

H-PLA: Hemp Filled Polylactic Acid

LAK: Dimethyl 5-sulfoisophthalate, potassium salt

LEED: Leadership in Energy and Environmental Design

NBC: National Building Code of Canada

OP: Oxygen Permeability

PBAT: Polybutylene adipate-co-terephthalate

PBS: Polybutylene succinate

PLA: PolyLactic Acid

SBS: Styrene Butadiene Styrene

WVP: Water Vapor Permeability

WVTR: Water Vapor Transmission Rate

Introduction

Material technology has seen a great progression over the years. With advances made in chemical engineering, society is able to benefit from a vast multitude of higher quality and better performing consumer goods. Ultimately, improvements in material technology has had benefits on the affordability and accessibility of materials found especially in the construction industry. This increase in quality and affordability has generated substantial production of construction materials such as roofing membranes. However, the increase in production has also led to increasing amounts of usage and disposal of old construction materials after the renovation and demolition of infrastructures. Today, construction, renovation and demolition (CRD) waste represents 12% of all waste that is disposed of in landfills each year. In 2014, this represented 592 tonnes of waste from CRD directed for landfilling (*Canada at a glance*, Statistics Canada, 2014).

In order to help attenuate this situation, our team is tasked to develop a bio-based roofing membrane made out of compounds found in recycled organic waste and/or biologically derived polymers. Not only will this have the added benefit of reducing our dependence on petroleum, but it will also try to respect the concept of a circular economy through the revalorisation of previously discarded materials. The advances made in this project will be able to contribute towards reducing the amount of waste generated and have a global positive impact on the environment. This report will seek to conclusively assess the usage of three bio-based materials as possible alternatives to traditionally fabricated roofing membranes composed of petroleum that can act as a suitable replacement. The report will therefore, at first glance, address the role of the targeted client in the project, elaborate an assessment of environmental, social, economic and occupational considerations. Furthermore, the report will also present a potential material composition of a bio-based membrane as well as a manufacturing guide in order to prototype and evaluate samples through the use of standardized tests.

1. Our Client's Company: Soprema

With the idea to pursue our project topic on the bio-based roofing membrane, we decided to contact a leader in the industry. We were able to establish contact with M. Pierre-Andre Lebeuf, project manager for the department of sustainable development at *Soprema*. *Soprema* is an international manufacturer of construction materials founded in 1908 in Strasbourg, France that has operations in over 60 countries worldwide. With their canadian research and development center located in Drummondville, Quebec it would give our team the opportunity to design, construct and test our membrane in a purpose built facility in the province of Quebec. *Soprema* specializes in waterproofing, insulating and sound deadening construction materials. The company also has expertise in developing and providing materials for sustainable constructions. This includes materials suitable for LEED® certification such as high quality insulating materials and products used to house green vegetation in building designs. *Soprema's* vision statement consists of being “the leader in the area of development, production and sale of products that meet and exceed the requirements of our markets”. With a focus on integrity, respect, commitment and the environment, they are one of the few players in Quebec pushing towards more sustainable constructions and construction materials. With experience in the development and manufacturing of bio-based roofing membranes, our team will seek to identify an alternative solution towards incorporating green materials in the specified product. *Soprema's* research and development team has the ability to test our designed product with the use of artificial weathering devices in the laboratories. Furthermore, they also have the technical knowledge required for the manufacturing process of various components that would lead to a commerciable product (fire retardants, reinforcing matrix, adhesives, aggregate surfacing etc.).

2. Design Approach

The membrane composition must be designed in a way that integrates bio-based polymers and/or organic waste compounds as a substitute to petroleum based compounds. Although it will be composed primarily from organic derived material, it will still need to incorporate other elements in order for the end product to be successful. This includes UV stabilisers for protection against oxidation and degradation from the sun's radiation. Secondly, plasticisers will need to be incorporated in order to improve the mechanical properties of the membrane so that properties that impact the material's flexibility are within production standards. The filler material is also crucial because it will have a role of improving its tensile strength, its resistance to abrasions and improving its thermal stability. We must limit ourselves to materials and additives that will be able to be utilised with the existing manufacturing equipment and processes located at *Soprema's* research and development headquarters in Drummondville, Quebec. This criteria has great value for our design since the usage of a drop in substitute results in less economical and logistical burdens. Once the composition is defined with the optimum concentration of ingredients, it will be imperative that the prototype membrane be constructed in order to validate the specifications of the membrane with material tests found in roofing membrane standards supplied by *Soprema*. The various tests aim to predict the durability of the membrane and its material performance. On one hand, simple mechanical tests can be performed in McGill's establishments because of their convenience like tensile strength, elongation, strain energy, tear resistance, static and dynamic puncture resistance as well as dimensional stability. On the other hand, artificial weathering tests are more complex and they require specific devices that *Soprema* possesses in their laboratories. Other evaluations to assess the sample's permeability, heat resistance and the wind resistance can be conducted by simulating conditions that replicate different stresses generated by various weather factors occurring during its service life. Once the selected tests are performed and the data is analyzed, we can then proceed to make an informed decision as to the final composition of the membrane. The research and development team of engineers at *Soprema* have the ability to assemble the various components of the membrane such as fire retardants, suitable adhesives, reinforcing

matrix and aggregate surfacing. Our team wants to adopt a circular design approach that takes into consideration the whole lifecycle of the product to ensure that its manufacturing, its utilisation and its disposal have relatively low environmental impacts.

3. Occupation Health and Safety Assessment of Alternatives

In regards to the project at hand, we hope to identify a potential material composition of a roofing membrane that has limited health and safety impacts on the manufacturing and installation process as well during the product's lifecycle. In theory, the substitution of petroleum based ingredients with bio-based compounds will have a beneficial impact on the environment. Creating a product that can be decomposed after its useful life reduces waste being disposed of in landfills or thermal incinerators. Both these options have negative environmental consequences and do not consist in sustainable practices. It will be crucial to identify a solution that achieves the desired membrane properties and specifications without sacrificing on health, safety and the environment. Despite being composed of biologically derived matter, it is also important that the membrane displays good physical properties and resist degradation, decomposition and failure due to the elements it is exposed to. Our membrane will need to adhere to ASTM Test method G21 in order to validate the material's fungal resistivity among other standardized testing methods in order to evaluate the mechanical properties of the membrane in question. The main properties of interest for this project are the tensile strength, Young's Modulus and the glass transition temperature. These can be evaluated using testing procedures outlined in the National Building Code of Canada (NBC). If the criteria above is not respected, the membrane in question will not be constructed to the standards of the industry and could ultimately fail prematurely resulting in water infiltration from rainfall. There are many other options available when designing and developing a watertight roofing membrane for building applications. In deviating away from traditional bituminous membranes, our project will focus primarily on biomass derived compounds in order to create a flexible rectangular membrane that can be adhered to existing roofing structure. Some alternatives to the flexible membrane include liquid based applications that are applied as a fluid and cure to form a compliant and watertight seal on

mostly leveled building rooftops. Our team will focus on bio-based alternatives to the traditional roofing membrane because a physical membrane will be able to be tested and manufactured more easily with the company's expert tutelage and assistance. In light of this, there exist many other alternatives to bitumen used in roofing membranes such as thermosets or thermoplastics which are composed primarily of synthetic rubbers. However, in trying to reduce the environmental impact generated from the construction industry, our client is interested in bio-polymers which will have the added environmental benefits as well as stimulating interest among investors and consumers looking for more sustainable construction materials.

4.0 Environmental, Economic and Social Considerations

There are many considerations that need to be taken into account when evaluating the feasibility of an engineering design project. In order to make a well informed decision, one must assess the economic, environmental, risk and safety criteria that each alternative displays. In design 2, the team conducted a thorough literature review on research that had been conducted on various bio-based materials and compositions that would be suitable as a petroleum substitute for the manufacturing of thin sheet membranes. The main groups consisted of a polyurethane polymer based from kraft lignin and castor oil, a castor oil polycaprolactone polyurethane biocomposite reinforced with hemp fibers, polycaprolactone polyurethane from high lignin content and finally a hemp filled polylactic acid bioplastic. A preliminary analysis of the various alternatives was conducted in order to identify that the best design consisted in the polylactic acid hemp bioplastic. The different alternatives will be characterized on a comparative basis based on their environmental, economic, health, safety and social impacts. This will serve as a ranking framework in order to objectively identify the alternative with the most benefits through the use of a pugh matrix. The weighting methodology must first be outlined in order to identify which parameters are of greater value to both the client and the design team.

The main goal of this project is to help develop a roofing membrane with respectable specifications and characteristics composed of biologically derived material. By choosing to design the membrane from biologically derived material, the product can maintain a lower carbon footprint than petroleum alternatives while having a more prosperous and sustainable life cycle. Although all the alternatives proposed comply with this design parameter, a more thorough analysis is needed in order to expose the environmental impacts that each base material exhibits.

4.1 Lignin

Lignin is one of the most abundant by-products of the paper and pulp industry worldwide. This uncharacteristic complex organic polymer is removed from the paper pulp because it reduces the paper's strength and darkens the color of the paper (Loutfi et al., 1991). Delignification is used to transform the structural lignin bonds into a soluble compound that is then used as an energy source in the paper and pulp manufacturing facilities. This process creates black liquor which is an aqueous solution composed of lignin and other additives. Unfortunately, this solution is used to recycle energy in the form of heat back into the systems through a series of boilers and heat exchangers (Vakkilainen et al., 2009). Most processing plants value this substance in the form of a no cost energy. Two alternatives presented in the BREE 490 final report sought to assess the benefits of using lignin from the paper and pulp industry as a material that can be recycled and incorporated into products as a petroleum substitute. In terms of lignin's environmental impact, it is one of the more environmentally beneficial alternatives proposed. By deviating this organic polymer from the paper and pulp industry, this is able to prevent the combustion of countless quantities of black liquor into the atmosphere (Vakkilainen et al., 2009). However, in order to make use of this material, companies need to devise strategies in order to further refine and sell the processed lignin into a form that can be easily incorporated into existing plastic manufacturing facilities. The paper and pulp industry would also be at a net energy deficit without the abundance of thermal energy it is able to generate with the black liquor it has sold. This energy would need to be recovered by other means from other combustible products or by the electrical grid supplying the paper and pulp plant. However, the lignin can be extracted from the black liquor before it is sold to be further refined as a base material. Extracting the lignin can help with the overall efficiency of the system by decreasing the heat load on the recovery boilers in order to produce more pulp (Vakkilainen et al., 2009). This is already being done in some plants, although the technology is still recent and requires an extensive investment from the paper and pulp industries. Lignin can be extracted from black liquor from membrane filtration and dewatering processes in order to preserve the energy density

of the mixture. The revalorization of this industrial waste makes this alternative a very environmentally sustainable way to extract a biopolymer from an existing industry. Overall, using lignin as a base material does have a very high environmental score because it is able to be sourced from a byproduct and revalorized while also maintaining the energy balance of the paper and pulp industry that uses it as a source of energy.

Although the lignin can be revalorized and transformed into a polyurethane that can be potentially used for our project's application, the main reason for not choosing it is due to the fact that it is not economically competitive with other options discussed within the scope of this project. Firstly, the lignin must first be commercially available as a pre-refined base material that has already been extracted from the black liquor. This requires a large capital investment from the paper and pulp industry to engineer a new system in order to filter or dewater the lignin from the black liquor. This would create a very long payback period for the manufacturing and extraction process of the lignin which in combination with a relatively limited market would result in increasing the cost of lignin even before it is processed for manufacturing commodities such as a roofing membrane (Loutfi et al., 1991). Much research has been done on lignin, but more is required in order to identify it as an economically viable option that displays interesting and tunable material properties which it currently lacks.

Economically, adopting lignin as a biopolymer for our design project would be infeasible from a chemical engineering perspective. Due to the structure and nature of kraft lignin, many key material parameters discussed in the previous design report are found to be lacking and require extensive chemical modifications which results in an increase in processing costs. Some interesting material compositions had good specifications however, this was the result of either low mass percent concentrations of lignin or extensive chemical modifications (Tavares et al., 2016). Furthermore, it was found that lignin did not react very well to the addition of common material additives (plasticizers, UV stabilizers) and that these had a tendency to wear off rapidly resulting in a quick degradation of the material's properties.

4.2 Castor Oil

Castor oil is a natural oil extracted from castor beans that is primarily harvested in China, india and brazil (Patel et al., 2016). This oil is used in various industries due to its beneficial chemical properties for a wide range of consumer products. Unlike lignin, castor oil is not found through a revalorization process, rather it is harvested in developing regions transformed and incorporated into a multitude of consumer products. In order to assess castor oil's environmental impact, it will be important to analyse castor oil's lifecycle as it is grown, processed and implemented as a consumer product.

Castor oil has been able to supply industries and manufacturers with a renewable source of hydroxylated fatty acid that serves a major purpose of increasing the viscosity and reactivity of a specific product (Patel et al., 2016). However, this resource is cultivated in only select areas with a majority of castor beans harvested in India. Castor beans are grown specifically for their oil, but do not constitute a source of edible food. This being said, their growth must still be supported by nutrients, energy, resources and labor. Cultivating crops for material transformations has the disadvantage of competing with crops grown for food for human consumption. There are also some challenges in regards to castor oil's sustainability as a biomaterial. Like most crops, climate change and disturbances in the weather and hydrologic patterns will be impacting castor bean cultivation. Castor oil is currently being grown in developing countries because of their favorable growing conditions and because the countries have sufficient labor that is required for harvesting of the beans (Patel et al., 2016). Global consumption and demand will continue to increase as more consumers move towards biologically derived materials and away from petroleum counterparts primarily due to consumer trends.

Castor oil does present some challenges if it is to become a mainstream biomaterial in the years to come. Firstly, it is cultivated using resources that are implemented for human crop consumption in developing countries with food security concerns. Secondly, the processing of castor oil involves the filtering of contaminants such as ricin naturally found in the castor bean (Macalino et al., 2017). Ricin is completely filtered in the countries where the crops are grown, however, this lethal poison has been known to contaminate its local environment by volatilizing into the air and contaminating the ground and water courses (Patel et al., 2016). The poison along with other impurities are removed from the end product and form the marsh (organic waste) from the processing process. Ricin can be inactivated by heating the compound to temperatures above 80 degrees celsius (Patel et al., 2016). The poison found in the bean has been impacting the health and safety of countless workers in both China, India and Brazil. Despite this toxin, the pomace generated from the castor oil extraction is used as a fertilizer and soil conditioner. Castor oil has seen such great success and will continue to see growth and demand as more manufacturers turn to it to fabricate products such as soap, lubricants and biomaterials that require hydroxylated fatty acids (Macalino et al., 2017). Nonetheless, castor oil faces some challenges due to climate change, the consumption of agricultural resources and the presence of an extremely deadly toxin found in the castor bean.

Economically, castor oil is a readily available commodity. Many manufacturers are using the product for a multitude of applications due to its ability to be easily tuned into elastic polyurethanes that can exhibit elastomeric properties (Macalino et al., 2017). The advantage of using castor oil as a building block for a bio-based membrane is that much research has been conducted on the topic. Castor oil as an elastic polyurethane has many advantages of being able to be designed with good physical, chemical and thermal properties in mind. Techniques such as coupling 1,6-hexamethylene diisocyanate with castor oil have been able to produce very good modulus of elasticity values, tensile elongation values without any further addition of plasticizing agents (Macalino et al., 2017). Castor oil has a market value of 1600\$ per ton which represents a feasible cost for our product's base material. Through the use of similar processing

techniques such as bitumen, castor oil has an economic advantage of being closer to a drop in substitute than lignin. Exhibiting good material properties, it would require less extensive chemical modifications. However, conventional roofing membrane additives could be incorporated into its elastic polyurethane structure.

4.3 Hemp

Hemp is a plant closely related to cannabis that has been grown and transformed into a vast variety of consumer products. It was commonly cultivated for textile purposes, but has found usage in other applications such as for paper, bio-based plastics and biofuels (Schlottenhofer et al., 2017). Hemp is not cultivated in every part of the world because it is closely tied to cannabis and also contains the active ingredient cannabidiol CBD. Countries like Canada have permitted hemp cultivation since the late 1998, but due to its strong ties with marijuana it is still considered a regulated crop (Mangino, 2018). Before the legalization of marijuana in Canada, licensed farmers were only able to harvest the seeds and stem of the plant in order to produce cooking oil, protein powder and edible seeds. Since then, farmers have been able to harvest the plant in its entirety in order to extract the CBD content among other benefits. This has also opened the doors to the conversion of hemp grain into plastics and fuels. In 2017, Canada cultivated 138 000 acres of land for the production of industrial hemp (Mangino, 2018). This crop is quickly becoming more and more interesting to farmers due to its large versatility in many industries. On an environmental basis, hemp is a good yielding crop that has less harmful effects on the environment than its main counterparts. Firstly, hemp requires much less water than its textile counterparts such as cotton. It is also naturally resistant to pests, insects and diseases making it a crop that can be easily cultivated with organic practices (Schlottenhofer et al., 2017). This crop also outcompetes weeds which eliminates the usage of herbicides on the plants and pesticide drifts into the environment. In comparison to petroleum materials, hemp derived products help sequester airborne carbon and the end product has the potential of being decomposable or compostable once the product's life has reached an end. Despite these

environmental benefits, hemp is still a commercial crop that uses resources, energy, nutrients and water in order to grow. The added benefit of this plant is that it is highly robust to crowing conditions found in Saskatchewan and Alberta. Hemp has an added benefit of being a legalized crop that is already being grown for other purposes. Having the crop in the same country as the manufacturing facility reduces the material's environmental footprint since it does not need to travel a long distance from its source to the manufacturer. Ultimately, like castor beans, hemp is a crop that is already being cultivated and fulfilling diverse market needs. However, the usage of hemp as a base material has a far more favorable impact on an environmental standpoint due to its proximity to the client's manufacturing facility (in the same country) and its robust growing characteristics. It also does not produce any deadly or highly toxic by-products that have health, safety and environmental impacts.

Economically, hemp is a valued resource that is transformed into a variety of products destined for human consumption and as a base material for novel products. Currently, there are a few companies such as *The Hemp Plastic Company* in Australia that refines Hemp grain into a pellet that can be incorporated into existing plastic extrusion machines. This already refined product is sold at a price of 5.42\$ per pound. The base material could potentially be melted, mixed with additives and extruded into a thin roofing membrane. One of the benefits of using this product is that our client will not need to invest funds in a system that processes the raw hemp into a pelletized format. Furthermore, polylactide acid is a polymer with high thermal stability that has exhibited great results from the addition of plasticizing agents that can be easily incorporated into the PLA hemp polymer (Mallegni et al., 2018). Lastly, for the research and development stages of this project, a drop in pelletized bio-based polymer is of high value to the client, because it is readily available, requires little processing costs and serves as a benchmark for future chemical modifications.

4.4 Conclusive Assessment of Alternatives

After having thoroughly analysed the various project alternatives, a sound assessment needed to be conducted in order to identify the bio-based material of choice. In order to do so, a Pugh matrix was constructed with the goal of comparing and contrasting the various alternatives consisting of the three proposed biologic materials (lignin, castor oil and hemp). In BREE 490, a comprehensive analysis of the various material properties was conducted. This information was summarized and weighed in the matrix under the “Performance” category. The evaluation criteria was determined based on the client’s goals and priorities. Due to the environmentally conscious nature of the project, a substantial percentage of the criteria was allocated to this category. Despite this, material performance and economic viability constitute valuable design criteria for any commercial product in a competitive market. Based on numerous research and consultations with experienced professionals, our team was able to weigh the alternatives against each other using weighted criteria. Additional weighting criteria was categorized using information summarized in sections 4.1 to 4.3 of the report under “Environmental”, “Economic” and “Social” categories. Although not very precise, the results should be quite accurate because they represent general observations that have been identified in various peer-reviewed journals. Finally, the three bio materials were compared to SBS modified bitumen which corresponds to a conventional roofing membrane material. All and all, hemp polylactic acid was identified as the best bio-material based on our client’s weighted evaluation criteria. Ultimately, more research is required to gain better insight and some quantitative parameters for certain evaluation criteria will be obtained once a material composition is outlined and the product prototyping phase has begun.

Table 1. Pugh matrix of the researched bio-materials in comparison with SBS-modified bitumen.

			Benchmark	Alternative Bio-Based Compositions		
	Evaluation Criteria	Weight Factor	SBS-Modified Bitumen	Lignin	Castor Oil	Hemp PLA
Economic	Raw Material Costs	3	0	3	-1	-3
	Processing Costs	3	0	-3	-1	-2
	Drop in Replacement	3	0	-2	-2	0
	Supplier Quality	3	0	-2	1	1
Environmental	Revalorized Resource	2	0	2	0	1
	Raw Material impact on atmospheric emissions	2	0	0	2	2
	Raw material impact on environment	4	0	3	1	1
	Production By-Products	2	0	0	-1	1
Social	Sustainability (Customer Acceptance)	3	0	3	3	2
Performance	Ease of Implementation	2	0	-2	-1	0
	Chemical properties	4	0	-2	0	-1
	Physical properties	4	0	-2	-1	-1
	Lifespan	4	0	0	0	0
Final Score				-2	0	1

5.0 Bio-Based Membrane Material Composition

After determining that the best alternative for our project is the hemp PLA based membrane, more research needs to be conducted on the possible manufacturing processes and material compositions. A study conducted by Mallegni et al. sought to identify possible compositions of PLA in order to manufacture a tear-resistant and flexible biodegradable film. This paper will identify material additives that can be further investigated for our usage as well as possible manufacturing processes to produce thin membranes.

As previously mentioned, the hemp PLA polymer has certain valuable characteristics as a starting material for our project. Through the social, environmental and economic assessment of alternatives, hemp PLA was identified as being the better base material on a comparative analysis. Furthermore, it has the potential as being biodegradable which would help reduce the waste generated by the construction and renovation industry. Despite the numerous advantages that this novel material presents, PLA still has certain disadvantages with regards to its mechanical and physical properties. PLA is conventionally used to manufacture rigid containers for the food industry, however modifications need to be conducted to allow the material to exhibit more flexibility and a lower glass transition temperature (Mallegni et al., 2018). Despite having a high melting temperature of 190 degrees celsius and good thermal stability the PLA needs to be designed in a more flexible material. This paper investigates possible additives that can be added to PLA in order to attain favorable mechanical properties.

Additives such as poly(butylene adipate-co-terephthalate) (PBAT), poly(butylene succinate) (PBS) and polypropylene glycol diglycidyl ether (EJ400) were incorporated in various concentrations to determine the most favorable composition. EJ400 was incorporated as a plasticizer that also served the purpose of adhering the other additives to PLA. The EJ400 compatibilizer's main purpose is to prevent the separation of the PLA with the plasticizing agents. They have a tendency of migrating away from each other and cause a rapid reduction in

material properties. In terms of the manufacturing challenges, PLA displays a high crystallization rate which can be problematic in large scale manufacturing facilities. This is remedied by the incorporation of nucleating agents that are able to decrease the time required for crystallization by half. The nucleating agent used was Dimethyl 5-sulfoisophthalate, potassium salt (LAK). Extruding experiments were conducted in order to assess the quality of the manufacturing process and the resulting impact it had on the material properties due to a lower crystallization rate.

In order to blend the materials, the individual pellets of each material were incorporated into a molten state and mixed into a cylinder containing the appropriate concentration of each polymer. This was conducted at temperatures of 190 degrees celsius at 100 rpm for 1 minute. This temperature also corresponds to the hemp PLA melting temperature index on the data specifications sheet from *The Hemp Plastic Company*. The fluid material was then transferred to an injection molder where the final sample was manufactured at 180 degrees celsius at a pressure of 700 bar for 20 seconds to produce ASTM D638 dogbone samples for material testing and analysis based on the material testing standards. The blown extrusion films were manufactured in a similar process. The pellets were mixed in a homogenous mixture in a twin screw extruder and fractured into small particles once cooled. The small particles were put through a blown extrusion machine with a screw speed of 30 rpm, temperature of 150 degrees celsius at a pressure of 150 bar in order to produce the blown film. These are very accurate values for the manufacturing settings that need to be established for preparing blown film samples. More research, experience and trial and error testing will ultimately be useful to fine tune the settings once the additives and plasticizers are determined. The incorporation of other materials will impact these settings that may need to be revised, however it remains a good starting point for the blown film extrusion process. More research will need to be conducted to identify if this manufacturing method is adequate for our product as well.

After testing the dog bone samples of the various compositions the PLA, EJ400, PBAT mixture yielded good results that displayed a Young's Modulus of 1.4 GPa and a tensile strength of 28.8 MPa. This was achieved with a concentration ratio of 67:10:23 of PLA, EJ400, PBAT respectively. Ultimately, hybrid designs may be chosen based on the optimization of certain properties. However, this mixture had the added benefit of being more stable, more flexible while still displaying adequate mechanical properties.

Table 2. Tensile tests performed on dog bone samples following ASTM D638 procedures (Mallegni et al., 2018).

Composition	Final Torque (N·cm)	Young Modulus (GPa)	Tensile Strength (MPa)	Elongation at Yield (%)	Stress at Break (MPa)	Elongation at Break (%)
PLA/PBAT 67/33	73	2.6 ± 0.2	38.8 ± 3.1	1.4 ± 0.5	31 ± 3	110 ± 20
PLA/EJ400/PBAT 67/10/23	69	1.4 ± 0.1	28.8 ± 0.9	1.2 ± 0.2	29 ± 2	140 ± 10
PLA/PBS 67/33	58	1.8 ± 0.2	45 ± 1	1.3 ± 0.5	32 ± 5	100 ± 20
PLA/EJ400/PBS 67/10/23	55	2.7 ± 0.2	37 ± 2	0.9 ± 0.1	30 ± 4	150 ± 40

The report also looked at ways to increase the crystallizing rate of the extruded homogeneous mixture. A nucleating agent such as LAK 301, an aromatic sulfonate derivative, was incorporated to increase the hardening and crystallization rate of the mixed polymers. This was done in order to fragmentize the extruded filament in a quick manner for the blown extrusion process. However, it was noted that the addition of the nucleating agent negatively impacted the elongation and stress at the failure point of each tested sample. This would result in membranes with failure points at a lower stress levels and they would experience failure in a more brittle manner. This would be an important consideration after the prototyping phase where efficiency gains in the manufacturing process could be financially advantageous.

PLA does have a high glass transition temperature of 60 degrees celsius, however adding PBS or PBAT with glass transition temperatures of -33 and -27 degrees celsius respectively is able to bring the total mixture levels to acceptable levels of -20 degrees celsius as reported by our client *Soprema*.

All and all, the compositions investigated proved to be of value to our design project. By being able to identify possible compositions of biodegradable polymers we are able to design a composition that respects the goal of the project while performing similarly as petroleum based materials. The additives used can help increase the mechanical properties of PLA while maintaining a low glass transition temperature. Furthermore, this paper identifies specifications and settings that can be used to extrude the film through blowing extrusion. Other manufacturing processes such as injection molding or flat die extrusion may be better suited for the manufacturing of a membrane. Further research and consultation will be needed to help determine the ideal manufacturing method for the prototyping phase as well as for the commercial manufacturing stage.

6.0 Processing Guide of a Hemp Filled Polylactic Acid Roofing Membrane

The following theoretical processing guide describes the handling and extrusion of a hemp filled polylactic acid (H-PLA) waterproofing membrane reinforced with cellulose nanocrystals (CNCs). The guide is intended for industrial manufacturers that are interested in the development of a drop-in alternative for modified-bitumen based and/or petroleum based elastomers conventionally used in systems for small-sloped roofs. The information herein may only serve as a starting point and it should be noted that the optimization of the process is recommended to find the optimal process conditions for the manufacturing of a membrane whose formulation diverges from the one described in the processing guide. The guide will elaborate on pre-drying methods, maintenance and purging, twin-screw extrusion compounding, as well as quality assurance test methods.

6.1 Pre-Drying Methods

Even though polymers from the group of polylactides are usually shipped in sealed moisture-barrier packaging by the suppliers, it is important to pre-dry the biopolymer pellets to maintain their semi-crystallinity before processing and to ensure optimal mechanical properties of the final product. It should also be noted that polylactides should be stored at temperatures below 50°C and direct contact with sunlight should be avoided to prevent ultraviolet degradation of the biopolymer. During the storage period, H-PLA pellets can reach a moisture content of 400 ppm despite the moisture-barrier packaging. It is therefore recommended to reduce the moisture content of the pellets to a level of less than 250 ppm, but the optimal moisture content is 100 ppm before melt-processing. In fact, after contact with the moisture of ambient air, polylactide homopolymers hydrolyzes which affects the melting process and results in reduced mechanical performances of the final product. In order to lower the moisture content of the pellets, conventional drying systems can be used. The preferred method uses a desiccant hot air dryer

system. A desiccant dryer uses special drying agent beads, namely a desiccant (i.e. silica gel or activated alumina), to absorb water vapor from an air stream. These air dryer units are often regenerative so that the drying agent doesn't need replacing in order to provide vapor-free compressed air consistently. Typically, a desiccant dryer system has a two-tower design. While both towers have thousands of desiccant beads, they perform two very different processes; One tower works to dry the compressed air by removing the water vapor while the second tower works to regenerate the desiccant. The goal of the regeneration cycle is to remove as much water from the compressed air as possible to bring it to a level where the water will not condense. The air compressor desiccant dryer is programmed to handle this process automatically based on dew point levels. It is important, however, to regularly check to make sure that the air dryer is functioning correctly. This can be done by simply looking through an inserted glass window located on the desiccant air dryer system. Through the window, indicator beads can be seen and they will change color if there is too much water in the air. The particularity of a desiccant hot air system is that it uses a fan that blows hot air on the desiccant as a way to dry the beads and ensure a continuous process. Another important consideration in this part of the process is to equip the desiccant hot air system with a filtering system. In order to ensure a regenerative process that runs smoothly, a multi-filtering system consisting of a condensation trap, a water filter to keep the water as clean as possible before it enters the air dryer as well as a dust filter to remove desiccant dust, which could damage the equipment over time, should be installed. The time required to dry the polylactide homopolymer depends on its level of crystallinity. Typical drying conditions were determined by *Total Corbion PLA* which specializes in the distribution of polylactide based polymers for industrial applications. The parameters for various crystallinity levels are compiled in the following table.

Table 3: Typical Polylactide Homopolymer Drying Conditions, 2019, *Total Corbion PLA*

Parameter	Amorphous PLA	Pre-crystallized standard PLA (Luminy® LX175)	Crystalline PLA homopolymers (Luminy® L105, L130, L175)
Drying time	24 hours	4-6 hours	4-6 hours
Air temperature	40°C	85°C	100°C
Air dew point	< -40°C	< -40°C	< -40°C

After drying, the actual moisture content of the biopolymer can be determined from the principles of Karl-Fischer or the Brabender Aquatrac Method. The principles of Karl-Fischer rely on a titration technique that is based on a reagent that reacts with water to transform it into a non-conductive chemical. Since the initial process deals with semi-crystallized standardized pellets that are solid, the volumetric Karl-Fischer method is more appropriate. In this method, samples are dissolved in a solvent before the titration begins and a reagent is then added until the water is removed. The moisture determination is therefore based on the volume of reagent used to convert the water into a non-conductive chemical. This method is simple, fast and requires minimal handling since volumetric titrators automatically display the actual moisture content of the sample under study. On the other hand, the Brabender Aquatrac method uses an electronic moisture analyzer that works on the principle of heat drying in circulating air (oven drying method). In this method, the sample's loss of weight resulting from the drying procedure is determined. Indeed, water and calcium hydride react with each other under hydrogen development in a closed reaction vessel. The gas is then evacuated before the measurement with a built-in vacuum pump and electrically heated during the measurement. The water vapor released by the heating reacts with the calcium hydride and the pressure in the measuring system increases due to the developing hydrogen. The gas pressure is proportional to the amount of water introduced, as the reaction is specific to water. The ratio of pressure to sample weight is calculated and the result is finally displayed in percentage, ppm and milligrams of water content. Once the actual moisture content of the batch sample is determined and appropriate for the next step of the processing, it is recommended to process the biopolymer pellets as soon as possible to prevent moisture uptake. In fact, the moisture take-up curve of polylactide homopolymers, found below, shows that it only takes 15 minutes for a 100 ppm moisture content sample to reach the critical level of 250 ppm moisture content after exposure to ambient conditions. In order to prevent the moisture uptake by the dried pellets, a closed system from the drier to the twin-extruder feeder or simply a drier over a twin-extruder feeder are preferable options to limit the time of exposure of the pellets to the ambient conditions before melt processing.

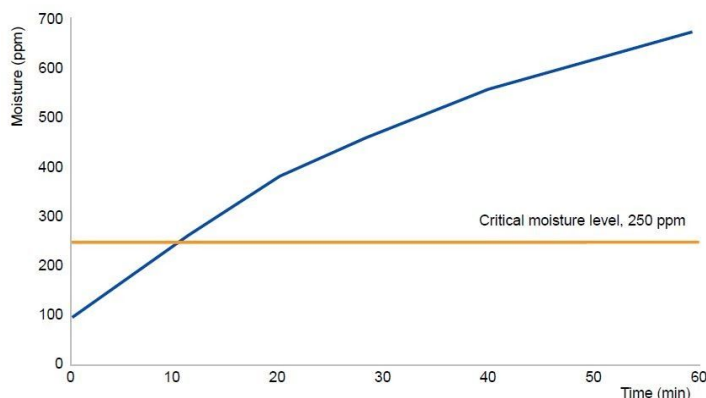


Figure 1: *Polylactide Homopolymer Moisture Take-Up Curve*, 2019, Total Corbion PLA

6.2 Cleaning and Purging

In an industrial setup, it is not uncommon to see that manufacturers process multiple different feedstocks with the same equipment. However, in order to prevent cross-contamination between different batches, it is important to carefully clean and purge the equipment. Therefore, a good manufacturing practice before starting-up the polylactide polymer melt process is to proceed to purging. The first important step before even purging is to check if another polymer from previous batches, if applicable, is present in the machine. This step seems intuitive, but it prevents starting up the machine with non molten material that could clog the extruder die and/or damage the screw. In the event that a polymer other than a polylactide is present in the barrel, the temperature parameters of the machine should be set accordingly to process the latter polymer to melt it and empty the barrel. Once the barrel is empty and that no trace of non molten material is present, the purging can start. The purging procedure simply consists in extruding a purging compound followed by the polylactide homopolymer that is used for the final product. Common purging compounds used in twin screw extruder are ASAclean or Dyna-Purge, but for both compounds, the principle stays the same. The temperature range of the extruder has to be adjusted accordingly with the grade of the purging compound that is advised by the supplier for the kind of purging that is required. The following table briefly summarizes the temperature ranges of the extruder required depending on the purging compound grade.

Table 4: Temperature Ranges of Purging Compounds at ASAClean, 2019, *ASAClean*

Grade	°F	°C
U - Polypropylene/Polyethylene Resin Color Change	325-625	180-330
EX - High Scrubbing	390-625	200-330
HP - Polypropylene Color Change	340-570	170-300
SX - High Temperature Resin	570-700	300-370
NH - Mechanical Purging in Hot Runner Cleaning	355-625	180-330
E - Residue Sensitive and/or Low Temperature Resin	340-570	160-330
NC - Mechanical Purging Scrub	355-625	180-330
PX2 - High Temperature Super-Engineered Resin Purging	535-790	280-420
PF - High Temperature Super-Engineered Resin for Material Sealing and Equipment Shutdowns	535-570	280-420
NF - Glass-Filled Mechanical Purging Compound for Carbon Deposits	355-625	180-330
NB - Mechanical Purging Compound with Foaming activity to Dislodge Contaminants	355-625	180-330

Once the appropriate temperature range is obtained, the barrel can be started and the hopper can be fed with the purging compound for an equivalent of 1 or 2 barrel capacity depending on the extent of the contamination. Screens and dies can be left on the extruder for unfilled purging compounds, but it is recommended to remove them if a filled purging compound (i.e. glass-filled) is used to prevent clogging and damaging of the equipment. The purging starts at low screw speed until the purging compound is coming out of the die or the head of the extruder. Once, the cleaning resin is visible, the screw speed can be increased at maximum safe level.

At regular intervals, the screw can be stopped to allow the purging compound to settle a few minutes after which the screw speed is reestablished at maximum allowable speed. This operation lasts until the purging compound is fully processed. A final visual inspection of the cleaning resin to determine if the machine is free of contamination. If the purging pile towards the end of the process is visually clean, it means that the extruder is purged and the polylactide homopolymer can be introduced for the batch purging. If contaminants are still visible, the process is repeated with the purging compound until the cleanliness is satisfactory. The second purging requires the barrel temperatures to be adjusted for the polylactide homopolymer that is used. In the case of hemp filled polylactic acid (H-PLA), the purging procedures are the same as for the purging compound but the temperatures need to be adjusted as compiled in the following table. Once the run is done, it is important to clean the extruder from any polylactide residue because the homopolymer can degrade into polylactic acid which can lead to corrosion of the equipment.

Table 5: Extrusion Temperature Profile for Hemp Filled Polylactic Acid (H-PLA), 2019, *The Hemp Plastic Company*

Parameter	Temperature (°F)
Feed Zone	260-290
Melt Zone	300-330
Mixing and Conveying	320-350
Die Head	330-360

6.3 Twin-Screw Extrusion Compounding

Twin-screw systems can be used in a variety of ways, but most notably for compounding, devolatilization and reactive extrusion. This particular step of the process involves the transfer of heat and mechanical energy to provide a continuous mixing of fillers and additives with the polymer matrix to obtain an end product with the desired enhanced properties. Since we want to reinforce the polymer matrix to obtain higher shear resistance and tensile strength while

maintaining the waterproofing capacity of hemp filled polylactic acid, cellulose nanocrystals (CNCs) will be added in a conveying zone of the extruder destined for split feeding of fillers. In order to optimize the grafting process of the cellulose nanocrystals with the polymer matrix, factors such as the choice of corotation versus counterrotation, screw design parameters, downstream-pelletizing-system configurations as well as the weight percentage attributed to the compounds of the formulation are all important design criteria for a successful grafting when employing a twin-screw equipment.

Twin-screw compounding extruders used for commercial applications are offered in three different modes; corotating intermeshing, counterrotating intermeshing, and counterrotating nonintermeshing as shown in the figure below.

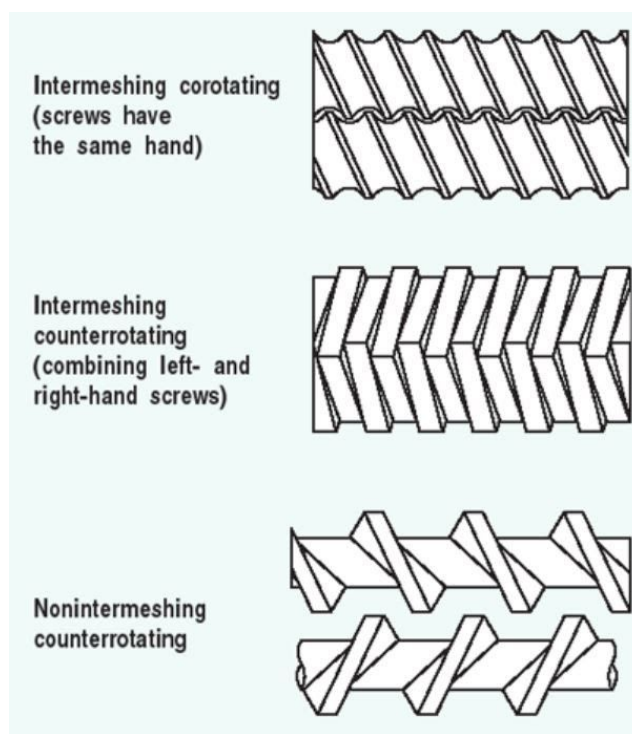


Figure 2: Commercial twin-screw extruder modes, 2000, *Accumold*

Although each mode has certain attributes that make it suitable for particular applications, the two intermeshing types are generally better suited for dispersive compounding making it a better choice for enhanced grafting. However, corotating assemblies have the advantage of having

self-wiping screws, so standard metallurgies for screws and barrels can be used, such as hardened tool steels and powder metallurgies for increased abrasion resistance. This accounts for a greater durability of the equipment and a better dispersion of the cellulose nanocrystals in the polymer matrix which ensure a homogeneous end product. It should also be noted that metal parts in the extrusion process that have stagnant flow areas (i.e. adapters, screen changers and dies) should be made of stainless steel and/or hard-chrome plated for increased corrosion resistance.

In regards of the screw layout in the barrel of the extruder, it is important to understand the main compounding steps in a twin-screw extruder, that is, feeding, melting, conveying, mixing, venting and extrusion of the homogenized product (Bernd and Geilen, 2018). In the feed zone, air is removed and material with low density is compacted. In the next step, the material is moved forward and is heated up in a partially filled and unpressurised conveying section. In the mixing zone, the material is molten, then plastified and it completely fills the barrel. The processing of hemp filled polylactic acid reinforced with cellulose nanocrystals requires our design to implement a conveying zone that is used for the split feeding of the cellulose nanocrystals. Then, an alternating mixing and conveying section follows to achieve a homogeneous product. A last conveying section is used for venting volatiles and air either at ambient pressure or by vacuum. Finally, the role of the extrusion section is to build up pressure and shape the material, which in this case would be a film that is destined for blown extrusion. A schematic of the extrusion screw layout as described above is represented in the figure below.

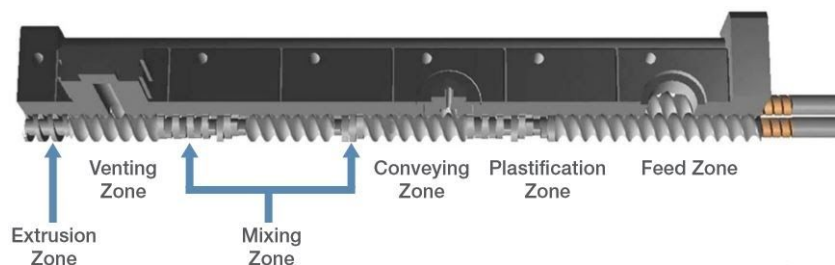


Figure 3: Screw layout of a twin-screw compounding extruder, 2018, Bernd and Geilen, Thermoscientific

The recommendations from the supplier of hemp filled polylactic acid *The Hemp Plastic Company* give a general idea of the extrusion profile in regards of temperature, pressure and screw speed. It should be noted that the following parameters should be optimized by the manufacturers to ensure that the compounding process yields a homogeneous film. The use of terms like “Moderate”, “High” and “Fast” to designate the pressure and the screw speed respectively were used intentionally by the supplier in the technical data sheet to allow the manufacturers to adjust their extrusion parameters in a way that is convenient for them and that minimally disrupt the efficiency and continuity of their production line. The supplier also notes that “due to the complex nature of design and processing, observation on a trial and error basis may be required to achieve desired results” (*The Hemp Plastic Company*, 2019).

Table 6: Extrusion Parameters for Hemp Filled Polylactic Acid, *The Hemp Plastic Company*, 2019

Temperatures (F)		Pressures		Other
Back	260-290	Injection	Moderate	Injection Rate: Moderate
Middle	300-330	Hold	Moderate – High	Screw Speed: Moderate-Fast
Front	320-350	Back	Moderate	
Nozzle	330-360			
Mold	80 - 100			

In regards to the downstream system, since we want to obtain a continuous film directly out of the twin-screw compounding extruder, the screw speed would have to be adjusted slower than recommended and the feeders should be filled more than usual. Another option is to join a gear pump to the twin extruder. This would allow to generate pressure within the barrel and to stabilize the compounding process. In fact, to optimize the compounding efficiency, the twin screws are most likely to be operated in a starved manner at high speeds, with a zero pressure gradient along much of the barrel. This can result in inconsistent or low pressure to the die, which is unacceptable for extruding a product. Therefore, it is recommended to cope with these conflicting process goals by lowering the screw speed while maintaining a higher feeding rate to

generate more pressure within the barrel. The end of the extruder also has to be equipped with a film die to obtain the desired end product destined to blown-extrusion. Concerning the use of cellulose nanocrystals, Karkhanis et al. investigated the water vapor properties of extrusion-blown polylactic acid/cellulose nanocrystals nanocomposite films by varying its filler content from 0 wt% to 2 wt% in increments of 0.5 wt% (i.e. 0; 0.5; 1.0; 1.5; 2.0 wt%). The water vapor transmission rate (WVTR) of the films was measured gravimetrically, according to the desiccant method in ASTM E 96 with the following relation;

$$WVTR = \frac{\Delta W/t}{A}$$

Where, ΔW is the weight gain of the cups at time t (24 h); and A is the effective area of exposed film ($31.67 \times 10^{-4} \text{ m}^2$). The obtained WVTR values were normalized by the thickness (l) and difference in partial pressure of permeant across the sample (Δp) to calculate the *Water Vapor Permeability* (WVP) as follows:

$$WVP = \frac{WVTR \times l}{\Delta p} = \frac{WVTR \times l}{p_1 - p_2} = \frac{WVTR \times l}{p_{sat} \cdot (RH_{out} - RH_{in})}$$

where p_1 and p_2 are the partial vapor pressures of the permeant (water vapor) on the outside and inside of the test film, respectively and can be given as $p_1 = (p_{sat} \cdot RH_{out})$ and $p_2 = (p_{sat} \cdot RH_{in})$, respectively. RH_{out} and RH_{in} are the relative humidities of the external (test RH) and internal sides ($\approx 0\%$) of the film and p_{sat} is the saturated vapor pressure at the test temperature.

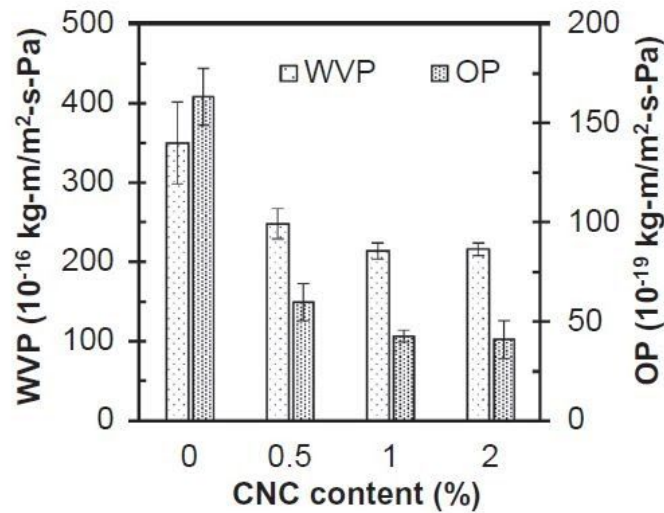


Figure 4: Effect of CNC content on the Water Vapor Permeability and Oxygen Permeability of PLA films. Karkhanis et al., 2018

The previous figure illustrates the effect of cellulose nanocrystal (CNC) content on the water vapor permeability (WVP) and oxygen permeability (OP) of PLA films. Karkhanis et al. concluded that the WVP decreased as the CNC concentration increased up to 1% and remained constant thereafter. “Significant improvements of approximately 39% in WVP were observed by adding only 1% CNC into PLA matrix. This improved barrier performance of the nanocomposite films is likely due to the presence of highly crystalline CNCs which acted as efficient nucleating agent resulting in higher degree of crystallinity as well as impermeable regions in the matrix” (Karkhanis et al., 2018). Therefore, the addition of 1 wt% of cellulose nanocrystals should be considered during the twin-screw extrusion compounding process to allow a grafting that optimizes the water vapor permeability to the desired level. As a final reminder, the cellulose nanocrystals should be inserted in the conveying zone of the extruder through a second feeder hopper destined for split feeding of fillers.

In order to obtain a finalized waterproofing roofing system, the extrudate can be applied on a frame made of fiberglass, non woven polyester or a combination of both. This formulation is commonly used in the industry as a reinforcement and allows for greater durability of the product. Our work with *Soprema* inspired the design of a manufacturing process that highly resembles the manufacturing of their *Styrene Butadiene Styrene* (SBS) modified bitumen roofing systems. Our contact at *Soprema* provided us with the manufacturing process diagram of such a system, in which we replaced *Styrene Butadiene Styrene*, bitumen and fine particles with hemp polylactic acid and cellulose nanocrystals. The only difference in our manufacturing process is the use of a bio-based extrudate that is destined to coat a saturated fiberglass frame. The combination of the frame and the extrudate is processed in a series of calendar machines to obtain a homogeneous surfacing. The calendaring is followed by a second coating of mineral granules and sand which act as antiadhesive agents for the cap and base surfaces of the roofing system. The product is then cooled, winded into standardized rolls and palletized for shipping. The modified manufacturing process diagram gives a general overview of the steps that follow the twin-screw extrusion compounding process, but it should be noted that the latter steps are

usually well mastered by the manufacturers in the industry. Since our design considered the drop-in compatibility aspect of the product, it was important that its processing relied on well known technologies to ease its adoption by the manufacturers in the industry and to foster a progressive transition towards more environmentally-friendly alternatives of construction materials.

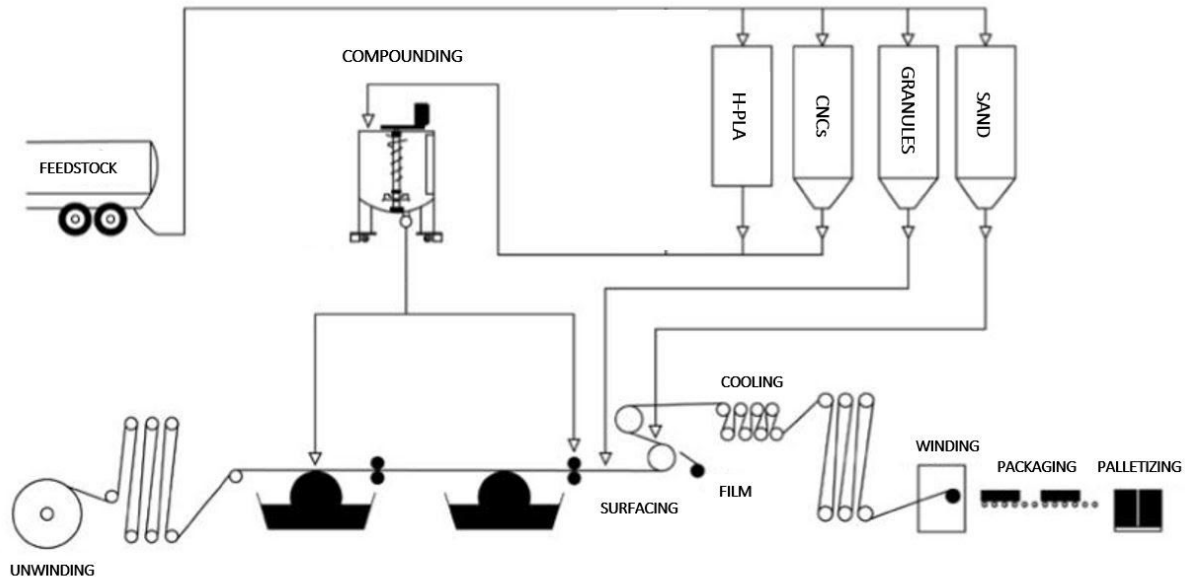


Figure 5: Manufacturing process diagram of a CNC reinforced H-PLA waterproofing roofing system, Environmental Product Declaration, Soprema, 2014

Standardized Quality Assurance Tests

In order to have a product that complies with the norms of the industry, the *Standard Test Methods for Sampling and Testing Modified Bituminous Sheet* designated as ASTM D5147/D5147M – 18 are recommended to proceed to the quality assurance tests for each shipment. It is recommended to randomly sample a number of rolls equal to one half the cube root of the total number of rolls in the lot. The latter test methods cover procedures for sampling and testing prefabricated, reinforced, polymer-modified bituminous sheet materials designed for single- or multiple-ply application in roofing and waterproofing membranes. Since our design is

very similar to a SBS modified-bitumen roofing system and is destined to be a drop-in compatible replacement for fossil fuel based roofing systems, the testing procedures from ASTM D5147/D5147M – 18 should be considered as a good framework for quality assurance tests. The most relevant test methods are presented in the following section.

Load Strain Properties

This test method determines the tensile elongation and the strain energy of a hemp filled polylactic acid sample. The test method requires five specimens of 25 millimeters wide by at least 150 millimeters long for sheet material. The specimens are first conditioned for two hours at the selected test temperature. The recommended test temperatures are $23 \pm 2^\circ\text{C}$ and $-18 \pm 2^\circ\text{C}$ respectively. A constant rate of elongation (CRE) tension testing machine should be used, preferably with automatic load and strain recording equipment, and clamps that permit a uniform clamping pressure on the specimen without slipping. The initial clamp separation should be 75 ± 2 millimeters for sheet material. The rate of separation should be of 5.0 mm/min for specimens tested at $23 \pm 2^\circ\text{C}$ and 2.0 mm/min for specimens tested at $-18 \pm 2^\circ\text{C}$. The percent elongations of each specimen at break and peak loads are determined using an extensometer, or by calculating the percent elongation at specimen break and also at peak loads from the chart of the stress versus time knowing the speed of the chart drive and the jaw separation rate. The percent elongation at break is calculated with the following relation;

$$\% EL_{break} = \frac{a-b}{b} \times 100\%$$

Where, a is the jaw separation at break and b is the initial jaw separation. Similarly, the percent elongation at peak is determined with the following relation;

$$\% EL_{peak} = \frac{c-b}{b} \times 100\%$$

Where, c is the jaw separation at maximum load and b is still the initial jaw separation. The average percent elongation at break and peak loads are then determined based on the total

number of measurements taken. The average strain energy at peak load and at break in each direction and the standard deviation of the strain energies in each direction are calculated based on the total number of measurements taken. Then, one can determine the ultimate elongation using data obtained from tests conducted previously. The ultimate elongation is defined as the elongation measured on the load-elongation curve at which point the load has dropped to 5 % of its maximum value, after the peak load has been reached. Once the load strain properties are determined, it is important to report for each specimen the temperature of the test, specimen size, and individual measurements of peak load in kN/m [lbf/in.], percent elongation at peak load, breaking load in kN/m [lbf/in.], percent elongation at break, method of determining elongation, strain energy in kNm/m [inch-pound /in.] at peak load, strain energy in kNm/m [inch-pound /in.] at break, and method of determining elongation.

Tear Strength

This test method determines the tensile tear strength of five specimens with dimensions that are identical to the ones previously described in the section *Load Strain Properties*. The test procedure should also be in accordance with the one previously described, except that the rate of jaw separation should be adjusted at 50 mm/min for testing at $23 \pm 2^{\circ}\text{C}$. The average tear strength in each direction and the standard deviation of the tear strength in each direction are calculated based on the total number of measurements taken. One can then report the individual specimen values, average, and estimated standard deviation of the specimens in each direction.

Water Absorption

This test method determines water absorption of five specimens measuring approximately 100 by 100 mm [4 by 4 in.] from each sample roll. The procedure starts by immersing the specimens in a distilled water bath maintained at $50 \pm 2^{\circ}\text{C}$ for 100 ± 4 h. The specimens are then removed and the surface water is blot off with a dry cloth. The specimens are then reimmersed

in technical grade acetone for 2 ± 1 second, and permitted to air dry in the laboratory for 15 ± 2 minutes at $23 \pm 2^{\circ}\text{C}$ and $50 \pm 5\%$ RH. The mass of each specimen can then be determined to the nearest 0.1 g after immersion. The moisture content is determined in accordance with Test Method D95 and is water expressed as a percent of dry mass. One can obtain the total percent of moisture gained by subtracting the moisture content as obtained in Section 9 from the moisture content after immersion as determined in this section. The average percent of moisture gain and the standard deviation of percent of moisture gains based on the total number of measurements taken can finally be calculated. The individual specimen values, average, and estimated standard deviation are reported.

Dimensional Stability

This test method determines a dimensional stability five specimens from each sample roll: one specimen from each edge of the sheet and three randomly across the sheet. The specimens are conditioned in an oven maintained at $80 \pm 2^{\circ}\text{C}$ for $24\text{ h} \pm 15$ minutes. After oven conditioning, the specimens are cooled and measured as indicated in Test Method D1204. This Then, one can calculate the absolute dimensional change based on the absolute difference between the initial measurements and the measurement after conditioning for each specimen. The average absolute dimensional change in each direction and the standard deviation of the absolute dimensional changes in each direction based on the individual results can also be calculated. Finally, the initial measurements of the individual specimens, the measurements of individual specimens after conditioning, the dimensional change in each direction for each specimen, the absolute dimensional change in each direction for each specimen, the absolute average, as well as the estimated standard deviation in each direction are reported.

Conclusion

Despite the unfortunate turn of events, our team was able to make the best out of the situation in order to advance the project. After having consulted with the client, our team was able to identify the needs and priorities that the design project needed to respect. After having identified and researched three potential bio-materials (lignin, castor oil and hemp), our team was to assess and evaluate the various alternatives based on an evaluation criteria reflecting the client's views. Hemp PLA was deemed favorable for the construction of a bio-based membrane, however its formulation and manufacturing process needed to be identified. Although somewhat rigid, PLA can be incorporated with EJ400 and PBAT in a 67:10:23 ratio respectively in order to improve on some of the fundamental physical properties displayed by flexible and watertight roofing membranes. Once identified, the manufacturing process could be assessed and outlined in order to produce a sheet like membrane. A pre-drying process followed by a cleaning and purging stage need to be adequately conducted before the manufacturing process can begin. It was determined that the twin-screw extrusion compounding with the addition of cellulose nanocrystals nucleating agent (1 wt%) would be able to produce a sheet membrane with industry standards dimensions. Ultimately, optimization of the composition and manufacturing process will be required in order to improve the end product. To do so, standardized quality assurance tests can be used to evaluate fundamental properties of the roofing membrane during the prototyping phases of the project. All and all, our team was able to follow through the design process in an effective manner and nonetheless present the course instructor (Dr. Chandra Madramootoo) and our client (Pierre-André Lebeuf from *Soprema*) with a respectable report outlining the project's developments.

Appendix A



H25CPLA1 TECHNICAL DATA SHEET

PRODUCT: HEMP PLA 25%

Description:

H25CPLA1 is a 25% hemp filled polylactic acid (PLA). This product is generally used in injection molding, but may be used for other forming methods as developed by individual users. HEMP PLA is designed to be a drop-in replacement for conventional fossil fuel based polymers.

Natural color is medium brown; pelletized. Refer to molding recommendations below; limiting back pressure and injection speed as much as process will allow is optimal for working with this material.

Property:	Typical Value:	Units:	Test Method:
Specific Gravity	1.27	g/cc	ASTM D 792
Tensile Strength @ Break	4,080	psi	ASTM D 638
Tensile Elongation @ Break	2.27	%	ASTM D 638
Flexural Modulus (2% secant)	380,000	psi	ASTM D 790
Melt Flow Index, 190C/2.16Kg	82	g/10 min	ASTM D 1238
Izod Impact	0.34	ft. lbs/in	ASTM D 256
Garner Impact	28	ft*lbs	ASTM D 5420

General Recommendations:

Temperatures (F)		Pressures		Other
Back	260 – 900	Injection	Moderate	Injection Rate: Moderate
Middle	300 - 330	Hold	Moderate – High	Screw Speed: Moderate-Fast
Front	320 - 350	Back	Moderate	
Nozzle	330 - 360			
Mold	80 - 100			Pre-drying is recommended before molding to avoid potential for splay

Data are obtained from tests performed under carefully controlled conditions from representative samples of the compound described herein. Properties may be materially affected by molding techniques applied and by the size and shape of the item molded. No assurance can be implied that all molded articles will have the same properties as those listed.

This information serves only as a guideline for processors, users and manufacturers. Due to the complex nature of design and processing, observation on a "trial and error" basis may be required to achieve desired results.

No information supplied by The Hemp Plastic Company (THPC) constitutes a warranty regarding product performance or use. Any information regarding performance or use is only offered as an approach for investigation for use, based upon THPC or other customer experience. THPC makes no warranties, expressed or implied, concerning the suitability or fitness of any of its products for any particular purpose. It is the responsibility of the customer to determine that the product is safe, lawful and technically suitable for the intended use.



Safety Data Sheet

Hemp Filled PLA

1 PRODUCT AND COMPANY IDENTIFICATION

Product Identifier: Hemp Filled PLA
Common Name: Filled PLA
SDS Number: NA
Revision Date: 8/23/2019
Version: 1

Supplier Details: The Hemp Plastic Company
 1495 Canyon Blvd. Boulder, CO 80302

Phone: (888) 608-8472
Email: info@hempplastic.com
Web: www.hempplastic.com
Emergency: (720) 548-6327

2 HAZARDS IDENTIFICATION

Classification of the Substance or Mixture

GHS Classification in Accordance with 29 CFR 1910 (OSHA HCS):
 None, None, None

GHS Label Elements, Including Precautionary Statements

GHS Signal Word: NONE

GHS Hazard Pictograms:

No GHS pictograms indicated for this product

GHS Hazard Statements:

H000 - None

GHS Precautionary Statements:

P103 - Read label before use.

3 COMPOSITION/INFORMATION OF INGREDIENTS

Chemical Ingredients:		
CAS#	%	Chemical Name:
557-05-1	<1%	Zinc stearate
31570-04-4		Phenol, 2,4-bis(1,1-dimethylethyl)-, phosphite (3:1)
6683-19-8		Tetrakis [methylene (3,5 di-tert-butyl-4-hydroxyhydrocinnamate)methane]

4 FIRST AID MEASURES

Inhalation: NA - Material is not airborne by nature of particle size
Skin Contact: Wash with soap and water.
Eye Contact: Rinse with water.
Ingestion: Call poison control.

5 FIRE FIGHTING MEASURES

Flammability: Comparable to other PP resins. Use standard precautions.

6 ACCIDENTAL RELEASE MEASURES

7	HANDLING AND STORAGE
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Storage Requirements: Keep in a cool, dry location.

8	EXPOSURE CONTROLS/PERSONAL PROTECTION
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Personal Protective Equipment: HMIS PP, A | Safety Glasses

9	PHYSICAL AND CHEMICAL PROPERTIES
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Appearance:	Green/Brown Pellets	Odor:	Organic, often described as smelling like bread baking
Physical State:	Solid		
Spec Grav./Density:	1.1 g/cc		

10	STABILITY AND REACTIVITY
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11	TOXICOLOGICAL INFORMATION
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12	ECOLOGICAL INFORMATION
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13	DISPOSAL CONSIDERATIONS
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14	TRANSPORT INFORMATION
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15	REGULATORY INFORMATION
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This product does not contain chemicals known to the State of California to cause cancer, birth defects, or other reproductive harm.

16	OTHER INFORMATION
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HMIS III: Health = 0, Fire = 1, Physical Hazard = 0
HMIS PPE: A - Safety Glasses

HMIS		
HEALTH	0	
FLAMMABILITY	1	
PHYSICAL HAZARD	0	
PERSONAL PROTECTION	A	



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References

- Vakkilainen, E., Välimäki, E. (2009). Effect of Lignin Separation to Black Liquor and Recovery Boiler Operation. DOI: 10.13140/2.1.2039.6485. Retrieved from https://www.researchgate.net/publication/267755667_Effect_of_Lignin_Separation_to_Black_Liquor_and_Recovery_Boiler_Operation
- Loutfi, H., Blackwell, B., Uloth, V. (1991). Lignin recovery from kraft black liquor: Preliminary process design. *Tappi Journal*., 74(1), 203-210. Retrieved from https://www.researchgate.net/publication/284087847_Lignin_recovery_from_kraft_black_liquor_Preliminary_process_design
- Tavares, L. B., Boas, C. V., Schleder, G. R., Nacas, A. M., Rosa, D. S., Santos, D. J. (2016). Bio-based polyurethane prepared from Kraft lignin and modified castor oil. *Express Polymer Letters*, 10(11), 927-940. Retrieved from: <http://dx.doi.org/10.3144/expresspolymlett.2016.86>
- Patel, V. R., Dumancas, G. G., Kasi Viswanath, L. C., Maples, R., Subong, B. J. (2016). Castor Oil: Properties, Uses, and Optimization of Processing Parameters in Commercial Production. *Lipid insights*, 9, 1–12. <https://doi.org/10.4137/LPI.S40233>
- Macalino, A. D., Salen, V. A., Reyes, L. Q. (2017). Castor Oil Based Polyurethanes: Synthesis and Characterization. *IOP Conf. Ser.: Mater. Sci. Eng*, 229. <https://doi.org/10.1088/1757-899X/229/1/012016>
- Schluttenhofer, C., Yuan, L. (2017). Challenges towards Revitalizing Hemp: A Multifaceted Crop. *Trends in Plant Science*, 22(11), 917-929. <https://doi.org/10.1016/j.tplants.2017.08.004>

Mangino, E., Lupescu, M. (2018). Industrial Hemp Production Trade and Regulation. Retrieved from https://apps.fas.usda.gov/newgainapi/api/report/downloadreportbyfilename?filename=Industrial%20Hemp%20Production%20Trade%20and%20Regulation_Ottawa_Canada_12-14-2018.pdf

Mallegni, N., Phuong, T. V., Coltelli, M. B., Cinelli, P., Lazzeri, A. (2018). Poly(lactic acid) (PLA) Based Tear Resistant and Biodegradable Flexible Films by Blown Film Extrusion. *Materials (Basel, Switzerland)*, 11(1), 148. <https://doi.org/10.3390/ma11010148>

Brabender Messtechnik. (2016). *Discontinued - the successor AQUATRAC-V*. Retrieved from: <https://www.brabender-mt.de/en/service/discontinued/aquatrac-3e>

ASAClean (2020). *Extrusion Process Purging Procedures*. Retrieved from: <https://www.asaclean.com/purging-procedures/extrusion/cleaning-of-screw-for-extrusion/>

Martin, Charlie. (2000). *In the Mix: Continuous Compounding Using Twin-Screw Extruders*. Medical Device and Diagnostic Industry. Retrieved from: <https://www.mddionline.com/mix-continuous-compounding-using-twin-screw-extruders>

Martin, Charlie. (2014). *Compounding PLA on Twin-Screws: What Testing Reveals*. Plastics Technology. Retrieved from: <https://www.ptonline.com/articles/compounding-pla-on-twin-screws-what-testing-reveals>

Bernd, Jakob. Geilen, Tom. (2018). *Relevant Process Parameters for Twin Screw Compounding*. Thermoscientific. Retrieved from: <https://assets.thermofisher.com/TFS-Assets/CAD/Application-Notes/LR70-e-Relevant-process-parameters-twin-screw-compounding.pdf>

Soprema, (2007). *Membrane de Bitume Modifié au SBS Pour Toiture*. Environmental Product Declaration. PDF.

American Standards and Test Methods. (2018). *Standard Test Methods for Sampling and Testing Modified Bituminous Sheet Material*. D5147/D5147M – 18. PDF.