INVESTIGATION OF BIOPOLYOL SPRAY FOAM INSULATION MODIFIED WITH NATURAL FIBERS

By

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

Faculty of Forestry
University of Toronto

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Abstract

Rigid spray foam insulation is widely used as wall insulation in construction industry. Replacing synthetic polyether and polyester polyols with bio-based polyol and using water as blowing agent, would provide eco-friendly spray foam which is good for the environment and make buildings a safer place to live. The objectives of this work were to produce sustainable spray polyurethane foam insulation from soy-based polyol, derived from agricultural product and enhance its properties by incorporation of wood and cellulose fibers, a consumer forest product. The composite foam systems and the neat foam prepared in this manner were evaluated in terms of their thermo-mechanical properties, morphological characterization, and also their resistance contribution to overall structural integrity of the buildings against natural shear forces.

Wood fiber and cellulose fiber were incorporated as reinforcement in foaming in three stages, 13php, 26php, and 40php. The fiber size, dispersion and concentration within the matrix affected the reinforcing quality. The interactions and the effects of fiber in composite foams were observed at cellular level by Fourier transform infrared and scanning electron microscopy to evaluate their performances. The results indicated incorporation of fiber had an impact on the...
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CHAPTER 1.0

General Introduction
1.1 Background

Polyurethanes were developed by Bayer Company around the year 1950. It was a success story and formed the basis for a multi-billion dollar business in the world today [1]. Since then manufacturers and pioneers of polyurethane tried to apply a more scientific approach to that research work but in spite of many discoveries there has been little change to the original work.

Polyurethane (PU) foams are widely used in different applications depending on its category such as flexible, semi-rigid and rigid foaming. They are mostly used in transportation, furniture, and construction industries. Spray polyurethane foam (SPF) is rigid foam currently used as wall insulation in residential and commercial buildings. It is an effective thermal insulation material due to its ability to reduce the heat loss through walls and save energy for home owners. It is an excellent air/moisture barrier because of its superior adhesion to wall frame. Spray Polyurethane foam insulation has two components, component ‘A’ as isocyanate and components ‘B’ as polyol. They come together at the nozzle of a gun and spray on the wall. It expands many times of its volume and solidifies in seconds sealing the wall.

Most commercial polyols used in SPF insulations are polyether or polyester polyols derived from petro-chemicals. Rigid foams manufacturers use approximately 1.3 billion pounds of polyols out of total 2.6 billion pounds of annual production in North America [2]. In recent years high petroleum prices along with sustainability of resources have prompted the researchers to look for alternative renewable resources to produce eco-friendly insulation foam to be used in construction.

1.2 Literature review

Rigid and flexible polyurethane foam
Polyurethanes have a wide variety of commercial applications. They are seen everywhere in furniture, packaging, automobile, footwear, and as insulation in construction industry and their consumptions are increasing day by day in the world.

Polyurethane is a polymer formed by the reaction of a polyol with two or more hydroxyl functional groups per molecule with an isocyanate that has more than one reactive isocyanate group per molecule (diisocyanate). The main raw material of commercial diol polyols such as ethylene glycol and propylene oxide are derived from petro-chemical products that are not sustainable and facing challenges due to the environment issues. To meet the increasing polyurethane demand, researchers are continuously searching for alternative natural resources that are renewable, less costly and more ecofriendly for production of polyols.

The bio-polyols synthetized from vegetable oils such as soybean oil, Caster oil, and palm oil are attractive alternatives for this purpose and has drawn considerable attention [3]. These vegetable oils must however, be chemically modified to introduce hydroxyl groups in their structure for formation of polyols. Castor and palm are relatively expensive vegetable oils to produce in North America but soybean oil has been widely explored for polyol synthesis by polyurethane manufacturers. In addition to being abundant and inexpensive soybean oil is highly unsaturated oil and its unsaturation number is higher than other vegetable oils. The average number of double bonds per molecule is about 4.6 and makes it a good candidate for polyol production.

Dr. Ramani Narayan, a pioneer in this field, produced different types of biopolyols from vegetable oils and lipids. In one attempt he synthesized high-value low molecular weight polyol using protein obtained from microalgae. Microalgae are used as sustainable feedstock to produce biofuels. This polyol was supplemented (up to 5%) with other bio-based polyols to produce polyurethanes with improved properties [4], but fiber was not used in this project.
In another attempt Tran P, Graiver D, and Ramani N, synthesized composites from natural biofibers such as kenaf with chemically modified soybean oil without supplementing the soy matrix with other bio-based polyols. He prepared the composites with the combination of two soy-based polyols in presence of treated kenaf fibers with the help of HMD cross-linking amine catalyst to enhance cross-linking in the matrix. The mechanical properties of the composite have been enhanced and attributed to the use of HMD as the right cross-linker to improve fiber/matrix adhesion [5].

Four major companies are global players in natural oil polyols production. Cargill with headquarter in Minnesota manufactures BiOH Polyols from soybeans. Dow Chemical based in Michigan produces Renuva family of polyols, also from soybean oil. BASF in Michigan and Bayer in Pennsylvania both produce castor oil-based polyols.

Currently, petro-chemical polyols are partially blended with soy-based polyols to produce polyurethane foam for automotive, furniture and adhesives. Ford Motor Company has been a pioneer in researching bio-based foams for use in automobile body and interior parts. The soy-based foam is currently in foam seats of every 2014 Ford vehicles [6]. Researchers continue to produce foams with soy based blended polyols to characterize their mechanical properties to prove they are appropriate for other industrial applications [7].

Polyurethanes are unique polymer materials with variety of physical and chemical properties but they have also disadvantages, such as low thermal stability and mechanical strength. To overcome these disadvantages, a great deal of research has been devoted to incorporation of natural fibers and clay as reinforcement in recent years. For example, Silva et al used industrial residue of cellulose pulp fiber at low concentration as filler in foaming and reported decreasing thermal conductivity and cell size reduction in fiber foam system [8]. Luo X et al embedded
refined wood pulp as reinforcement in foaming using soy-based and petrochemical polyols. The study exhibited improvement in compressive strength but reduction in bulk density of the composite foam as compared to the pure foam [9]. Cao X et al incorporated clay in polyurethane foam and demonstrated that presence of clay increased the cell density and reduced the cell size and also some improvement in compressive strength as compared to no fiber foam [10]. Banik et al added cellulose fiber in soy-based polyurethane foam and observed enhancement in bulk density and urethanes formation [11]. Racz et al reinforced polyurethane foam with wood flour and showed that the strength and modulus of the composite foam improved with fiber content [12]. Yuan et al developed wood-polyurethane composite of up to 20php fiber and demonstrated that presence of fiber improved the compressive properties of the polyurethane foam but decreased its tensile properties. The thermal stability of the composite foam was also enhanced [13].

**Spray Foam Insulation**

Spray foam insulation originally was developed to be used in military airplanes in 1940s [14]. Then it was started to be used as insulation in residential buildings in 1970s. It was soon discovered that the isocyanate one of the main component of SPF was a toxic substance, causing health problems. The government authorities restricted the usage of SPF insulation in homes. Manufacturers of PU foams did an extensive research and modified isocyanate to a safer substance so that it could be used again. Once more its usage was permitted in homes around the year 2004, due to energy savings for home owners.

Spray foam insulation (SPF) is rigid foam used in building construction as an alternative to traditional fiberglass insulation. It is different compared to other types of rigid foams because its
foaming reactions are faster and it sets quicker. It is relatively a new technology gaining popularity for sealing the wall cavities providing effective thermal insulation.

As sustainability and green permeated almost every industry, people begin to like low-energy homes that are more comfortable and affordable to operate. The Equilibrium Housing Initiatives led by Canada Mortgage and Housing Corporation (CMHC) promoted such homes that reduces energy demand and utilizes renewable materials in housing [15]. Natural Sciences and Engineering Research Council of Canada–Industrial Research Chairs (NSERC-IRC) is providing leadership in improving performance standards in promoting and encouraging natural and sustainable products through funding such as this research project.

National Research Council of Canada – Institute for Research in Construction (NRC-IRC) in collaboration with SPF producers and contractors conducted a study to determine the energy rating of SPF insulated walls [16]. This would take into account the effect of air leakage and thermal transmission characteristics of SPF walls. The industry was promoting SPF as an effective air barrier system in addition to its thermal insulation characteristics. To address this issue NRC-IRC constructed walls with SPF and fiber glass batts and performed thermal resistance and air leakage standard tests according to ASTM C-518 and ASTM E-283 respectively. It was concluded that there was little or no air leakages flow for SPF walls whereas there was air leakage through fiber glass walls.

The U.S. Department of Agriculture is implementing a BioPreferred program to promote the increased purchase and use of biobased products [17]. It states that “The program spurs economic development -- creating new jobs and providing new markets for farm commodities. The increased development, purchase, and use of biobased products reduce our Nation's reliance
on petroleum, increase the use of renewable agriculture resources, and may contribute to reducing adverse environmental and health impacts”.

Although there were few studies in literature regarding the use of blended soy-based polyol and use of fiber as reinforcement in flexible and rigid foaming, the concept of developing biocomposite spray foam has not been studied to date and remain unexplored. The above research papers [8-13] demonstrated that there was improvement in foam properties when fiber was introduced. Therefore, the development of a novel method to produce fiber reinforced biocomposite spray foam insulation seemed to be promising. As natural fibers are rich in –OH groups and can potentially react with –NCO groups of isocyanate [18-21] it would be interesting to study such combination. We expect addition of fiber would increase cell density in composite foam and delay moisture permeability. Further, the interaction between polyurethane and fiber would improve interfacial adhesion and trap more carbon dioxide in composite foam which enhances R-value. Hence, this study would develop a novel process methodology to produce the biofoam insulation from soy-based polyol and incorporate natural fiber to investigate thermo-mechanical properties. It will also study the effect of natural fiber in soy-based water-blown biofoam insulation as well as its contribution to the structural integrity of the building against lateral forces.

1.3 Objectives and scope of the study

SPF is currently prepared by mixing isocyanate with petroleum based polyol using auxiliary blowing agents such as chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC). They are currently facing challenges to eliminate these harmful substances due to environmental issues and replace them with natural products in spray foaming.
The goal of this study was to prepare spray foam insulation from soy-based polyol using water as blowing agent and to introduce fiber in foaming process to improve its properties. Soybean oil is a natural product that can be converted into polyol through epoxidization process. Distilled water can act as blowing agent and react with isocyanate to produce carbon dioxide required to expand the foam during polymerization reaction replacing auxiliary blowing agents. Therefore, main objectives were:

- To better understand the fiber-polyurethane interactions and their effects on thermo-physical and morphological properties of spray foam insulation.
- To investigate the effect of chemical and fiber compositions on the foaming characteristics.
- To optimize the flow behavior of chemicals as a function of fiber content.
- To develop a prototype wood / cellulose fiber filled sustainable foam and validate their structural, thermal and moisture stability.
- To evaluate contribution of SPF wall insulation in structural integrity of a building against shear loads.

The expected outcome and benefits are:

- To achieve a balance between environment and building insulation quality.
- To engage in creating sustainable building structure.
- To encourage use of sustainable and green materials in SPF that reduces CO2 emission.
- To reduce home energy use while increasing safety, durability, and comfort in buildings.

Scanning electron microscopy (SEM) images of foam samples were studied to investigate fiber-matrix interfacial adhesion. Fourier transform infrared spectroscopy (FTIR) was utilized to identify the nature of functional groups present in foam material to investigate foam internal
structure and compatibility between fiber and resin. It may be noted that the scope of this study is not limited to open-cell SPF mainly used as wall insulation in residential and commercial buildings, but closed-cell foam has also been used in structural integrity experimentation for higher strength foaming.

This thesis is composed of seven chapters. First chapter includes objectives of this study, foam formulation and preparation including photographs of fiber and non-fiber foams prepared in the lab. It assesses full analysis of wood fiber used as reinforcement.

Chapter 2 deals with the determination of optimum amount of water to be used in foaming as blowing agent as well as the effects of wood fiber size and concentration on cell morphologies of the foam insulation with respect to non-fiber (neat) foam. Fiber was embedded in foaming at different aspect ratios in different stages of fiber concentration and their effects on cell size and density were investigated.

Chapter 3 is concerned with reinforcing effect of wood fiber on thermal stability and mechanical properties of the foam insulation at different fiber content and levels. Thermal degradation temperature, compressive strength and tensile strength of the composite foam system were compared with neat foam. The impact of water content which affected thermal stability was also considered here.

Chapters 4 and 5 choose a particular fiber size (400 micron) and the optimum amount of water (6.7php) as blowing agent to be used in core study. A comprehensive characterization and thermo-mechanical properties of the composite foam systems were investigated and compared with neat foam. Chapter 4 deals with the impacts of wood fiber as reinforcing agent in insulation
foam while chapter 5 considers the impacts of pure cellulose fiber as an alternative reinforcement for comparison.

Chapter 6 addresses the contribution of fiber and none fiber spray foams as wall insulations in overall structural integrity or shear resistance against wind and seismic loads applied to the buildings.

Finally, chapter 7 summarizes the key findings of this project together with major conclusions and recommendations for further research. Appendix 1 includes summary table of thermal degradation temperatures for composite and neat foam system while Appendix 2 provides statistical analysis details for density and compressive strength of foam systems.

1.4 Raw materials

Two major raw materials in foam process are polyol and isocyanate.

1.4.1 Soy-based polyol

Most commercial polyols used in rigid foams are polyether or polyester polyols derived from petro-chemicals. In recent years, price of petroleum polyols escalated due to increase in crude prices and created an opportunity for their substitution. The consumption of petro-chemical substances also releases more carbon dioxide into the atmosphere and contributes to the global warming. Hence, researchers are prompted to look for alternatives from renewable resources such as soy-based polyol prepared from soybean oil.

Soy bean oil can generate high -OH value polyol, with high activity secondary -OH groups. It contains saturated and unsaturated fatty acids in its chemical structure. Using chemicals (biophasic catalytic system with H$_2$O$_2$ for epoxidation and H$_2$SO$_4$ for hydroxylation), the unsaturated fatty acids (triglycerides) are modified to introduce hydroxyl functional groups
converting vegetable oil into polyol. Application of soy-based polyol depends on the oil source if highly unsaturated or saturated. This is just one example and there are other methods using other chemicals to synthesize biopolyol. Preparation of soy based polyol is a two-stage process - conversion of double bond to single bond through epoxidation followed by hydroxylation process to introduce -OH groups in its molecular structure (Figure 1).

Figure 1. Shows a typical chemical method to produce soy-based polyol [3].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyl Value</td>
<td>69 mg KOH/g</td>
</tr>
<tr>
<td>Functionality</td>
<td>Bi-functional</td>
</tr>
<tr>
<td>Viscosity @ 25°C</td>
<td>2040 cps</td>
</tr>
<tr>
<td>Acid Value</td>
<td>2.5 mg KOH/g</td>
</tr>
<tr>
<td>Moisture Content</td>
<td>0.04 %</td>
</tr>
<tr>
<td>Bio-renewable content</td>
<td>98 %</td>
</tr>
<tr>
<td>Appearance</td>
<td>Orange</td>
</tr>
</tbody>
</table>

(Source: Urethane Soy Systems)
1.4.2 Isocyanate

Isocyanate is the most important component in foaming. It is a highly reactive substance and can react with any compound containing a hydrogen atom attached to an electronegative atom. The reactivity of isocyanate depends on polyol functional group. The rate of reaction is 3 times faster if functional group (-OH) is primary rather than secondary position. Therefore, catalyst for gel reaction should be carefully chosen to balance the reaction.

Two major isocyanate used in PU foam marketing are Toluene diisocyanate (TDI) and Diphenylmethane diisocyanate (MDI) with market share of 30% and 60% respectively [2]. They are aromatic compounds with chemical structures shown below. Polymeric MDI is more reactive than MDI having higher average functional groups. It not only reacts with hydroxyl groups, but also with other hydrogen containing compounds such as water, and amines. When PMDI reacts with polyol functional group (-OH) it increases cross-linking density, producing a bigger and stronger three-dimensional foam network.

Rubinate M or polymeric diphenylmethane diisocyanate (PMDI) is an aromatic compound, brownish liquid with slight aromatic odor. It is manufactured for using as ‘A’ component material in spray polyurethane foam insulation. It shows excellent compatibility with Polyol to produce light color foam. In polyurethane foam the chemical reaction is considered completed when all the initially free (–N=C=O) groups are bound within the polymer network and are considered to be non-toxic.
Chemical Structure of Diisocyanate - Aromatic

<table>
<thead>
<tr>
<th>2,4-TDI (C₉H₈O₂N₂)</th>
<th>4,4-MDI (C₁₅H₁₀O₂N₂)</th>
<th>Polymeric - MDI</th>
</tr>
</thead>
</table>

Characteristics of Polymeric Isocyanate (Rubinate M)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functionality</td>
<td>2.7</td>
</tr>
<tr>
<td>NCO content, %</td>
<td>31.5</td>
</tr>
<tr>
<td>Isocyanate Equivalent Weight</td>
<td>133</td>
</tr>
<tr>
<td>Viscosity at 25°C, cps</td>
<td>190</td>
</tr>
<tr>
<td>Specific Gravity at 50°C</td>
<td>1.23</td>
</tr>
</tbody>
</table>

(Source: Huntsman Corporation)

**Isocyanate index**

The actual amount of Isocyanate to be used during foaming process is calculated by isocyanate index formula (below) to ensure the complete reaction of polyol and water with isocyanate.

$$Isocyanate\ Index = \frac{(1/ E_{NCO}) \times W_{NCO}}{(Hydroxynumber_{polyol} / 56100) \times W_{polyol} + (2/18) \times W_{water}} \times 100$$

$E_{NCO} = $ Isocyanate equivalent weight

$W_{NCO} = $ The amount of isocyanate to be used

$W_{polyol} = $ The amount of polyol to be used

$W_{water} = $ The amount of water to be used
1.4.3 Blowing agent

The blowing agent produces gas bobbles. The bobbles get trapped in the polymer causing the polymer to expand many times of its original volume to form rigid foam insulation. This type of foam would have a good thermal insulation due to gas trapped inside cell bobbles. Auxiliary blowing agents such as Chlorofluorocarbons (CFCs) and other propellants are widely used as blowing agent in commercial insulation foam. They are high volatile liquids producing large amount of gas to generate bobbles during polymerization to expand the foam before solidification. These auxiliary agents have been phased out due to ozone depletion. An alternative candidate to replace auxiliary agents is distilled water in which it reacts with isocyanate and generates carbon dioxide to expand the foam during reaction. Distilled water is used as blowing agent in this study to make CFC free foam or water blown foam.

1.5 Polyurethane chemistry

Polyurethane foam process contains two main reactions- the polymerization reaction and the blowing reaction. A balance between these two reactions is essential for a stable structure with good physical properties. Catalysts I & II (Table 2) control these two reactions and prevent the foam from collapsing. If carbon dioxide evolution is rapid with respect to gel reaction, the foam will collapse and if the generation of carbon dioxide is not enough, foam-rise will be restricted.

The main component of foaming process is isocyanate with highly reactive group (-N=C=O) containing two double bonds. It reacts with electron donor and electron acceptor functional groups. Isocyanate undergoes two types of reactions known as - primary and secondary reactions.
1.5.1 Primary reactions

Reaction between the isocyanate and the polyol is usually referred as polymerization reaction, leading to the formation of a polymer with high molecular weight. In this reaction the isocyanate (-NCO) group reacts with hydroxyl (-OH) group of polyol to form urethane (-NH-CO-O-) linkage. It is an exothermic reaction. Simultaneously, another major reaction occurs between isocyanate and water to generate carbon dioxide gas to promote foam expansion. This reaction is referred to as blowing reaction. The blowing reaction itself contains two reactions. First, isocyanate group (-NCO) reacts with water to generate Carbamic acid which is unstable and immediately decomposes, forming an amine and carbon dioxide. The amine (R-NH₂) reacts again with another isocyanate group to produce urea linkage (Scheme I).

\[
\begin{align*}
R–NCO + R’–OH & \quad \longrightarrow \quad R–NH–CO–O–R’ \quad \text{(Urethane)} \\
R–NCO + H₂O & \quad \longrightarrow \quad R–NH–CO–OH \quad \text{(Carbamic Acid)} \\
R–NH–CO–OH & \quad \longrightarrow \quad R–NH₂ + CO₂ \\
R–NCO + R–NH₂ & \quad \longrightarrow \quad R–NH–CO–NH–R \quad \text{(Urea)}
\end{align*}
\]

Scheme I

1.5.2 Secondary reactions

Isocyanate reactive groups further react with urethane and urea groups to form allophanates and substituted biurets respectively. The secondary reactions of isocyanate leads to cross-linking, and the resulting polyurethane becomes more rigid. Thus temperature control during polyurethane synthesis is critical to control secondary reactions and thereby cross-linking. Allophanate linkages may or may not be reversible, depending on many factors such as the nature of catalyst or NCO/OH ratio. Secondary reactions were schematically shown below (Scheme II)

\[
\]
1.5.3 Hard and soft segments

The polyurethane structure is diverse and complex containing hard and soft segments and they determine the rigidity and elastomeric properties of the foam. In early stages of foaming process, the generated urea linkages from blowing reaction has tendency to initiate phase separation (hard segment) within the polymer due to its ability to form strong hydrogen bonds between themselves. As soon as the polyol-isocyanate reaction generates enough urethane linkages, the soft phase formation starts and urethane links bond the soft and hard segments together.

The hard segments are mainly crystalline, having urethane groups that are cross-linked through hydrogen bonding with urea and other urethane linkages through C=O and N-H active groups. The hydrogen bond energy or hydrogen bond strength between these groups is much higher than those in soft segment groups. The soft segments are the fatty acid linear sections of polyol structure stretched in coil shape within the polymer profile, and provide elastomeric quality within the matrix network. While hard segments are highly crystalline, the soft segments are comparatively mobile. The presence of these two phases in the same molecule can alter the foam properties.

1.6 Experimental approach

1.6.1 Fiber selection and analysis

Polyurethane foams are unique materials with wide range of physical and chemical properties. They have also disadvantages such as low mechanical strength and thermal stability. To
overcome these disadvantages, a great deal of effort has been devoted to incorporate fiber in foaming to enhance these properties. Fibers such as wood and cellulose fibers are plenty in nature and cost effective.

Just like polyol, cellulose natural fiber contains hydroxyl (-OH) group and isocyanate has a natural tendency to react with this group. Each repeating unit of cellulose has three hydroxyl groups (C6, C3, and C4) available for reactions. The compatibility of matrix with cellulose fiber depends on the involvement of these free -OH groups.

Cellulose fiber monomer and structure

Cellulose fiber – Macro fiber to micro fibril
The original white birch medium density wood fiber (MDF) was supplied by FPInnovations with the following fiber composition to be used in the study.

<table>
<thead>
<tr>
<th>Fiber Type</th>
<th>Mean Length (µm)</th>
<th>Aspect Ratio (L/D)</th>
<th>Cellulose Content (%)</th>
<th>Hemi-cellulose Content (%)</th>
<th>Lignin Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>White Birch MDF-8bar</td>
<td>1660</td>
<td>28</td>
<td>50</td>
<td>24</td>
<td>16</td>
</tr>
</tbody>
</table>

(Source: FPInnovations Data Sheet)

Although the long fiber provides better enforcement quality, high viscosity and dispersion became a problem even at lower fiber content. To eliminate these barriers, the original fiber had to be grinded to an optimum size around 400 µm to be able to incorporate it in foaming with lesser difficulties and still achieve a moderate reinforcement. The analysis of fiber length provided the data for average length of fiber within the reinforcing material.

_Fiber length analysis using SEM_

Wood fibers were analyzed in terms of diameter and length with Table top SEM (Hitachi TM-1000). A small amount of short wood fiber (400 µm) which was grinded previously with the mesh 40 was placed under electron microscopy to measure diameter and length of approximately 100 fibrils to draw fiber distribution diagram. Figure 2a and 2b show the distribution in terms of length and diameter. It is observed that fibrils diameter ranges between 5 to 55 µm with an
average of 30 µm, while fiber length range falls between 100 to 400 µm with an average around 200 µm. Therefore aspect ratio of the wood fiber was estimated to be around 6.5.

Table 1. Fiber length and aspect ratio analysis

<table>
<thead>
<tr>
<th>Method</th>
<th>Fiber Type</th>
<th>Avg. Length (µm)</th>
<th>Avg. Diameter (µm)</th>
<th>Aspect Ratio (L/D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FQ Analyzer</td>
<td>Wood fiber</td>
<td>270 (100-800)</td>
<td>60</td>
<td>4.5</td>
</tr>
<tr>
<td>SEM</td>
<td>Wood fiber</td>
<td>200 (100-400)</td>
<td>30 (5-55)</td>
<td>6.5</td>
</tr>
<tr>
<td>FQ Analyzer</td>
<td>Cellulose fiber</td>
<td>260 (100-800)</td>
<td>13.5**</td>
<td>20</td>
</tr>
<tr>
<td>Sigma Data Sheet</td>
<td>Cellulose fiber</td>
<td>200 (50-350)</td>
<td>13.5</td>
<td>15</td>
</tr>
</tbody>
</table>

*FPInnovations Data Sheet  **Sigma data sheet

Figure 2. Wood fiber length and diameter distribution histogram.

**Fiber quality analyzer (FQA)**

Fiber quality analyzer test would analyze fiber length of a particular fiber type. It has an integrated sensor unit capable of taking optical measurements. A small amount of wood fibers stirred well with 500 ml of water in a beaker and placed under the stirring device. It kept the fibers suspended in water, uptake them into the machine for analysis using the imaging sensor. In this technique, about 5000 short fibers were counted to estimate the average fiber length. Table 1
shows average fiber length and aspect ratio of each fiber class. Fiber length was observed to be within the range of 100-800 µm for both fibers.

### 1.6.2 Formulation and study design

The first set of experiments was carried out to produce neat foam insulation. Many samples have been prepared trying different catalysts and surfactants to arrive at an optimum formulation in which it could be used as base for neat as well as composite foam system. Observations indicated that catalysts K-15 makes foam more yellowish and Polycat-9 gives product a strong odor. On the other hand, 33-LV in combination with DMEA leads to a better performance in terms of balancing -NCO reactions with Polyol and water. Catalyst 33LV is responsible for the balancing reaction between Polyol and NCO. DMEA speeds up the reaction between NCO and water. The optimized ratio of DMEA to 33-LV was found to be 2/3. The amount of water had significant influence on the blowing behavior and formation of cell sizes. Table 2 shows the formulation for water-blown open-cell spray foam insulation.

<table>
<thead>
<tr>
<th>Components</th>
<th>Commercial Name</th>
<th>Php(^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyol</td>
<td>Soyol 2101</td>
<td>100</td>
</tr>
<tr>
<td>Catalyst I</td>
<td>DMEA</td>
<td>1.33</td>
</tr>
<tr>
<td>Catalyst II</td>
<td>33 LV</td>
<td>2</td>
</tr>
<tr>
<td>Surfactant</td>
<td>DC 5179</td>
<td>0.67</td>
</tr>
<tr>
<td>Blowing agent</td>
<td>H(_2)O</td>
<td>6.7</td>
</tr>
<tr>
<td>Isocyanate Index</td>
<td>Robinate M</td>
<td>120</td>
</tr>
</tbody>
</table>

\(^{1}\) Parts per hundred grams of polyol

However, the formulation has been modified in structural integrity experiments (chapter 6) to reflect stronger foam network (closed-cell foam) to better withstand the applied shear forces. The
polyol used in such formulation had higher hydroxyl groups to promote polyurethane solid structure with more closed-cells containing diffused gas trapped in.

**Neat and composite foam system**

At first neat polyurethane foam insulation was prepared using above formulation. Catalysts, surfactant, and water were mixed with polyol for 5 minutes and then isocyanate was added and stirred again for 30 seconds. The mixture was transferred into a mold and rose under free-rise method. The composite foam system was prepared using the same method as neat foam but wood or cellulose fiber was initially pre-mixed with polyol at 13php, 26php or 40php as per requirement for 20 minutes. The following scenarios were considered for analysis.

- Neat foam (no fiber)
- Fiber foam with 13php 400 µm Wood fiber
- Fiber foam with 26php 400 µm Wood fiber
- Fiber foam with 40php 400 µm Wood fiber
- Fiber foam with 13php 400 µm Cellulose fiber
- Fiber foam with 26php 400 µm Cellulose fiber
- Fiber foam with 40php 400 µm Cellulose fiber
Figure 3. Neat and composite foam samples
References


CHAPTER 2.0

Fiber Reinforced Soy-based Polyurethane Spray Foam Insulation.

Part 1: Cell Morphologies
Abstract

Environmentally friendly polyurethane (PU) spray foam insulation was prepared by substituting petrochemical polyol with soy-based polyol. The effects of adding wood fiber and water on the cell morphologies were studied. Cell size increased with the presence of wood fiber, but decreased with an increase of water (H2O). Still, shorter fiber decreased the foam density but increased the cell size and open cell content.

2.1 Introduction

Most sprayed polyurethane (PU) foams are used in the construction/building area (Bomberg and Kumaran 1999). PU spray foam insulation prevents air leakage and retains effective energy (Moore and Ference 1998). Compared to traditional insulation, sprayed-in-place PU foam quickly expands to many times its original liquid size in seconds to create an airtight environment by sealing and filling each cavity, crevasse, void, and cap, which overcomes some of the causes of energy loss in a building. This also improves indoor air quality by blocking harmful outside irritants and eliminates the particles that are emitted and developed from fibrous and dusty insulations. This sealed envelope can also improve sound abatement because airborne noise can no longer seep through the walls (Falke et al. 2001). In addition, PU spray foam has high R-value compared to common insulation materials (Anon, Honeywell technical document), which will lower heating cost in cooler regions of Canada (Anon, Dow technical documents). Still, PU insulation adheres well to almost any material, especially wood and steel studs (Lohman 2005).

Biodegradable foams lower society’s dependence on fossil fuels and have drawn attention in construction building industry to develop more environmentally friendly practices (Pollack 2004). Biofoam is a new, entirely sustainable and biologically degradable polymer made from
renewable bio-sources (Meyer 2011). Bio-based polyol has been prepared from biobased epoxidized vegetable oils (Tan and Chow 2010), that consumes less energy associated with the energy required for the fabrication process (Anon, Omni Tech International 2010) and reduces the carbon footprint by absorbing greenhouse gas during the plant lifecycle (Sleeckx 2006). The large output of soybean oil in North America motivates the use of soy-based polyol (Soyol) (USDA 2011; Allen 2009).

Soy-based PU spray foam is popular due to its good quality, superior adhesion, and fast dry-time. Soyol is derived from soybean oils which come from soybeans. The soy has achieved a higher yield due to advances in its biotechnology. According to the U.S Department of Agriculture (USDA) figures for 2010, 93% of all of soybeans produced in USA are genetically engineered for herbicide tolerance (USDA 2010), and 70% of the global productions are biotechnical soybeans (James 2008). The vast majority of genetically modified soybean oils are used for affordable soyol production by adding hydroxyl groups at the unsaturated sites (Monteavaro et al. 2005; Petrović et al. 2005). Since its invention, Soyol has been used in various PU foam applications due to its renewability (Sherman 2007). Natural fibers, which also are rich in hydroxyl groups, can be introduced for reinforcement (Silva et al. 2010; Gu et al. 2010; Bledzki et al. 2001) to give a better biodegradation (Silva et al. 2010). This study would investigate the cell morphologies of PU spray foam in presence of wood fiber.

2.2 Experimental

2.2.1 Materials and methods

*Soy-based Polyol (Soyol)*

Soyol, which is rich in triglycerides structures, was prepared from soybean oil by adding hydroxyls at the unsaturated sites. Low odor Soyol® 2102 was donated by Urethane Soy Systems
(Volga, South Dakota, USA). It is the 5th generation of polyol made using soybean oil. Its bio-renewable content is as high as 98%, as reported by ASTM D 6866. Its hydroxyl number was 63 mg KOH/g according to ASTM D4274-99 with the viscosity of 2181 cps at 25°C.

*Isocyanate*

Polymeric diphenylmethane diisocyanate (PMDI) having 31.5% NCO content was donated by Huntsman and used to produce sprayed foams. Its functionality was 2.7, as provided by the supplier.

*Wood pulp fiber*

Steam explosion pulp of trembling aspen (high energy, 8 bar pressure) was received from Forintek Canada Corp (Point-Claire, Quebec, Canada). This air-dried industrial aspen Chemical Thermal Mechanical Pulp (CTMP) was grinded by Thomas Wiley Laboratory Mill, Model 4, and screened into 20-35, 35-70, 70-100, 100-140, 140-200, and 200-325 mesh size ranges, respectively. Six selected fibers were introduced into PU spray foams as natural filler. This unbleached CTMP fiber imparts PU biofoam a dark-brown color.

*Catalysts*

Diamine was used as a foaming catalyst, which was received from Sigma Chemical Company. Tertiary amine donated by Air Products and Chemicals, Inc. (Allentown, Pennsylvania, USA) was used as a gelling catalyst.

*Surfactant*

Polysiloxane family based surfactant was used to achieve superior cell structures; these were donated by Air Products and Chemicals, Inc.

*Blowing agent*

Distilled water was used as a blowing agent to generate foams; this was prepared in our lab.
2.2.2 Foam preparation and evaluation

PU spray foams were prepared by a free-rise method with the formulations shown in Table 1. The amount of pulp fiber used was in terms of 100 parts of soyol. The soyol was manually mixed with the additives (catalysts, surfactant and H\textsubscript{2}O) for 5 minutes under ambient temperature, and then PMDI was added and mixed for another 20 seconds. The resultant mixture was quickly transferred into a mold for foaming to get neat PU spray foams. For the reinforced PU spray foams, wood fiber was pre-mixed with soyol for 20 minutes to wet completely. The process was the same as the preparation of neat foam. Finally, all the PU spray foams were kept at the room temperature and well post-cured overnight.

Obviously, the amount of H\textsubscript{2}O is expected to have significant influences on the cell performances. In this study, the amount of H\textsubscript{2}O was set in the range of 4.7 to 8.0php (parts per 100 parts) of Soyol. When a lower amount (less than 4.7php) of H\textsubscript{2}O was used, neat PU foams were shrinkable. Oppositely, neat PU foams would collapse when the amount of H\textsubscript{2}O was over 8.0php. From Fig. 1a-c, more H\textsubscript{2}O helped create a smooth plump appearance. With the addition of wood fiber, the foam shrank, as it can be seen by comparing Fig. 1b (no fiber) with Fig. 1d (20php fiber) with same 4.7php H\textsubscript{2}O content. Therefore, the amount of H\textsubscript{2}O was adjusted to 6.7php in order to get acceptable fiber reinforced foams as shown in Fig. 1e. Meanwhile, the foaming and gelling time was extended beyond 20 seconds when wood fiber was introduced according to our observations. In addition, longer curing time was required as more fiber was added. It demonstrated that wood fiber, in particular for CTMP fiber, had a delaying effect on urethane reaction.
Table 1. Formulation for PU spray foam insulation (Open-cell)

<table>
<thead>
<tr>
<th>Materials</th>
<th>Parts by weight, php</th>
<th>Neat PU spray foam</th>
<th>PU-Fiber spray foam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soyol</td>
<td>Soyol® 2102</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Diamine</td>
<td>1.33</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td>Tertiary amine</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Surfactant</td>
<td>Polysiloxane</td>
<td>0.67</td>
<td>0.67</td>
</tr>
<tr>
<td>Blowing agent</td>
<td>H$_2$O</td>
<td>4.7; 5.3; 6.7; 8.0</td>
<td>6.7</td>
</tr>
<tr>
<td>PMDI</td>
<td>NCO index</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Wood fiber</td>
<td>35-70 mesh</td>
<td>---</td>
<td>10; 20†; 30; 40; 50; 60</td>
</tr>
</tbody>
</table>

† Six select fibers were formulated

2.2.3 Fiber quality analysis (FQA)

The length of fiber particles and their distribution were measured by Fiber Quality Analyzer (Optest Equipment Inc. Hawkesbury, Ontario, Canada). The fiber count was over 5000.

2.2.4 Morphologies of PU spray foam

All the foams were conditioned at 23°C and 45% relative humidity, and then the foam slabs were extracted by cutting with a saw, followed by polishing with a belt sander (Model 31-710,
Rockwell International, Pittsburgh, USA). The size grit was 120. The length, width, and thickness were measured after polishing. The thickness is along the foam rise direction.

**Open cell content measurement and foam density**

10 small specimens (3cm×3cm×3cm) were used to get the foam densities according to ASTM D1622-09, and then the open cell percentage was determined by a Quantachrome Instruments Ultrapychometer 1000 (Boynton Beach, FL) according to ASTM D6226-05 under 23°C and 45% relative humidity.

**Scanning electron microscope (SEM) investigation**

Sample stub with thin foam slab was surface metalized by a sputter coating (BOT 341F) with evaporated gold (in 4nm thickness), and then was carried out by SEM (Hitachi S-2500, Hitachi High Technologies Inc., Tokyo, Japan) at an acceleration voltage of 15kV.

The cell morphologies were statistically analyzed by Image J including feret diameter and distribution.

### 2.3 Results and discussion

#### 2.3.1 Fiber quality analysis (FQA)

It has been reported that natural fiber can influence the performance of PU microfoams (Bledzki et al. 2001). However, PU spray foam is different from the reported PU foams due to its quick expansion and fast dry-time. In this study the effects of fiber concentration and fiber size in particular for fiber length on the sprayed foams were investigated. The length distributions of 6 classified fibers are shown in Fig. 2. The six select fibers had roughly the same diameter but distinguished length distributions and exhibited different average fiber sizes. Fibers in high mesh had short length and narrow distribution, such that they were more like particles rather than fibers. All these selected fibers were introduced into sprayed PU foam reaction system after pre-
wetting by soyol according to their fabrication process. The resultant foams were examined to reveal the changes in cell morphological structures and performances.

2.3.2 Morphological structures of PU spray foams

Effect of H$_2$O content on cell structures

In general the amount of H$_2$O dominated the cell structures of water-blown PU foams because the CO$_2$ gas was released from the reaction between water and –NCO groups of PMDI. But the influence of gas expansion should be neglected if the foam comprised mostly open cells and avoided “exotherm” problems, such as foam core-burning. In addition, the effect of the moisture of polyol could also be neglected due to its very low amount reported by its supplier (max 0.01%).

The effects of H$_2$O on foam density and cell structures are demonstrated in Fig. 3. In this study, the densities for the neat PU foams were varied depending on the amount of water as blowing agent. Figure 3 shows the variation in density and open cell content of the neat PU foams with 4.7-8.0php H$_2$O, which was based on the weight of Soyol. With the increase of H$_2$O from 4.7 to 8.0php, the densities of the neat PU foams decreased from 40.9 to 24.5 kg/m$^3$. This finding corresponded to the results of H$_2$O-blown foams based on polyester polyol (Thirumal et al. 2008; Li et al. 2006). However, there was some deviation in cell structures as the open cell content decreased from 90.6% of 4.7php H$_2$O to 87.3% of 6.7php H$_2$O. After that the open cell content rebounded to 90.2% again. This change was caused by the un-uniform distribution of H$_2$O molecules through the whole foam. In any case, the neat PU spray foam can achieve maximum closed cells in the presence of 6.7php H$_2$O.

Figure 4 shows the cell size distributions of the neat PU foams with different H$_2$O concentration. The distribution of cell size was narrowed on the downward size as more H$_2$O was introduced.
The decreased mean values of cells sizes have a linear relationship with an increase in H$_2$O amount, as computed in Fig. 5. The cell feret diameter decreased from 401 µm to 287 µm when the amount of H$_2$O increased from 4.7php to 8.0php. The decrease of cell size in biofoam with an increase of H$_2$O content is opposite to the result of petrochemical PU foam reported by Li et al. (2006). The relationship of cell size to H$_2$O content can be observed from the SEM images in Fig. 6. The cells became smaller and non-uniform as more H$_2$O was introduced. This finding was in accordance with the decrease of cell irregularity as shown in Fig. 5.

![Fig. 2. Average fiber length and distribution of selected fibers](image-url)
Fig. 3. Effect of H$_2$O on foam density and open cell content

Fig. 4. Effect of H$_2$O on cell size distribution

Fig. 5. Effect of H$_2$O on cell structure
Effect of wood fiber on cell structures

Due to the fact that polyols contained a high content of hydroxyl groups and natural fibers were well wetted by polyols, the foam matrix was compatible with wood fiber, as shown in Figs. 7-1a and 8b. When 20php fibers were introduced into the foams, most fibers were framed in cell walls, as observed in Fig. 8 (a, c and d) due to the good compatibility between the fibers and polyols. Natural fibers were compatible with isocyanate. They may react to form units of urethane; the existence of secondary interactions of the fiber with polymer polyurethane may also be possible. Therefore, the surface of the fibers was well covered with the polymeric matrix. Only fewer long fibers were isolated and located in the pores, as shown in Fig. 7. Wood fiber had the most significant impact on the cell structures, typically to cell supports and cell windows. In addition, woody color of pulp fibers was imparted to the fiber reinforced PU spray foams with
brownish-yellow color. This agglomeration of pulp fibers was clearly seen at the foam skin, as shown in Fig. 1e.

PU has a good adhesion to wood (Wake 1978; Phanopoulos et al. 1999; Somani et al. 2003; Frihart 2005), especially at high hydroxyl content (Desai et al. 2003). Naturally, the fiber reinforced PU spray foam is also expected to have a good compatibility between the introduced fibers and the foam matrix to improve house insulation (Lohman 2005).

Effect of fiber concentration on cell structures

The overall density of the foams increased steadily following an increase of wood fiber, as indicated in Fig. 10. The density of the fiber-reinforced foam achieved an increase of 3.8 times from 28kg/m$^3$ of neat PU spray foam up to 136kg/m$^3$ as 60php fiber incorporated. A similar result was also obtained in polyester polyol foam, as reported by Silva et al. (2010). Incorporating the right amount of fiber, such as 10-20php, the foam shrinkage can be prevented due to the support of stiffer fiber. Even though wood fiber was well wetted, some fiber destroyed cell structures high levels of fiber, as shown in Fig. 9.

![Fig. 7. Long fiber isolation in the cells](image)
From our observation, a typical effect of addition of fiber into the foam mixture was increase in its viscosity. Foaming delay, induced by wood fiber, was also observed, halting the foam expansion and increasing the foam density (Silva et al. 2010). When more fiber was introduced, a much greater degree of time-delay-induced effects caused high foam density. This increase in density can be observed in Fig. 10. In addition to foam density, small amounts of fiber increased the open cell content from 87.3% of neat PU spray foam up to 91.3% for foam with 10php fiber that was attributed to the high perforation behavior of wood fiber (Fig. 9a). However, the open-cell content decreased to 85.5% when 60php fiber was introduced (see Fig. 10) because some cell walls were overlapped into microvoids in a delayed foaming process (see Fig. 11c-f).
Fig. 9. Fiber existence in PU spray foam with high fiber loading

Fig. 10. Effect of fiber concentration on foam density and open cell content
The foam quality was dependent on the amount of fibers present because wood fiber can be framed into the cell structures, as described earlier. With more fibers employed, more cells became irregular and defective (Fig. 11) compared to the cells without fiber present (Fig. 6) (Silva et al. 2010). Stiff fiber also perforated the cell walls, which made it difficult to distinguish cells. It was hard to find an intact cell in the foam block in the presence of 60php fiber, as shown in Fig. 11f. In addition, more fiber concentration had increased the cell size (see Fig. 12). The distribution of cells also became inhomogeneous, which is shown in Fig. 13. Therefore, the increase in fiber content led to large irregular cells and a decrease of cell regularity (see Fig. 12) due to the gas releasing along the fiber axis.

**Fig. 11.** SEM images of the fiber reinforced PU spray foams in different fiber concentration (50×)
The contribution of cell size in the direction of foam rise increased obviously and more cells were broken when more fibers were incorporated. With the increase of fiber concentration, the cell size increased from 314µm of neat PU foam to 655µm of 50php fiber reinforced foam as shown in Fig. 12. This finding is contradictory to the finding in polyester polyol foams (Silva et al. 2010) because of different foam matrix, foaming technology and the lack of auxiliary blowing agent in our case. This increase probably came from the cell breakage, which was caused by the continuous connected fibers, especially for high fiber loaded foam.

**Fig. 12.** Effect of fiber concentration on cell structure

**Fig. 13.** Effect of fiber concentration on cell size distribution
Depth-of-field SEM images of the neat foam matrix (Fig. 14) clearly indicated polyhedral structures, which exhibited polygonal cell shapes (Bandyopadhyay-Ghosh et al. 2010) and three-dimensional cell wall structures (Fig. 14a) because of triglyceride molecule structure (Petrović 2008). Each polygonal cell-face was covered by a thin membranous window. The films are considerably thinner than the struts, as shown in Fig. 8a. In addition, the cell structure altered complex three-dimensional structures when fiber was introduced (Fig. 14b). Figure 14b shows a cross-section of broken struts, which were always formed at the junction of three windows (Dawson and Shortall 1982). The cross-sectional profile for the struts were seen triangular and described as a hypocycloid of three cusps (Jones and Fesman 1965). However, the nodes were always formed by four struts from their SEM images. The three struts seen at each node in Fig. 14 were accompanied by a strut out of the plane of the micrograph.

![Fig. 14. Three-dimensional cell structures](image)

a- neat PU spray foam; b- 20php fiber reinforced PU spray foam

The fiber reinforced PU foams had more broken windows due to the stiffness of wood fiber from the observations of Figs. 6, 11, and 14. Furthermore, three-dimensional structures contributed the foams with good dimensional stability. In our case of predominantly open-cell PU foams (over
85%), the open cells enabled the foam to breathe, ensuring cell gas equilibration to keep dimensional stability (Brown et al. 2010; Tylenda 1988).

Effect of fiber size on cell structures

The use of screened fibers as continuous threads in different oriented arrangements provided foams with different final properties. With the decrease of fiber size, the foam density reduced gradually from 32.7kg/m$^3$ for 20-35 mesh fiber-reinforced foam down to 27.4kg/m$^3$ for those with use of 200-325 mesh fiber, as shown in Fig. 15. This could be caused by the existence of much more smaller but numerous fiber particles. Unlike cell density, the open-cell content increased from 86% to 92% following the fiber size decreasing from 1.04 mm (20-35 mesh) to 0.175 mm (200-325 mesh). The small fibers can serve to increase cell amounts to large quantities by an enhanced heterogeneous nucleation (Ramesh et al. 1994; Rodrigue et al. 2001), which causes cell-cell borders overlaps, leading to a minor increase of open cell content.

The experimental measured cell size distributions for each sample were fitted in Fig. 16. With decreasing size of the fiber, the average cell size distribution increased. This deviation was exhibited clearly for the foam in a presence of 0.175 mm (200-325 mesh) fiber. Alternatively, the average cell diameter increased with decreasing fiber length, which was observed from Fig. 17. However, the effect of fiber size was not clear on the cell regularity.

Small fiber particles can accelerate the amount of foam cells as a nucleation agent. The thickness of cell wall was expected to be thin following the decrease of the foam density. Therefore, several crowded thin cells must crowded together to build large microcavities, as shown in Fig. 18. Shorter fibers contributed to a larger average cell size, which was computed in Fig. 17. The increase of cell diameter was hypothesized as coming from these overlaps. Unlike the fiber
content, the fiber size has less impact on the cell regularity. These findings indicated that the cell regularity mostly depended on the amount of fibers, not the fiber length.

Fig. 15. Effect of fiber size on foam density and open cell content

Fig. 16. Effect of fiber size on cell size distribution

Fig. 17. Effect of fiber size on cell structure
2.4 Conclusions

PU spray foams with varying density using water as a blowing agent were prepared via a free-rise method. The amount of water affected the cell structures by increasing the cell size. It was possible to prepare sprayed PU biofoams with wood fiber using a soy-based polyol. SEM images revealed that wood fiber was compatible with the foam matrix at interfaces due to their chemical reactions. The amount of fiber had significant effects on the cell structures, in particular the increase of cell size and of foam density. As fiber content was elevated the bulk density of the composite foam increased. In terms of fiber size, long fiber composite foam had slightly higher bulk density than that of short fiber foam. It is possible that the small fiber particles acted as nucleating agent producing thinner cell walls within the foam structure reducing the density. Presence of fiber had minor impact on Open-cell content. Open-cell contents of fiber and non-
fiber foams were observed to be in the range of 85% to 90% and remained at that level regardless of fiber size and concentration. In general, long fiber showed better enhancement, which was related to its high aspect ratio, contributing to complex structures that can act as a chain extender. Short fiber showed low aspect ratio.
References


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CHAPTER 3.0

Fiber Reinforced Soy-based Polyurethane Spray Foam Insulation.

Part 2: Thermal and Mechanical Properties.
Abstract

Biobased polyurethane (PU) spray foam insulation was prepared with soy polyol. The effects of adding wood fiber and water on the thermal and mechanical properties of the insulations were studied. The decomposition temperature ($T_d$) of the foams increased with fiber reinforcement due to a higher degree of crosslinking. Alternatively, different fiber length contributed to different crosslinking. The neat foams, which didn’t contain wood fibers, had exceptional thermal stability with the increase of the amount of $H_2O$ by forming more stable polyurea adducts. In addition, PU spray foam blown with a larger content of $H_2O$ had higher compressive strength by forming a stiffer phase. The spray foam reinforced with fiber also had superior compressive strength due to the fiber framing into the foam struts. The effect of the fiber length on the compressive strength was evaluated. The degree of complex networks was influenced by the fiber length. However, the tensile strength was weakened with the addition of wood fiber.

3.1 Introduction

Bio-based foams reduce risk from unpredictable and increasable prices of fossil fuel; such materials have moved into the mainstream for the construction building industry (Pollack 2004). Sprayed PU foam is mostly used in construction (Bomberg and Kumaran 1999) due to its effective energy saving (Moore and Ference 1998) and improved sound abatement (Falke et al. 2001). New sustainable bio-based PU spray foams are made from renewable bio-sources (Meyer 2011), thus consuming less energy and reducing carbon footprints.

Soy-based PU spray foam is being driven by large soybean output in North America (USDA 2011). Meanwhile, the agricultural industry will thrive by the growing demand for soy.
Furthermore, soy-based foam could achieve higher thermal and dimensional stability than petroleum-based foams due to their triglyceride structures (Javni et al. 2004).

Though PU foams based on vegetable oils have been reported (Banik and Sain 2008; Petrović 2008), there are no records for PU spray foams, especially for PU spray foams reinforced with wood fiber. Due to wood fiber being rich in –OH groups for potential reaction to –NCO groups of isocyanate, it would be wise to study the thermal and mechanical properties of PU spray foam in presence of wood fiber, in addition to the cell morphologies considered in Part 1 (Khazabi et all. 2011).

3.2 Experimental

3.2.1 Materials and methods

Soy-based Polyol (Soyol)
Soyol was prepared from soybean oil by adding hydroxyls at the unsaturated sites of its abundant triglycerides structures. Low odor Soyol® 2102 was donated by Urethane Soy Systems (Volga, South Dakota, USA). It is the 5th generation of polyol made using soybean oil. Its bio-renewable content is as high as 98%, as reported by ASTM D 6866. Its hydroxyl number was 63 mg KOH/g according to ASTM D4274-99 with the viscosity of 2181 cps at 25º C. Its moisture is less than 0.01% according to the data by the supplier.

Isocyanate
Polymeric diphenylmethane diisocyanate (PMDI) having 31.5% NCO content was donated by Huntsman and used to produce sprayed foams. Its functionality was 2.7, as provided by the supplier.

Wood pulp fiber
Steam explosion pulp of trembling aspen (high energy, 8 bar pressure) was received from Forintek Canada Corp (Point-Claire, Quebec, Canada). This air-dried industrial aspen Chemical Thermal Mechanical Pulp (CTMP) was cut and screened into 20-35, 35-70, 70-100, 100-140, 140-200, and 200-325 mesh sizes, respectively. Six select fibers were introduced into PU spray foams as natural filler. This unbleached CTMP fiber imparts a dark-brown color to the PU biofoam.

Catalysts
Diamine was used as a foaming catalyst, which was received from Sigma Chemical Company. Tertiary amine, donated by Air Products and Chemicals, Inc. (Allentown, Pennsylvania, USA) was used as a gelling catalyst.

Surfactant
Polysiloxane family based surfactant was used to achieve superior cell structures; samples were donated by Air Products and Chemicals, Inc.

Blowing agent
Distilled water was used as a blowing agent to generate foams which was prepared in our lab.

3.2.2 Foam preparation and evaluation
PU spray foams were prepared by a free-rise method according to the formulations listed in Table 1. The amount of pulp fiber used was in terms of 100 parts of soyol. The soyol was manually mixed with the additives (catalysts, surfactant and H2O) at ambient temperature for 5 minutes, and then PMDI was added and mixed for another 20 seconds. Afterwards, the resultant mixture was quickly transferred into a mold for foaming to get neat PU spray foams. For the PU spray foams in presence of wood fiber, wood fiber was pre-mixed with soyol for 20 minutes to
soak completely. The processes of the addition of the additives and foaming were same to neat foams. Finally, all the PU spray foams were kept at the room temperature overnight to be well post-cured.

According to our observation, wood fiber can delay the urethane reaction in particular for CTMP fiber from their longer foaming time.

Table 1. Formulation for PU spray foam insulation (Open-cell)

<table>
<thead>
<tr>
<th>Materials</th>
<th>Parts by weight, php</th>
<th>Neat PU spray foam</th>
<th>PU-Fiber spray foam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soyol</td>
<td>Soyol® 2102</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Diamine</td>
<td>1.33</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td>Tertiary amine</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Surfactant</td>
<td>Polysiloxane</td>
<td>0.67</td>
<td>0.67</td>
</tr>
<tr>
<td>Blowing agent</td>
<td>H₂O</td>
<td>4.7; 5.3; 6.7; 8.0</td>
<td>6.7</td>
</tr>
<tr>
<td>PMDI</td>
<td>NCO index</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Wood fiber</td>
<td>35-70 mesh</td>
<td>---</td>
<td>10; 20†; 30; 40; 50; 60</td>
</tr>
</tbody>
</table>

† Six select fibers were formulated

3.2.3 Fiber quality analysis (FQA)

The length of original fiber was measured by Optest Fiber Quality Analyzer (Optest Equipment Inc., Hawkesbury, Ontario, Canada) according to TAPPI T271. 5000 fibers were evaluated to compute an arithmetic mean fiber length. Each sample was tested twice.

3.2.4 Scanning electron microscope (SEM) investigation

Sample stub with thin foam slab was surface metalized by a sputter-coating (BOT 341F) with evaporated gold (in 4nm thickness), and then was carried out by SEM (Hitachi S-2500, Hitachi High Technologies Inc., Tokyo, Japan) at an acceleration voltage of 15kV.
3.2.5 Mechanical properties

Preparation of ASTM specimens

All the foams were conditioned at 23°C and 45% relative humidity, and then the foam slabs were extracted from a saw machine and polished with a sanding machine. The length, width and thickness were measured after polishing. The thickness is along the foam rise direction.

Mechanical tests

At least 6 type C specimens (5cm×5cm×3cm) were used for tensile strength test using a Zwick universal testing machine (Zwick/Z100, Zwick GmbH & Co. KG, Germany) according to ASTM D1623-09 under 23°C and 45% relative humidity (Fig. 1). The rate of crosshead movement was 1.3mm/min.

More than 15 specimens (5cm×5cm×3cm) were tested for compressive strength using an Instron universal testing machine (Model 3367, Instron) according to ASTM D1621-04a under 23°C and 45% relative humidity. The rate of crosshead movement was 2.5mm/min, and the value at 10% deformation was recorded as compressive strength.

Fig. 1. Tensile test of PU spray foams
3.2.6 Thermal analysis

Thermal analyses for PU spray foams were performed with thermo gravimetric analyzer (TGA Q500) of TA Instruments. Runs of TGA were conducted in the ramp mode from room temperature to 700° C under air condition at 60mL/min flow rate. The heating rate was 10° C/min. Sample weights of TGA were approximately 5 mg in its original state. Runs of DSC were performed in the temperature range of -60 to 200° C under nitrogen protection at 50mL/min flow rate. The heating rate was 10° C/min in the ramp mode. Samples weights of DSC were approximately 6 mg after fractured in liquid nitrogen.

3.3 Results and discussion

It has been reported that natural fiber can affected the mechanical properties of PU microfoams (Silva et al. 2010). Although PU spray foam is definitely different from PU microfoams due to its quick expansion and fast dry-time, the influences of wood fiber were expected to impact sprayed foam quality. The average length of 6 classified fibers is shown in Fig. 2. The 6 select fibers had same width due to cutting the same original fiber source. Obviously, fibers in high mesh categories had short length, which were more like particles rather than fibers. Thermal and mechanical properties were investigated after the select fibers were introduced into sprayed PU foam.
DSC analyses of foam samples were performed to evaluate the effects of wood fiber and blowing agent on foaming. The typical DSC curve of PU spray foam with fiber introduced, which combined the DSC behaviors of pure fiber and neat spray foam, is shown in Fig. 3. Both beta and glass transition temperatures observed from DSC analyses were reported in Fig. 4. Though the DSC trace showed a decreased beta transition with the increase of H$_2$O or wood fiber (Fig. 4a and b), the identifications were absolutely different. The increase of the amount of H$_2$O can generate more stiff urea adducts during the reaction of –NCO groups. Rigid urea structures had difficult movement of molecules, exhibiting high $T_g$ temperature as shown in Fig. 4a. The $T_g$ increased linearly with the amount of H$_2$O.

In general, the –OH groups of wood fiber would react with –NCO groups of PMDI. The beta transition of PU spray foam in the presence of fiber decreased due to this reaction, leading to conformational changes in the side groups of the matrix backbone (Fig. 4b). This reaction led to additional barriers to free segmental motions. In our study, the $T_g$ shifted to a high temperature from 57º C up to 85º C, with additional reaction of wood fiber with –NCO (Fig. 4b'). Similar to the function of H$_2$O, the increase of $T_g$ was also in linear proportion with the amount of fiber.

Unlike the functions of H$_2$O and fiber amount, the fiber size had different behavior on beta transition. Shorter fibers probably formed shorter chain groups rather than long molecular chains. It is known that the beta transition is related to the molecules of polyol long chains and short backbone chains. It was reasonable to demonstrate high beta transition with the decrease of fiber size due to the formation of shorter chains. This estimation was verified by the experimental result as shown in Fig. 4c. Though shorter fibers might generate shorter chain groups amidst the
foam matrix, shorter fiber containing more fiber ends can produce more bonds at these ends (Hsueh 1989). More chemical formations between the fibers and –NCO groups caused high limitation of segmental rotation exhibiting higher $T_g$, as shown in Fig. 4c.

Fig. 3. Typical DSC curves of PU spray foams
Fig. 4. Effect of the H₂O and fiber on DSC behaviors of PU spray foams

**Effect of H₂O on cell thermal properties**

Although this spray-on material had a skin, the quality of the skin was not controllable. As well, we studied the thermal properties of the foam core. The cell structure had an important effect on foam thermal behavior. TGA analyses of foam samples have been carried out to justify the effect
of H$_2$O concentration as shown in Fig. 5. The thermal degradation temperatures observed from TGA curve are reported in Table 2.

The decomposition temperature ($T_d$) was correlated with increasing H$_2$O. Urea formation was a dominant factor in the H$_2$O-blown PU foam, especially during initial stages of foam rise (Li et al. 2006; Grünbauer et al. 1992). This finding was supported by the data in Table 2. A typical decomposition curve of PU foam with two distinct steps is shown in Fig. 5. The primary degradation associated with urethane linkages would happen at lower temperature (about 310º C) leading to collapse of the cellular structure (Saber et al. 2010). The secondary degradation associated with polyurea and polybiuret linkages would be cleaved at higher temperature (about 420º C). The $T_d$ at 5% weight loss ($T_{d5}$) was closer to the decomposition of urethane bonds, whereas the $T_d$ at 50% weight loss ($T_{d50}$) was mostly correlated with the degradation of polyurea linkages and polyol bonds. In either case, the degradable behaviors of soy-based PU foam are very similar to the hydrolysis of petro-based foams (Dai et al. 2002; Gerlock et al. 1980). The $T_{d50}$ was expected to increase from 415º C to 440º C with the increase of H$_2$O from 4.7 to 8.0php due to more polyurea and polybiuret generated (Li et al. 2006). However, there was almost no change for the $T_{d5}$ temperatures of neat foams as shown in Table 2, which demonstrated that H$_2$O was used to build polyurea and polybiuret linkages in sprayed fast foaming procedure. Alternatively, the urethane formations would not benefit from the increase of H$_2$O. The increase of $T_{d50}$ indicated that more H$_2$O blown PU spray foam had higher thermal stability (Thirumal et al. 2008). Urea adducts have been reported to be more thermally stable than urethane structures (Banik and Sain 2008).
**Fig. 5.** Effect of H$_2$O on thermal behavior of PU spray foams

**Table 2.** Effect of H$_2$O on cell thermal degradation

<table>
<thead>
<tr>
<th>H$_2$O, php</th>
<th>Td$_5$, °C</th>
<th>Td$_{50}$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.7</td>
<td>254</td>
<td>415</td>
</tr>
<tr>
<td>5.3</td>
<td>257</td>
<td>416</td>
</tr>
<tr>
<td>6.7</td>
<td>254</td>
<td>429</td>
</tr>
<tr>
<td>8.0</td>
<td>259</td>
<td>440</td>
</tr>
</tbody>
</table>
Effect of fiber concentration on foam thermal properties

Wood fibers will start to decompose at 200° C (Kim et al. 2005) and showed two distinct stages with maximum weight loss at 328° C and 445° C in Fig. 6. Wood fiber was completely decomposed at 445° C. So, the foams were exposed to the low temperature thermal decomposition of wood fiber. However, the degradable pattern was variable due to the –OH groups of wood fiber reacting with –NCO groups of PMDI in exothermal reactions.

The pattern of the decomposition of the fiber-reinforced PU spray foam showed that there was also two-stage weight loss behavior accompanied with two endothermic peaks, as shown in Fig. 7. These indicated the thermal decomposition of PU foams consisted of a two-stage degradation of urethane adducts and polyurea bonds. But, this degradable pattern shifted to higher temperature with the increase of fiber. It demonstrated that the employment of wood fiber had important influence on thermal behaviors. The thermal degradation temperature observed from TGA analysis was reported in Table 3.
Different structures had different degradation temperatures, which were portrayed by their break-off peaks. According to Fig. 7, the amount of fiber had significant effects on the thermal decomposition. When a lesser amount of fiber was introduced, it had little effect on the foam decomposition. But, this improvement was enhanced when high content fiber was present. The employment of wood fiber alleviated the creaming reaction, which was expected to form more urethane adduct formations because the tertiary amine significantly promoted the polyol-urethane reaction after the fast blowing reaction caused by diamine. In addition, the extra hydroxyl groups in wood fiber were also involved in the urethane reaction. Afterwards, the $T_{d5}$ increased because the initial stage of weight loss was dominated by the urethane-urea blocks and wood fiber degradation from 300º C. Still, the delayed gelation time and extended cure time were purposed to contribute PU foam with more trimerization opportunities exhibiting high $T_{d50}$, which governed the second stage around 500º C. The enhancement of $T_{d5}$ and $T_{d50}$ indicated that the fibers contributed PU spray foam with superior thermal stability. Alternatively, the functions between the reactive –OH groups containing wood fiber and PMDI contributed more thermally stable structures by reacting chemically and extending post-curing time.
**Table 3.** Effect of fiber concentration on cell thermal degradation

<table>
<thead>
<tr>
<th>35-70 mesh fiber, php</th>
<th>$T_d$, °C</th>
<th>$T_d^{50}$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>254</td>
<td>429</td>
</tr>
<tr>
<td>10</td>
<td>258</td>
<td>429</td>
</tr>
<tr>
<td>20</td>
<td>256</td>
<td>439</td>
</tr>
<tr>
<td>30</td>
<td>260</td>
<td>437</td>
</tr>
<tr>
<td>40</td>
<td>262</td>
<td>437</td>
</tr>
<tr>
<td>50</td>
<td>265</td>
<td>468</td>
</tr>
<tr>
<td>60</td>
<td>274</td>
<td>467</td>
</tr>
</tbody>
</table>

**Effect of fiber size on foam thermal properties**

TGA data were measured using six consecutive fiber lengths. The $T_d$ varied with the fiber particle size, which was seen in Fig. 8. It was observed that the PU spray foam with long fiber had higher thermal stability, attributed to the fact that long fiber contained more –OH groups exposed to the matrix forming a more complex network structures and functioned as both chain-extender and cross-linkers. Short fiber will decrease the actual contact surface of the fibers with the foam matrix, leading to less complex structural networks and were mostly cross-linkers. To verify the above observations, the thermal degradation at 5% and 50% were recorded in Table 4. The $T_{d50}$ decreased from 443° C to 410° C when the fiber length decreased from 1.04 mm (20-35 mesh) to 0.175 mm (200-325 mesh). Moreover, their relationship was very delicate. Unlike the effect of fiber content, the fiber particle size had little influence on the $T_{d5}$. This finding proved that wood fibers were involved in building high thermal stability structures regardless of their length.
Fig. 8. Effect of fiber size on thermal behavior of PU spray foams

Table 4. Effect of Fiber Particle Size on Cell Thermal Degradation

<table>
<thead>
<tr>
<th>Fiber particle size, 20php</th>
<th>Td5, °C</th>
<th>Td50, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20-35 mesh</td>
<td>255</td>
<td>443</td>
</tr>
<tr>
<td>35-70 mesh</td>
<td>256</td>
<td>439</td>
</tr>
<tr>
<td>70-100 mesh</td>
<td>255</td>
<td>426</td>
</tr>
<tr>
<td>100-140 mesh</td>
<td>256</td>
<td>427</td>
</tr>
<tr>
<td>140-200 mesh</td>
<td>256</td>
<td>429</td>
</tr>
<tr>
<td>200-325 mesh</td>
<td>251</td>
<td>410</td>
</tr>
</tbody>
</table>

3.3.2 Mechanical properties of PU spray foams

Foam cell morphology has direct influence on foam mechanical properties, such as compressive strength and tensile strength. Good cellular structure helps in dispersing tension under compression and the applied stress. In our case, H2O blown PU spray foam had fine cell structure (see Fig. 9a). With the increase of H2O amount, the compressive strength had a linear increase.
The cell walls of neat H₂O blown foam were thinner with the increase of H₂O concentration. In chapter 2, section 2.3.2 it was observed that higher water content in foaming led to lower foam density in which could be attributed to thinner cell walls. This nature of the cell walls could not bear the tensile stress and broke, which led to a loss in tensile strength as shown in Fig. 10.

Although a small amount of fiber will not destroy the whole cell structure (see Fig. 9b), some stiff fibers still perforated the cell walls (Fig. 9c) and also built disconnected struts (Fig. 9d). The fiber reinforced PU spray foam had inferior compressive strength at low fiber quantities comparing to neat foam, where the compressive strength decreased from 30 kPa for neat foam down to 20 kPa for the foam with 10php fiber. On the other hand, the stiff fibers also interfered with the cell nodes (see Fig. 11) by framing into the struts, even though the frames of the cells were not uniform according to its increased foam density and cell size. Therefore, as more fiber was introduced, they provided stiffer cusps to bear high compressive stress, exhibiting superior compressive strength as shown in Fig. 12. This finding in soy-based PU spray foams corresponds to the behaviors of conventional PU foams with the introduction of fiber residue reported by Silva et al. (2010).
Fig. 9. Three-dimensional cell structures

a) Neat PU spray foam; b) 20php fiber reinforced PU spray foam; c) fiber isolation in cells; d) struts disconnection due to fibers

Fig. 10. Effect of H₂O on foam mechanical properties.
Unlike PU resin composites, PU spray foams have different reinforcement behaviors because a high hydroxyl value polyol in PU resin composites leads to better bond strength (Desai et al. 2003). Obviously the –NCO groups of PMDI will react with primary –OH groups in polyol with priority (Ionescu et al. 2008), and then react with secondary –OH groups on the fiber surface.
(Pigman and Wolfrom 1948). Thus, wood fiber can interfere with the reaction between polyol and PMDI. Moreover, the stiff fibers destroyed the cell structures (Fig. 9c-d), leading to the decrease of the tensile strength as soon as a small amount of fiber was presented. The value of the tensile strength decreased from 95 kPa for neat PU spray foam to 70 kPa as 10php fiber was employed. Furthermore, the tensile strength continued to decrease as more fiber was introduced after temporary improvement (Liu et al. 2009). Clearly, the destructive effect of wood fiber on cell morphologies was determined by its amount.

Maximum compressive stresses at 10% deformation for six select fiber particles are recorded in Fig. 13 for 20php fiber loading. The trend of compressive strength decreased in a linear relationship thereafter. The compressive strength decreased by 47% from 20.6 kPa for the 20-35 mesh fiber to 10.9 kPa for the 200-325 mesh fiber. Therefore, PU spray foam with 20-35 mesh fiber showed a superior compressive strength. In addition to the compressive strength, a similar trend was also observed in the tensile strength curve. Although the refined fiber particles have high surface area to expose more –OH groups in wood fiber to the foam matrix, the fiber size greatly affects the mechanical properties of foams. The reinforced foam had achieved an inferior tensile strength (89 kPa) due to the destructive effect of fiber by isolation in the foams as described in Fig. 9c. Like a chain extender, 20-30 mesh fiber would be expected to contribute to three-dimensional structures as well as seemingly high crosslinks exceptional to the above mentioned destructions. Consequently, 35-70 mesh fiber produced superior tensile strength at the value of 103 kPa from its moderate length and better cell morphologies. Actually, very small fiber particles will be powdered as a nucleation agent to create more effective nucleation sites (Guo et al. 2008). So, it was assumed that the shortest fibers acted as a nucleation agent rather
than extenders. Spray foams with the shortest fibers had more cells expand more rapidly and melt into large microvoids easily, leading to inferior tensile strength.

![Graph showing effect of fiber particle size on foam mechanical properties]

**Fig. 13.** Effect of fiber particle size on foam mechanical properties

### 3.4 Conclusions

The amount of water present during foam preparation affected the cell thermal stability by forming more urea/biuret adducts. The more urea/biuret structures increased the hard phases in the foams, exhibiting high compressive strength but inferior tensile strength because of poor cell quality.

The amount of fiber had significant effects on foam qualities. As more fibers were introduced, the foam had inferior tensile strength. However, Due to the fiber framing within the three-dimensional foam structure higher fiber concentration produced superior compressive strength. Meanwhile, the fiber reinforced PU spray foam had better thermal stability following the increase of fiber according to their TGA results. Long fiber showed better comparative properties, to short fiber, by acting as a chain extender, which contributed the foam with an improved thermal stability.
References


CHAPTER 4.0

Morphological and Physico-thermal Properties of Soy-based Open-cell Spray Polyurethane Foam Insulation Modified with Wood Pulp Fiber
Abstract

Replacing polyether and polyester polyols with soy-based vegetable oil, using water as a blowing agent, would provide environmentally friendlier spray foam insulations, making buildings safer places to live in. The objective of this work was to produce sustainable open-cell spray polyurethane foam insulation from soy-based polyol and enhance its properties by incorporation of wood pulp fiber. The effect of wood fiber in composite foam was investigated in terms of its morphology by Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM), and Thermo-gravimetric Analysis (TGA). The changes in foam properties such as bulk density, compressive strength, water vapor permeability and thermal resistance were observed. Addition of fiber as reinforcement improved bulk density, moisture permeability and thermal degradation, but slightly reduced the comprehensive strength and thermal resistance of the insulation foam.

4.1 Introduction

High petroleum prices over the last two decades, along with sustainability of resources have prompted the researchers to look for alternative renewable resources to produce eco-friendly insulation foam to be used in buildings. Soy oil, palm oil and castor oil - to name a few, exist in plenty to be considered as potential replacements for petrochemical polymers. Soy-based polyol generated from soy bean oil is gradually gaining industrial importance as it contains high -OH value make it more suitable for obtaining good quality spray foam insulation.

Soy-based polyurethane (PU) foams are produced by the reaction of isocyanate with polyol. For water blown polyurethanes, foaming process involves two basic reactions where isocyanate reacts with a) polyol to generate the urethane linkages leading to curing and b) water to form urea and carbon dioxide to expand the polymer. Rigid and flexible foams are the two main
categories in polyurethane industry. Open-cell spray polyurethane foam (SPF) is a rigid type of foam, widely used as wall insulation in residential and commercial buildings. It has the ability to reduce heat loss and provide a good air/moisture barrier with respect to traditional fiber glass insulation, and to save energy for home owners. Two main components, component ‘A’ as isocyanate and component ‘B’ as polyol, mixed with catalysts including blowing agents, come together at the nozzle of a gun and are sprayed between the struts of the wall. It expands many times of its liquid volume and solidifies in seconds sealing the wall.

In general, the performance of PU foam depends on hard and soft segment ratio in copolymers. Hard segments are those formed by the reaction of di-isocyanate with short-chain diols. They contain high density urethane groups of high polarity, and for that reason, the foam becomes rigid. On the other hand, soft segments are shaped by the reaction of di-isocyanate with the long-chain diols, having low density urethane groups and polarity, and therefore, are flexible. They usually have a phase separation due to the incompatibility between the hard and soft segments. The high polarity of hard segments generates a strong attraction between them which forms a high concentration and order in this phase, generating crystalline regions within flexible matrix\(^1\). The crystalline areas have high levels of elasticity and act as cross linkers, whereas the flexible or soft chains are more chain extenders and give longitudinal strength to the polymer. When a load is applied to the foam material, the soft segment phase would stretch while the hard segment would carry the load and release it when the stress is removed.

The objective of this study was to develop an optimum formulation to produce open-cell soy-based SPF insulation in the laboratory and to introduce wood fiber into it as reinforcement. The fiber was incorporated in 13, 26, and 40 per hundred grams of polyol (php). Many research studies have demonstrated that fiber has strength and its addition would enhance foam properties.
Though this effect has been reported for flexible and rigid foaming, little is known about introducing fiber in spray foam insulation. It was expected that addition of wood fiber would reduce moisture permeability and would enhance R-value of the composite foam. In this study an attempt has been made to incorporate fiber in open-cell spray foam insulation and try to understand the fiber-polyurethane interactions at morphological level, as well as its effect on the physio-chemical properties of spray foaming. The benefits would be to encourage the use of sustainable and green materials, to reduce CO$_2$ emissions, and to increase safety and comfort in buildings.

4.2 Experimental

Materials

Bi-functional soy-based polyol (Soyol R-2101) was obtained from Urethane Soy Systems, Volga, USA. Its viscosity @ 25° C was 2040 cps with hydroxyl value 69 mg KOH/g. The aromatic polymeric diphenylmethane di-isocyanate (Robinate M) was donated by Huntsman PU Geismar, LA, USA having functionality of 2.7, NCO content 31.5%, and viscosity @ 25° C 190 cps. The surfactant and catalysts I & II were also donated by Air Products and Chemicals, Allentown, USA. Distilled water was used as blowing agent. Mechanically pulped medium density wood fiber with average 1600 µm in length was donated by FPInnovations, Canada. It was grinded by Thomas Wiley Laboratory Mill, Model 4, to 400 µm in length to reduce the impact of viscosity. The aspect ratio was estimated to be around 8.

Foam Preparation

Spray foam specimens were prepared by mixing soy-based polyol and other ingredients with isocyanate at room temperature in laboratory, which was poured into a mold for free rise. After
After two hours, the samples were removed from the mold and left for 48 hours for full curing under ambient temperature. It may be mentioned that the quantity of all ingredients used in the formulation was expressed as part per hundred grams of polyol (php). In case of composite foam, at first fiber was mixed thoroughly with polyol and then other ingredients and isocyanate were added.

The first set of experiments was carried out to obtain neat foam. Many samples were prepared trying out different catalysts and surfactants of varying quantities to arrive at the optimum formulation. The amount of water had significant influence on the blowing behavior and formation of cell sizes. Then wood fiber was incorporated as reinforcement in 13php, 26php, and 40php. Attempt has been made to increase the concentration of wood fiber as much as possible to reduce the amount of raw materials and make the biofoam more environmentally friendly. At least four scenarios were prepared - one for neat foam and the others for fiber foam at the above quantities.

Foam has been characterized by Fourier transform infrared (FTIR) spectroscopy to determine the behavior of different functional groups present in the polymer structure. Brucker infrared spectrometer with resolution of 4 cm\(^{-1}\) and 32 scans for signal averaging was used to record the spectra of the samples. Cellular structural observations have been made with Hitachi S-2500 as well as Hitachi TM-1000 Table-top scanning electron microscopy (SEM). Thermal degradation of neat and composite foam samples have been investigated using Thermo-gravimetric Analyzer Q 500 at heating rate of 10°C/min. in nitrogen atmosphere. Decomposition temperatures at different weight loss percentages have been recorded. The Brookfield Viscosity Test (BVT) was utilized to measure the viscosity of polyol with added ingredients known as component ‘B’. The ingredients were catalysts, blowing agent, surfactant and fiber (where applicable). The mixture
was poured into a glass jar and placed under a viscometer. The tests were performed for 30 seconds at ambient temperature with spindle number 64 and running speed of 50 and 100 RPM and averaged.

The American Society for Testing and Materials (ASTM) procedures were utilized to evaluate the effect of fiber on physical and mechanical properties of foam samples. At least five samples were considered for each test with ±3% error. The bulk density of the foam was estimated by direct measurement of volume and weight of the samples according to ASTM-D1622. The compressive strength was determined in accordance with ASTM-D1621. The test was carried out using INSTRON 3367 equipment with crosshead speed of 2.5 mm/min. and cell load of 2 kN. The square specimens of 50 mm x 50 mm cross-sectional dimensions and 25 mm thickness were used for both tests. Water vapor transmission property plays an important role in assessing moisture permeability of foam insulation. The test method is specified in ASTM-E96. A foam specimen of 25mm thickness, was sealed to the open mouth of an impermeable dish containing water and placed in a desiccator containing saturated calcium nitrate (as desiccant) to maintain a relative humidity of 50% at all times. The whole assembly was placed in atmospheric temperature. The test dish was filled with water to a level 25 mm from the specimen having a mouth area of 12.6 cm X 12.6 cm. and defined as the area of the specimen exposed to the water vapor. Periodic weighing of dish assembly determined the rate of water flow through the specimen. As foam insulations are rated in terms of their resistance to heat flow, the thermal resistance and R-value of foam samples were determined in accordance with ASTM-C518, by means of the heat flow meter apparatus and in conjunction with ASTM-C1045 standard practice for calculating thermal transmission. Laser Comp FOX314 Heat Flow Meter instrument was used.
4.3 Results and discussion

A series of neat and wood fiber SPF samples were prepared to evaluate the effect of wood fiber on physical and mechanical properties. They are summarized in Table 1. The same formulation was used in preparation of all samples including fiber foam. It was observed that addition of fiber delayed foam creaming compared to the neat foam and increased the bulk density as fiber content was raised. During foaming process fiber could be acting as a heterogeneous nucleating agent producing smaller cell sizes, thereby increasing the foam density\(^2\). To verify this reduction due to addition of fiber, the average cell diameters of samples were measured utilizing SEM images and Image J software. It was determined that it had decreased from 184 \(\mu\)m for the neat foam to 170 \(\mu\)m for the fiber foam (Figure 4). On the other hand, compressive strength of fiber foam was reduced compared to neat foam. The strength reduction was about 7\% to 28\% depending on fiber content. Higher fiber content resulted in lesser reduction in strength. The presence of fiber as nucleating agent not only generated smaller cell sizes, but also reduced the cell wall thicknesses and lowered the compressive strength.

The performance of PU foam also depends on the quantity and quality of cross-links formed within the polymer network. Higher cross-links give rise to higher compressive strength\(^4\). Reaction of di-isocyanate with multifunctional polyol and water leads to the formation of urethane and urea linkages that are highly cross-linked network. Urethanes are elastomers with combination of hard and soft segments whereas urea polymers are hard short chains and bridge urethane units. In a more balanced and stable polyurethane structure, urethane chain formations are greater or equal to that of urea production in order to create a good hydrogen bonding between N-H groups (acceptors) and C=O groups (donors) within the network\(^5\). They are cross-
linked together into a single networked molecule that is hard to break and can withstand the pressure in a more effective manner\textsuperscript{6}.

To understand the chemistry between these two hard segment groups, foam samples were analyzed by FTIR spectroscopy. Figure 1 represents peak absorptions of urethane carbonyl groups at 1740 cm\textsuperscript{-1} and urea carbonyl groups at 1660 cm\textsuperscript{-1}. It was observed that for the neat foam the concentration of urethane carbonyl groups had increased, while that of urea carbonyl groups had decreased. This is an enhancement to the foam. The addition of fiber had reversed this process by decreasing the absorbance of urethane carbonyl groups followed by increasing the urea carbonyl groups. For an unknown reason, fiber hysterically hindered the reactivity of isocyanate with polyol causing less formation of urethane linkages and promoted the blowing reaction increasing the urea. They did not interact in an efficient manner. Thus the fiber foam network did not generate enough urethane elastomers to support a strong network to carry the applied stress and thus lowered the compressive strength\textsuperscript{7,8}. It may be noted that this slight reduction in compressive strength is less important in spray foam as wall insulation.

Thermal resistance and degradation of sample materials have been investigated to observe the behavior of fiber in foaming. According to the US Department of Energy, insulations are rated in terms of their resistance to heat flow (also known as R-value). The higher the resistance, the greater is the insulating effectiveness. The analysis revealed that thermal resistance of the foam has decreased slightly when fiber was embedded. The lower reactivity of polyol with isocyanate has diminished the foam cell strength and formed a weaker three-dimensional structure of cell walls. The cross-linkages in polyurethane solid structure were weakened to such extent that less carbon dioxide could be trapped inside the foam during foaming process. Thermal resistance of foam would be greatly improved if more diffused gas could get trapped inside. As more air
replaced the escaped carbon dioxide, the thermal conductivity of the material was increased and resulted in lower thermal resistance and R-value\(^9\). However, both thermal resistance and R-value measurements of open-cell spray foam with or without fiber matched the commercial foam values and were in accordance with minimum requirements specified by CAN/ULC-S706-09.

Thermal gravimetric analysis determined degradation behavior of biofoam. Temperatures at different percentages of weight loss were recorded as shown in Table 2. Both neat and composite foams experienced a two-stage weight loss behavior supplemented by two major endothermic peaks representing urethane and urea bond degradation. The initial degradation of foam started at about 250°C (at 5% weight loss, T5), and was delayed slightly at higher levels of fiber content. As temperature was increased, urethane linkages and urea bonds started to decompose, as indicated by two endothermic peaks\(^10\). The recorded data indicated that degradation temperatures have been delayed at 50% and 75% weight losses (T50 & T75) for the fiber foam. All samples experienced significant weight losses at 600°C at relatively same percentage. Hence, it was obvious that the fiber had positively influenced thermal behavior of the foam and delayed its degradation temperature. This effect increased as fiber content was increased. This suggested that some O-H groups on the surface of fiber must have reacted with N-C-O groups of isocyanate, increasing urethane formation beyond polyol and isocyanate reaction. FTIR spectra in Figure 2 also revealed that free N-C-O group peaking at 2270 cm\(^{-1}\) were diminished in fiber foam system. Therefore, fiber foam system had more thermal stability than the neat foam.

Water vapor transmission property plays an important role in assessing moisture permeability of foam insulation. This is the rate of water vapor flow through unit area of a flat material of unit thickness under specified temperature and relative humidity condition\(^11\). As water vapor moves from a warm interior through the insulation material to a cooler surface, it gets condensed as
liquid water. The condensed water not only reduces the thermal effectiveness of the insulation but also damages the foam structure\textsuperscript{12}. In order to measure water permeability through each foam samples, an apparatus was constructed and the flow of water vapor was measured during different time intervals. The effect of moisture permeability on various foam samples were determined and tabulated in Table 1. It was demonstrated that presence of wood fiber in foaming would enhance the foam quality by restricting the flow of water vapor through the foam. The permeability was decreased with increase in fiber content suggesting that fiber acted as moisture barrier in foam insulation. Although the incorporation of wood fibers increased the water vapor barrier property of the foam, it might increase the water absorption attracting molds. However, this effect can be minimized by addition of antifungal agents in foaming.

To justify the effect of fiber in foaming structure, SEM observations have been made. Figure 3(a-b) represents SEM images at 13php and 0php wood fiber content. It was observed that the non-fiber foam had cell structures generated in random and irregular shapes, whereas the fiber foam cells formation were smaller and more homogeneous. The average cell diameter of fiber foam system was estimated and is shown in Figure 4. SEM images also revealed the interaction of fiber with matrix polymer as indicated in Figure 3(c-f). Fiber interacted with matrix polymer and dispersed within cell walls but it was also detected standing freely within the foam structure with no interaction. The O-H groups on the surface of the fiber reacted with N-C-O groups of isocyanate just like O-H groups of polyol and exhibited some compatibility with the polymer\textsuperscript{13}. This effect has been seen by the reduction of free N-C-O groups at 2275 cm\textsuperscript{-1} in FTIR observation. However, this interaction between the fiber and polymer matrix was not significant to create enough adhesion to improve compressive strength and R-value of the composite foam system. This effect could be attributed to the presence of waxes and to some extent to lignin and
hemi-cellulose in wood fiber. Lignin –OH is difficult to access and hemi-cellulose is short chain with lower molecular weight so, interaction is less.

Presence of fiber also influenced creaming behavior during the foaming process and reduced slightly the rising height of the foam. This was attributed to the decreased formation of urethane linkages in presence of wood fiber.

Aspect ratio and concentration of fiber play an important role in foam reinforcement. Although longer fiber length would provide better reinforcement, it would create high viscosity problems in polyol component and could not be sprayed with conventional spray guns. Thus, pulp fiber had to be grinded to optimum length of 400 µm to keep viscosity increase of polyol component at minimum. As the fiber content was increased, so was the viscosity. It was observed that the increase in viscosity would be about 10% if fiber concentration remains under 20% php and it could still be sprayed by conventional guns. Incorporation of more fiber percentages in foaming requires modification to present spray foam system, when it would become possible to spray the fiber simultaneously with the polymer matrix.

4.4 Conclusions

Spray Polyurethane foam was successfully produced in the laboratory with soy-based polyol matrix and water as blowing agent. The neat foam was reinforced with wood fiber as much as possible and its impact as reinforcement was investigated. The biofoam made by this formulation had comparable properties; same or even better than commercially available spray foams. When fiber was embedded in spray foam, the analysis indicated that pulp wood fiber was less compatible with the matrix, and its presence slightly interfered with hydrogen bonding between urethane linkages during foam formation. As cross-linked urethane elastomers were not
promoted enough, the comprehensive strength and thermal resistance of the fiber foam were not enhanced in comparison to the neat foam. However, the density of fiber foam was increased as more homogenous and smaller cells were formed as a result of nucleating effect. Addition of fiber also enhanced the foam and delayed the thermal degradation. The moisture permeability was greatly improved in fiber foam system indicating that fiber acted as a good moisture barrier enhancing the foam quality. Although this property was improved it might have absorbed moisture and increased the possibility of mold formation. This effect could be minimized by antifungal agents in foaming. Though it was possible to achieve high fiber content spray foam of up to 40php without major impact on foaming reactions, the analysis demonstrated that the fiber content may not exceed more than 26php in order to achieve optimum viscosity to be able to spray with conventional spray gun system. However, the spraying technology could be improved to accommodate more fiber content in foaming.
Table 1
Physico-thermal properties of neat and composite polyurethane spray foams.

<table>
<thead>
<tr>
<th>Foam type</th>
<th>Average Density (kg/m³)</th>
<th>Average Compressive strength (kPa)</th>
<th>Water Vapor Transmission (g/h·m²)</th>
<th>Thermal Resistance at 25mm thickness (K·m²/W)</th>
<th>R-Value (US) (h·ft²·°F/Btu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Foam</td>
<td>20.99</td>
<td>23.70</td>
<td>3.77</td>
<td>0.604</td>
<td>3.43</td>
</tr>
<tr>
<td>13php wood fiber foam</td>
<td>20.60</td>
<td>17.02</td>
<td>2.50</td>
<td>0.535</td>
<td>3.05</td>
</tr>
<tr>
<td>26php wood fiber foam</td>
<td>24.80</td>
<td>18.35</td>
<td>2.25</td>
<td>0.550</td>
<td>3.11</td>
</tr>
<tr>
<td>40php wood fiber foam</td>
<td>26.97</td>
<td>22.10</td>
<td>2.18</td>
<td>0.500</td>
<td>2.85</td>
</tr>
</tbody>
</table>

Table 2
Thermal degradation analysis of spray foam insulation.

<table>
<thead>
<tr>
<th>Foam Type</th>
<th>Degradation Temperature (° C)</th>
<th>Residue in % @ 600° C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T5</td>
<td>T50</td>
</tr>
<tr>
<td>Neat Foam</td>
<td>253</td>
<td>376</td>
</tr>
<tr>
<td>Fiber Foam WF13php 400</td>
<td>250</td>
<td>370</td>
</tr>
<tr>
<td>Fiber Foam WF26php 400</td>
<td>247</td>
<td>380</td>
</tr>
<tr>
<td>Fiber Foam WF40php 400</td>
<td>261</td>
<td>384</td>
</tr>
<tr>
<td>Wood Fiber only</td>
<td>206</td>
<td>353</td>
</tr>
</tbody>
</table>
Figure 1. FTIR spectra peak of urethane carbonyl at 1740 cm$^{-1}$ and urea carbonyl at 1660 cm$^{-1}$.

Figure 2. FTIR spectra of free N-C-O absorption peak at 2275 cm$^{-1}$. 
Figure 3. SEM foam cell structure (a) 13php fiber foam (b) Neat foam (c) Fiber detection (d) Fiber compatibility with matrix (e-f) Fiber embedded in foam.
**Figure 4.** Average foam cell size (micron).

**Figure 5.** Water vapor transmission for the foam system.
References


CHAPTER 5.0

Morphological and Thermo-mechanical Characterization of Open-cell Spray Polyurethane Foamed Wall Insulation Modified with Cellulose Fiber
Abstract

Open-cell spray polyurethane foam insulation was prepared using soy-based polyol and water as blowing agent. Cellulose fiber was embedded in polymer matrix as reinforcement and the effects of fiber on morphological changes, as well as thermal and mechanical properties of the foam insulation were investigated. The foam was characterized at cellular level by FTIR and SEM and it was demonstrated that incorporation of cellulose fiber in open-cell foam insulation altered the foaming structure. Cell density increased and became more homogeneous. Compressive strength and thermal resistance of the composite foam were improved at lower fiber concentration. Moisture permeability was reduced. At higher fiber content the reinforcement effect weakened due to agglomeration of fiber.

5.1 Introduction

Polyurethanes were developed by Bayer Company around the year 1950. It was a success story and formed the basis for a present multi-billion dollar business in the world today [1]. Since then manufacturers and pioneers of polyurethane dedicated a great deal of research for improvements, but in spite of many discoveries, there has been little change to the original work. Polyurethane foams are currently used in many applications depending on their categories such as flexible, semi-rigid and rigid. They are mainly used in transportation, furniture, and construction industries. The control of parameters such as chemical composition, functionality of the materials and molecular weight would produce a wide variety of foam types with significant differences in properties.

Spray polyurethane foam (SPF) is a type of rigid foam widely used as wall insulation in residential and commercial buildings. It is applied in-situ with a special blending machine and a
spray gun. It has two components, component ‘A’ as isocyanate and component ‘B’ as polyol. They come together at the nozzle of a gun, which is then sprayed on the wall. It quickly expands to many times its original volume and solidifies in seconds, effectively sealing the wall. Although it sets in about an hour, full curing is reached after 24 hours. It adheres well and has the ability to reduce heat loss through walls, thus saving energy for home owners. It acts as an air and moisture barrier, and provides effective thermal insulation. Its performance is superior to commonly used fiber-glass insulation. It also contributes to the structural stability of the building, due to its superior adhesion properties. Many studies in USA indicated that the racking strength of building structures can be increased by applying SPF insulation.

Main raw materials used in the preparation of PU spray foam are derived from petro-chemical products. Efforts to replace them with alternative natural and sustainable resources have been accelerated during recent years. Polyols derived from vegetable oils are considered a potential replacement due to their attractive properties. As spray foam insulation is gaining popularity, enhancement of mechanical properties becomes an important consideration as they are usually weak. Many researchers have demonstrated that addition of fiber has contributed to the foam quality in flexible and rigid foaming, but little is known about introducing fiber in spray foam insulation. In this study, an attempt has been made to produce SPF from soy-based polyol and water as blowing agent with incorporated cellulose fiber in polymer matrix as reinforcement. The potential improvement of SPF properties and the effects and interaction of fiber in foaming process were investigated. The benefits would be to encourage the use of sustainable and green materials to increase safety and comfort in buildings.

5.1.1 Open-cell Vs closed-cell foam
SPF is either closed-cell or open-cell, referring to the internal structure of the foam. In closed-cell forms almost all the foam bubbles remain closed and the gas that forms during the foaming process gets permanently trapped in the cells. In open-cell forms the bubbles are mostly open or ruptured and the diffused gas could escape from the cells during the foaming process. The advantages of closed-cell foam with respect to open-cell foam include its strength, higher R-value, and greater resistance to the leakage of air or water vapor. The disadvantages are that it is denser, requires more material, and is, therefore, more expensive. The choice of foam can also be based on the requirements of performance or application specific characteristics such as strength, vapor control, available space, etc. Open-cell SPF has an R-value around 3.3 per inch and typically weighs about 0.4-0.6 lb./cu. ft. and is usually used indoors. Closed-cell SPF has an R-value of around 6.0 per inch and typically weighs about 1.5-2 lb./cu. ft. and is mainly used outdoors.

5.1.2 Polyurethane foam reactions

The isocyanate group (-N=C=O) is an unsaturated and highly reactive group containing two double bonds. It can react with both electron acceptor and electron donor functional groups. The main groups reacting with isocyanate are hydroxyl, carboxyl and amino groups. Isocyanate undergoes two types of reactions in the foaming process - primary and secondary.

*Primary Reactions*

Primary reactions are fast and performed at lower temperatures compared to secondary reactions. At first, the isocyanate (-NCO) group reacts with the hydroxyl (-OH) functional group of polyol to form urethane (-NH-CO-O-). This reaction is an exothermic polymerization reaction. During this exothermic process, the isocyanate reacts with a blowing agent such as water to generate carbon dioxide, as per the reaction scheme I below, to cause the foam to rise during
polymerization reaction. First isocyanate group (-NCO) reacts with water to generate Carbamic acid which is unstable and immediately decomposes, forming an amine and carbon dioxide. The amine (R-NH₂) reacts again with another isocyanate group to produce urea linkage.

\[
\begin{align*}
R\text{-NCO} + R'\text{-OH} & \rightarrow R\text{-NH} - CO - O - R' \quad \text{(Urethane)} \\
R\text{-NCO} + H_2O & \rightarrow R\text{-NH} - CO - OH \quad \text{(Carbamic Acid)} \\
R\text{-NH} - CO - OH & \rightarrow R\text{-NH}_2 + CO_2 \\
R\text{-NCO} + R\text{-NH}_2 & \rightarrow R\text{-NH} - CO - NH - R \quad \text{(Urea)}
\end{align*}
\]

Scheme I

PU foam reaction is a unique process in which polymerization and foam blowing occurs simultaneously. Polymer structure forms rapidly in order to support the fragile foam, but not fast enough to burst the bubbles.

**Secondary Reactions**

Isocyanate reactive groups further react with urethane and urea groups to form allophanates and substituted biurets respectively [2]. The secondary reactions of isocyanate leads to cross-linking, and the resulting polyurethane becomes more rigid. Thus temperature control during polyurethane synthesis is critical to control secondary reactions and thereby cross-linking. Allophanate linkages may or may not be reversible, depending on many factors such as the nature of catalyst or NCO/OH ratio as schematically shown below (Scheme II)

- \[
R\text{-NH} - CO - O - R' + R\text{-NCO} \rightarrow R\text{-NH} - CO - NR - CO - O - R' \quad \text{(Allophanate)}
\]

- \[
R\text{-NH} - CO - NH - R + R\text{-NCO} \rightarrow R\text{-NH} - CO - NR - CO - NH - R \quad \text{(Biuret)}
\]

Scheme II
5.1.3 Hard and soft segments

The structure of PU contains hard and soft segments which contribute to its rigidity and elastomeric properties, depending on the ratio of these segments in copolymers. In the early stages of polymerization, the reaction of polyol with isocyanate is slower than that of isocyanate with water due to secondary hydroxyls present in soy-based polyol. The generated urea linkages from the later reaction are able to start phase separation (hard segments) from the liquid matrix due to its ability to form strong hydrogen bonds between themselves. As soon as the polyol-isocyanate reaction proceeds, the soft phase formation starts and urethane links bonds the soft and hard segments together.

The hard segments are mainly crystalline, having urethane groups that are cross-linked through hydrogen bonding with urea and other urethane linkages [3]. The soft segments are the fatty acid linear sections of polyol structure stretched in coil shape within the polymer profile, and provide elastomeric quality within the matrix network. While hard segments are highly crystalline, the soft segments are comparatively mobile. The presence of these two phases in the same molecule can alter the properties of flexible and rigid foaming. Upon mechanical deformation, the soft segments are stressed by uncoiling, and the hard phases become aligned in the stress direction. This reorientation of hard segments and powerful hydrogen bonding contributes to high strength, elongation, and tear resistance of the foam structure [4, 5].

5.1.4 Fiber as reinforcement

Polyurethanes are reinforced with synthetic or natural fibers to enhance their properties. Synthetic fibers such as nylon and glass fibers are made of petro-chemicals with a good elasticity and strength. As society becomes more environmentally conscious, natural fibers such as wood and cellulose fibers replace synthetic fibers. Their benefits as reinforcement in composite
materials are sustainability, low cost, biodegradability and low energy consumption. The effect of reinforcement depends on a variety of parameters, such as nature of fiber, aspect ratio and interaction of fiber with the polymer.

In recent years, a great deal of research has been dedicated to the use of cellulose fiber as reinforcement in polymers. It is extracted mainly from wood, highly available around the globe as a sustainable resource, and used in various applications. This study focuses on the incorporation of cellulose fiber in spray foaming at low and high concentrations, and evaluates its impacts in foaming. The average length of cellulose fiber is 350 micron with aspect ratio of about 26 which provides the best compromise between viscosity increase and reinforcement.

5.2 Experimental

5.2.1 Raw materials

Multi-functional soy-based polyol (bio-polyol-X500) was purchased from Cargill Industrial Oils & Lubricants, Chicago, USA. Its viscosity @ 25° C was 3200 cps with hydroxyl value 56 mg KOH/g. The polymeric diphenylmethane di-isocyanate (Robinate M) was donated by Huntsman PU Geismar, LA, USA having NCO content 31.5%, viscosity @ 25° C 190 cps, and functionality of 2.7. The catalysts I & II, as well as the surfactant, were donated by Air Products and Chemicals, Allentown, USA. Blowing agent used was distilled water. The cellulose fiber was purchased from Sigma-Aldrich having the average length of 350 µm.

5.2.2 Foam preparation

Spray foam specimens were prepared by mixing soy-based polyol and other ingredients for 5 minutes, then adding the isocyanate and mixing it for an additional 30 seconds in the laboratory. The mixture was poured into a mold for free rise. After one hour, the samples were removed
from the mold and left for 48 hours for full curing under ambient temperature. It may be mentioned that the quantity of all ingredients used in the formulation was expressed as per hundred grams of polyol (php). Then cellulose fiber was embedded in foaming in 13php, 26php, and 40php concentration. At first fiber was mixed thoroughly with polyol for 20 minutes and then other ingredients and isocyanate were added accordingly. Attempt was made to increase the concentration of cellulose fiber as much as possible to make the bio foam more environmentally friendly and to reduce the amount of raw materials.

5.2.3 Characterization

The bulk density of the foam was measured in accordance with ASTM-D1622 with sample size of 50 mm x 50 mm x 25 mm, and an average of six measurements was recorded. The density was calculated by dividing the weight of the sample by its volume. Water vapor transmission of foam was measured using a desiccator containing saturated calcium nitrate for maintaining a relative humidity of 50% at all times. A foam specimen of 25mm thickness was sealed to the open mouth of an impermeable dish containing water and placed inside the desiccator under ambient temperature. The test dish mouth had an area of 126 mm x 126 mm, defined as the area of the specimen exposed to water vapor. Periodic weighing of dish assembly and the test method specified in ASTM-E96 determined the rate of water flow through the specimen. The cellular morphologies of the foam system samples were investigated by Hitachi S-2500 as well as Hitachi TM-1000 Table-top scanning electron microscopy (SEM). Samples were freeze-fractured in liquid nitrogen and coated with gold before observation. Image J software was used to determine cell sizes. Viscosity of polyol components was measured under normal temperature of 25° C using Brookfield Viscosity Machine (BVT). The ingredients were polyol, catalysts, blowing agent, surfactant and the fiber (where applicable). The mixture was poured into a glass
jar, placed under the viscometer, and the test performed for 30 seconds with spindle number 64 and running speed of 50 and 100 RPM, and then averaged. Fourier transform infrared (FTIR) spectra of the foam samples were recorded using Brucker infrared spectrometer to measure the concentration of functional groups in polymer structure. A total of 32 scans were taken with a resolution of 4 cm\(^{-1}\) in frequency range of 4000 – 400 cm\(^{-1}\). The thermal resistance and R-value of the specimens was measured using Laser Comp FOX314 Heat Flow Meter instrument according to ASTM-C518. The compressive strength and modulus of the foam system was measured by INSTRON 3367 equipment in accordance with ASTM-D1621. The crosshead speed was 2.5 mm/min. and cell load of 2 kN with sample dimensions of 50 mm x 50 mm x 25 mm. The force required for 10% deformation of the original thickness has been considered as the compressive strength of the foam.

5.3 Results and discussion

5.3.1 Effect of viscosity during foaming process

Viscosity of a liquid is its resistance to flow. The presence of fiber in the polymer reduced the ease of flow and increased the viscosity of the matrix to a tar-like consistency. High viscosity affected the rising height and gel time of the foaming process. Gel time is the starting point of gel formation and production of urethane cross-links till the full expansion of the foam. Gel time increased with fiber concentration in foaming, suggesting that diffusion was reduced across the interfaces [6]. The rising height is the height of a free-rise cellular plastic to achieve its ultimate expansion under certain conditions [7]. The rising height of the foam samples were examined and recorded after each curing time. The results indicated that as the fiber content was increased the rising height of the fiber foam system was reduced proportionately compared to the neat
foam. This obviously led to the foam volume reduction as a whole. The viscosities of the polyol components with various fiber contents were measured (by Brookfield) and shown in Table 1

Table 1. Impact of cellulose fiber concentration as reinforcement in foam insulation.

<table>
<thead>
<tr>
<th>Item</th>
<th>Neat Foam</th>
<th>13php cellulose foam</th>
<th>26php cellulose foam</th>
<th>40php cellulose foam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rising height, (cm)</td>
<td>15.5</td>
<td>15</td>
<td>13</td>
<td>11</td>
</tr>
<tr>
<td>Reduction in Volume (%)</td>
<td>0</td>
<td>3</td>
<td>13</td>
<td>28</td>
</tr>
<tr>
<td>Gel Time (Second)</td>
<td>40</td>
<td>50</td>
<td>60</td>
<td>75</td>
</tr>
<tr>
<td>Viscosity Increase (%) (Polyol Component)</td>
<td>0</td>
<td>10</td>
<td>16</td>
<td>175</td>
</tr>
</tbody>
</table>

The orientation, concentration and aspect ratio of fiber would affect the performance of the reinforced composite foam. Although longer fiber length would provide better reinforcement, the optimum fiber length was found to be around 400 micron in which to obtain reasonably good fiber dispersion without increasing the matrix viscosity significantly. The results showed that if the fiber concentration remained below 26php, the viscosity increase would be about 16%, and it would still possible to spray it using conventional spray guns. Incorporation of fiber more than this amount requires technological advancement to the present spray foam system.

5.3.2 Density and compressive strength

Both neat and composite foam samples were prepared with the same formulation and analyzed to investigate the changes in density and compressive strength properties. They are illustrated in Figure 1–4 and presented in Table 2. Incorporation of cellulose fiber increased the bulk density
of the composite foam significantly (up to 60%) compared to the neat foam. The effect of fiber on density is more pronounced for lower dosage of fiber, and this effect becomes practically insignificant with further increase in the fiber content beyond 26%. The initial increase in foam density might be attributed to cell nucleation and heavier mass of the fiber. It is hypothesized that the presence of fiber led to the process of heterogeneous nucleation, producing smaller homogeneous cell sizes within cellular foam and thus increasing the cell density [8-10]. Surfaces promote nucleation because of wetting. Using Image J software, the average diameter of the cells in composite foam was observed to be smaller than the neat ones by up to 8%. Secondly, when fiber was embedded in foaming, although there was interaction on the surface of fiber with the polymer, fiber remained as a heavier solid material within the foam and could contribute to the density increase too [11]. As density was determined by mass over volume, the increase in foam mass was proportional to the fiber content. The fiber mass alone was estimated to be at least ten times heavier than the neat foam mass.

It was further evidenced that addition of fiber led to the shrinkage of the composite foam compared to foam without fiber. The rise-height was reduced by 3% for 13php, 13% for 26php, and 28% for 40php in the fiber foam system. It appeared that fiber influenced the molecular chain packing and mobility in the composite foam system.

![Figure 1. Effect of fiber content on density of the foam.](image-url)
Figure 2. Polynomial fitted line plot of density as a function of fiber content

Figure 3. Effect of fiber content on compressive strength of the foam.

Figure 4. Polynomial fitted line plot of compressive strength as a function of fiber content.
When a load is applied on a foam material, it will gradually be compressed, and the stress-strain curve experiences three regions of deformation - linear elasticity, plateau and densification [12]. The behavior is linear elastic under 5% of strain and as the load is increased, the foam cell walls begin to collapse (plateau region), until the opposing walls in the cells meet one another to elevate stress rapidly (densification region). Under the load, the urethane soft segments stretch, while the urethane hard segments carry the load and release it when the stress is removed. Therefore, it is important to have sufficient amount of urethane linkages that contain both segments within the network structure of PU foam.

The compressive strength of the composite foam system showed improvement with incorporation of cellulose fiber. It can be explained by the fact that cellulose fiber containing a large number of hydroxyl groups could form hydrogen bonds or other chemical bonds with the matrix, contributing to the foam enhancement. There were three free hydroxyl groups available in each monomer of cellulose chain which could easily interact with isocyanate active groups at the interfaces, and increase cross-linking within the foam network. As illustrated in Figure 5a & 5b of the SEM images, fiber was well embedded in the cell wall and interacted firmly with the matrix. This suggested that high strength of cellulose fiber, along with efficient interaction between matrix and the fiber, enhanced the composite foam compressive strength. However, as fiber concentration was increased above 26php, dispersion became a problem. The hydrophilic cellulose fiber was agglomerated and resulted in less number of available hydroxyl groups for fiber-matrix interactions.

Figure 6 represents FTIR spectra of neat (without fiber) and composite foams. The absorption peaks of urethane at 1740 cm\(^{-1}\) and urea at 1660 cm\(^{-1}\) indicated a good balance between the hard and soft segment production during foaming process. It seemed that for every urea link, an equal
amount of urethane was generated to link them together and eliminate the phase separation [13]. As a result a strong network structure was formed which could carry more load capacity.

Table 2. Mechanical and thermal properties of open-cell spray PU foam insulation*.

<table>
<thead>
<tr>
<th>Foam Type</th>
<th>Density (Kg/m$^3$)</th>
<th>Compressive strength (kPa)</th>
<th>Modulus of Elasticity (kPa)</th>
<th>Water Vapor Transmission (g/h·m$^2$)</th>
<th>Thermal Resistance (K.m$^2$/W)</th>
<th>R-Value (US) (h.ft$^2$.F/Btu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Foam</td>
<td>35 (±4)</td>
<td>40 (±10)</td>
<td>700</td>
<td>3.77</td>
<td>0.61</td>
<td>3.43</td>
</tr>
<tr>
<td>CF 13 php</td>
<td>46 (±1)</td>
<td>54 (±1)</td>
<td>908</td>
<td>2.15</td>
<td>0.65</td>
<td>3.69</td>
</tr>
<tr>
<td>CF 26 php</td>
<td>57 (±2)</td>
<td>50 (±5)</td>
<td>861</td>
<td>1.63</td>
<td>0.57</td>
<td>3.19</td>
</tr>
<tr>
<td>CF 40 php</td>
<td>54 (±2)</td>
<td>50 (±4)</td>
<td>846</td>
<td>1.30</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*Number of samples tested for water vapor transmission was 1 and for thermal resistance were 2.

Figure 5. SEM cellular foam images a) and b) Fiber compatibility c) Free fiber detection.
Figure 6. FTIR spectrum peaks of urethane carbonyl groups at 1740 cm$^{-1}$ and urea carbonyl groups at 1660 cm$^{-1}$.

Statistical Analysis

Properties of bio foam insulation vary with fiber content. To establish a relationship between variable Y (property) and variable X (fiber content) and to assess the validity of that relationship, the regression analysis has been performed. The observed data were plotted with their best fitted lines. $R^2$ value for density of cellulose fiber was 0.90, which was statistically significant at 95% confidence level ($\alpha=0.05$), representing inter-dependence between both variables. The regression fitted line indicated that density would increase with addition of fiber in foaming. On the other hand, the $R^2$ value of compressive strength was found to be 0.37 which was statistically insignificant and could not be explained by the model. However, the trend line showed that addition of cellulose fiber slightly improved the compressive strength of the composite foam.
5.3.3 Thermal resistance and R-value

Thermal resistance of a material is its resistance to heat flow. Foam insulations are rated in terms of their resistance to heat flow or R-value. The higher the resistance, the greater is the R-value and insulating effectiveness. The open-cell foam samples were analyzed by heat flow apparatus in terms of their heat conductivity and heat resistance, and determined their R-values. Table 2 shows R-values of the foam samples with and without fiber.

Results revealed that thermal resistance and R-value of the composite foam system have been slightly enhanced at 13php fiber content, and then reduced slightly at 26php. Thermal resistance of the foam would be greatly enhanced if less air could get into the system and be replaced by the escaped carbon dioxide [14]. During polyurethane foaming reaction the reaction rate of soy-based polyol with isocyanate is slower than the reaction between water and isocyanate. As fiber embedded in foaming, the viscosity increase further delayed this polyol-isocyanate reaction, forming a weaker three-dimensional foam network which was less capable of holding the pressure of carbon dioxide generated from the reaction. This delay was measured during foam preparation by gel time. The gel time was increased from 40 seconds (neat foam) to 50 seconds for 13php, to 60 seconds for 26php, and 75 seconds for 40php fiber foams (Table 1, section 5.3.1). Although the cell density increased in composite foam, most cells are raptured in open cell foam (85% to 90%) and the diffused gas could easily be replaced by air convection (especially when polymerization reaction is retarded) and increase thermal conductivity [15]. Natural fibers are also perforated materials and their presence in foam provides additional passages for the diffused gas to escape. Therefore, fiber foam with lower carbon dioxide content could have lower R-value and higher thermal conductivity. However, both thermal resistance and
R-value measurements of the neat and composite foams were above the minimum requirements specified by CAN/ULC-S706-09.

5.3.4 Moisture permeability

Open-cell spray polyurethane foam is airtight foam insulation. Once it is cured, it acts as a good moisture barrier layer. However, condensation occurs when water vapor moves through the insulation from warmer to a cooler area and affects the thermal efficiency of the insulation. Therefore, moisture permeability becomes an important property of the foam insulation and can be measured by the rate of water vapor flowing through the foam material of unit area and thickness under particular temperature and humidity conditions [16].

Water vapor transmission test was carried out to measure moisture permeability of the foam system. An apparatus was built and the permeability of water vapor through the foam sample material was recorded during different time intervals. It was observed that the passage of water vapor through the composite foam materials was significantly reduced compared to the non-fiber foam (Table 2), suggesting that cellulose fiber restricted the flow of water vapor. The moisture permeability was proportionally decreased with the increase in fiber concentration. Figure 7 illustrates slope of the lines representing rate of water vapor transmission for the foam system.

![Figure 7. Rate of water vapor transmission for the foam system](image-url)
The reduction in moisture permeability could be attributed to two factors. Firstly, as water vapors were permeated through the composite foam, some were absorbed by the fiber, allowing less water vapor to pass through. Cellulose is known for high moisture absorption because of hydrogen bonding between hydroxyl groups in fiber cell wall and water molecules. This action led to fiber swelling or moisture build-up in the fiber, and also in the fiber-matrix interface [17]. Secondly, incorporation of fiber increased the cell density of the composite foam and generated smaller cells (as discussed in section 5.3.2) and delayed the water vapor flow through the voids.

5.4 Characterization of composite foam system

The knowledge of foam cellular structure aids in improving its thermal and mechanical properties. Addition of fiber requires morphological analysis to observe the effects of fiber in foam insulation.

5.4.1 Morphological characterization of composite foam

The fiber used in PU foam must have a good compatibility with the selected resin in order to provide a good reinforcement. Synthetic glass and nylon fibers are synthesized from petrochemical substances and are mostly hydrophobic and strong, making them compatible with the resin and improving the strength of the matrix. But natural cellulose and wood fibers compatibility have always raised question amongst researchers. Almost all resins are hydrophobic and not compatible with hydrophilic character of natural fibers. This creates weakness in adhesion and wettability between the fiber and the polymer, and results in poor mechanical properties of the composite products.

Fiber size and dispersion of fiber within the matrix significantly affect the strength of the composite foam as well. A small fiber size with low aspect ratio holds a larger surface area
which could be non-reactive to the matrix, creating more stress points and resulting in weak material strength. While long fibers provide more reinforcement than short fibers, the latter have less impact on the viscosity of the mixture. Thus a greater amount of short fiber could be incorporated in the mixture at a given viscosity to achieve higher reinforcement. Short fibers also provide a better dispersion within the matrix than long fibers. The confocal microscopy image (Figure 8) shows that although the fiber was distributed fairly within the composite foam, the dispersion was not uniform. The agglomeration of fiber (dark areas) could be clearly seen.

Figure 8. Confocal microscopy image of fiber dispersion.

It is well known that hydrogen bonding contributes a great deal to the strength and modulus of PU foam network. If foam molecules react with cellulose fiber through the reaction between the isocyanate –NCO groups and the –OH groups on the surface of the fibril they generate additional cross-links. This is a positive effect. If the fiber could not participate in the reaction, it would interfere with hydrogen bonding between urethane molecules, causing a negative effect (as observed in SEM image in Figure 5c, some fibers did not interact with the resin). The overall performance of composite foam depends on the competition between the positive and negative effects. The morphological observations and enhancement in compressive strength proved that
the positive effect dominated here, enhancing cross-linking within the fiber foam system network. This effect was also demonstrated by Xia Cao et al, 2005 [6], in trying to incorporate clay in foaming. This interference may be illustrated below in Figure 9.

![Diagram of hydrogen bonding between urea and urethane linkages](image)

Figure 9. Hydrogen bonding between urea and urethane linkages

The reaction between isocyanate active groups and the hydroxyl groups of cellulose fiber could also be demonstrated by FTIR spectra changes as shown in Figure 10. The free –NCO absorption peaks at 2270 cm$^{-1}$ were lowered in composite foam with 13php and 26php fiber contents compared to the neat foam without fiber, indicating reactivity between the fiber and free –NCO groups. The unreacted isocyanate amount was increased at 40php fiber concentration as viscosity of the matrix was elevated significantly and interfered with foaming process.

![FTIR spectra of free –NCO absorption peaks at 2275cm$^{-1}$](image)

Figure 10. FTIR spectra of free –NCO absorption peaks at 2275cm$^{-1}$
5.5 Conclusions

Spray foam insulation was produced using sustainable soy-based polyol and water as blowing agent. Cellulose fiber was incorporated in foaming up to 40php in three stages and its impact was investigated in terms of mechanical and thermal properties as well as foam morphological characterization. It was demonstrated that presence of fiber in foaming increased cell density due to nucleation process and increased the bulk density of the composite foam. The increased cell density reduced moisture permeability in composite foam. Good adhesion between resin and fiber at interfaces enhanced the compressive strength of the composite foam system. The interaction of fiber and polymer was efficient at lower fiber concentration and slightly improved the thermal resistance of the insulation foam. At higher fiber concentration, the viscosity increase and also agglomeration of fiber (due to its hydrophilic nature) which provided open channels, allowed more diffused gas to escape from the material and slightly reduced thermal resistance of the composite foam. Pre-treatment of fiber would help to separate fibers from each other, and eliminate hydrogen bonds holding them together. As fiber was embedded in the matrix, the increased viscosity affected the foaming process through ease of flow. Although the impact was not significant, the gel time was increased and resulted reduction in composite foam volume proportionate to the fiber content. The polyol viscosity was significantly increased with incorporation of fiber above 26php.
References


CHAPTER 6.0

Novel Bio-based Polyurethane Spray Foam Insulations for Light Weight Wall Panels and Their Performances under Monotonic and Static Cyclic Shear Forces
Abstract

This work was dedicated to investigation of the effects of bio-based polyurethane (PU) foam cores (neat and composite foams) on the performance of small-scale wooden wall panels under monotonic and static cyclic shear loads. Adding wood fiber resulted in a reduction in compressive properties of the foam while tensile modulus slightly increased. Monotonic and static cyclic shear tests showed that inclusion of the foam core increased the maximum strength of the panels significantly. Panels containing composite foam cores had the highest shear strengths.

6.1 Introduction

Rigid polyurethane foams have gained a growing attention in a variety of applications due to their unique set of characteristics such as excellent thermal insulation properties, durability, and relatively high specific mechanical properties (strength to weight ratio) [1-3]. Performance of PU foams can be optimized for a wide range of applications by a well-designed formulation of polyols, isocyanates, catalysts, surfactants, and blowing agents. A change in formulation could alter the properties of the foams by changing their cellular structure and also properties of the polymer constituent [4,5].

During the past decades, concerns caused by the environmental impacts of petroleum based polyurethane foams have driven researchers towards fabrication of these foams utilizing renewable resources. As a result, use of bio-based polyol derived from chemically modified plant oils, especially soy bean oil, has been suggested in a number of research works [6-13].
Production of soy-based polyol is possible via the introduction of functional groups (hydroxyl groups) into unsaturated sites in triglyceride molecules which are present in the oil. Several techniques have already been proposed for the production of polyol from soybean oil [10-12].

Inclusion of natural fibers to PU foams has also been proposed to reduce their environmental impacts, reduce their cost, and possibly modify their properties [5,7,14-20]. Main advantages of natural fibers over synthetic fibers include their low cost, low density, renewability, abundance, and low equipment wear during production. Natural fibers are known to have poor compatibility with hydrophobic polymers [21-23]. In case of PU based materials, however, creation of chemical bonds between hydroxyl groups on the surfaces of natural fibers and isocyanate is expected to create strong interfacial adhesion between fibers and the PU matrix [24,25].

Introduction of natural fibers to PU foams has also been reported to increase the rate of their biological degradation after disposal [26]. Due to their cross-linked structure, thermosetting polymers cannot be readily recycled which adds to their environmental issues. Thus, biodegradability is especially important in case of thermosetting polymers, including PU foams.

Earthquakes and high winds are the main sources that apply lateral forces to the wall panels which are parallel to the direction of the force (shear walls) [27]. In wood-frame buildings, which are particularly common in residential and low-rise commercial buildings of North America, distortion of shear walls due to such lateral forces is a common phenomenon. As a result, such forces are usually referred to as racking forces. Lightweight wooden wall panels are usually made of a lumber frame, sheathing materials on one or both sides of frames (usually plywood or gypsum), and fasteners [28,29]. Performance of these wall panels determines the structural integrity of the entire building during hurricanes or seismic forces [30]. Due to the fact that a
majority of North American population lives in hurricane prone regions, improving the racking performance of the shear walls is believed to be absolutely necessary.

Despite the extensive use of PU spray foams as insulating materials inside wall panels [31,32], the authors noticed a significant lack of research regarding the contribution of foam cores to the shear force capacity of wooden wall panels. As a result, this work has been devoted to the characterization of structural behavior of small scale wooden wall panels under monotonic and static cyclic racking forces, before and after the introduction of a rigid bio-based polyurethane foam core. The measurement of racking performance of small scale panels is a common method for evaluation of structural performance of full scale (8 ft× 8 ft) walls [28]. Effects of inclusion of wood fibers in PU foam on strength of the panels have also been evaluated. This study also provides information on the density, tensile properties and compressive properties of the prepared bio-based PU neat and composite foams.

The formulation was modified in structural integrity experiment to reflect a stronger foam network (closed-cell) to withstand the applied shear forces. The polylol used in structural integrity experiment had a higher hydroxyl groups than that of polylol used in other experiments in other chapters to enhance polymerization reaction. As more –OH groups of polylol participated in the polymerization reaction, polyurethane solid structure would increase to such extent that more closed-cell bubbles would form. Promoting this reaction would increase the bubble formation rather than bubble expansion with more carbon dioxide entrapped inside the cells. This would enhance the foam properties especially density and compressive strength in the wall panels and would increase shear resistance of buildings against applied lateral forces [33-35]. Open-cell and closed-cell foams were discussed in section 5.1.1.
6.2 Preparation and characterization of foams

6.2.1 Materials

Commercially available soybean oil based polyol (X-0110) was provided by Cargill. Other ingredients of the foam including isocyanate, catalyst, co-catalyst and surfactant were all selected from commercially available sources [3]. Distilled water was used as the blowing agent. Wood fiber from White Birch was supplied by FPInnovations, Canada. Fine wood fibers were collected after grinding and passing through a 30 mesh sieve.

6.2.2 Preparation of PU neat and composite foams

PU neat foams, with an isocyanate index of 140, were produced according to the formulation (Table 1) suggested by Faruk et al. [3] using free rise pouring technique. In case of neat PU foam, without wood fiber, 100g of soy-based polyol was mixed with suitable amounts of the additives (catalyst, co-catalyst, surfactant, and distilled water). The mixture was homogenized for three minutes at room temperature. Isocyanate was then added to the mixture followed by 20 seconds of vigorous mixing. At this point, the mixture was transferred to a wooden mold with dimensions of 20×18.5×11.5 cm$^3$.

<table>
<thead>
<tr>
<th>Components</th>
<th>Commercial Name</th>
<th>Php$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyol</td>
<td>BiOH X-110</td>
<td>100</td>
</tr>
<tr>
<td>Catalyst I</td>
<td>Polycat 9</td>
<td>0.26</td>
</tr>
<tr>
<td>Catalyst II</td>
<td>33 LV</td>
<td>2</td>
</tr>
<tr>
<td>Surfactant</td>
<td>DC 5357</td>
<td>1.50</td>
</tr>
<tr>
<td>Blowing agent</td>
<td>H$_2$O</td>
<td>2.0</td>
</tr>
<tr>
<td>Isocyanate Index</td>
<td>Robinate M</td>
<td>140</td>
</tr>
</tbody>
</table>

$^1$ Parts per hundred grams of polyol

In case of composite foams containing wood fiber, the processing of foam was as follows: (i) 100g of polyol was mixed with 20g of wood fibers for 6 minutes in order to fully disperse the
fibers, (ii) additives were then added followed by 3 more minutes of mixing, (iii) in the end, isocyanate was added and mixing was continued for 20 seconds before transferring the mixture into the wooden mold.

6.2.3 Characterization of the neat and composite foams

Densities of the foams were obtained according to ASTM D1622-09 using specimens with dimensions of 5×5×3 cm³.

Tensile properties of the neat and composite foams were measured according to ASTM D1623 using five type C specimens (with dimensions of 5×5×3 cm³) for each sample. The tests were done using a Zwick universal testing machine (Zwick/Z100, Zwick GmbH & Co. KG, Germany) at a crosshead speed of 1.3 mm/min. Average values of the tensile modulus, tensile strength, and tensile elongation at break of the samples were reported.

Compressive properties of the foams were measured according to ASTM D3574 using five specimens (with dimensions of 5×5×2.5 cm³) for each sample. The measurements were done using Instron universal testing machine (Model 3367) at a crosshead speed of 2.5 mm/min. Average values for compressive modulus and compressive strength of the samples were reported.

6.2.4 Properties of neat and composite foams

Densities, compressive properties, and tensile properties of neat PU foam and PU composite foam are summarized in Table 2. One of the most important characteristics of PU foams is their density. Addition of wood fiber decreased the density of the foam. Density of the neat rigid foam was 68.6 kg/m³ compared to 52.5 kg/m³ for the composite foam (23% reduction in density). This behavior could be attributed to the introduction of wood fiber in foaming which increased the gel time (from 40 sec. to 55 sec.) and delayed the polymerization reaction. Fewer bubbles were
formed due to less ease of flow. This later effect decreased polyurethane solid structure resulting in reduction of bulk density of the fiber foam. Banik and Sain [10] reported that the introduction of 8 parts per hundred parts of polyol (php) refined paper fiber to bio-based polyurethane foam caused a reduction in the density of the foam. Using IR spectroscopy, they also reported that the composite foams had a higher concentration of urea linkages compared to the neat foam which proves that the chemistry of the foaming reaction was altered.

Table 2 shows the inclusion of the wood fibers caused a reduction in the compressive properties of the foams. Compressive modulus and strength of neat PU foam were reduced about 30%. Such reduction in the compressive properties of the foam can be linked to the reduction in its density (which signals a reduction in the cell-wall thickness). On the other hand, it is shown in Table 2 that inclusion of 20 php of wood fiber to the neat bio-based foam increased its tensile modulus slightly. Tensile modulus of the neat foam was increased from 38.6 MPa to 41.1 MPa after the inclusion of wood fibers. Tensile strength and elongation at break of the composite foam were only slightly lower than the neat foam due to a reduction in deformability. The fact that the tensile properties of the foam were not reduced upon inclusion of the fibers is due to the reinforcing effect of the fibers which seems to have neutralized the negative effects of the reduction in cell-wall thickness. The results from Table 2 suggest that wood fibers had a more noticeable reinforcing ability under tensile loads compared to compressive loads.

If we statistically normalize the value of tensile strength and compressive strength of the composite foam with respect to density (68.6/52.5 = 1.3) and recalculate the values, the tensile strength increases, which signifies fiber as reinforcement for foamed composite.
Stress-strain curves of neat and composite foams under tensile and compressive loads are also shown in Figure 1. It is clearly shown that although compressive properties of the neat foam were noticeably higher, the tensile behaviors of the two foams were very similar.

Table 2. Characteristics of the neat and composite foams.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (kg/m$^3$)</th>
<th>Tensile properties</th>
<th>Compressive properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Modulus (MPa)</td>
<td>Strength (kPa)</td>
</tr>
<tr>
<td>Neat foam</td>
<td>68.6 (0.9)$^a$</td>
<td>38.6 (2.2)</td>
<td>317 (21)</td>
</tr>
<tr>
<td>Composite foam</td>
<td>52.5 (1.1)</td>
<td>41.1 (2.5)</td>
<td>309 (17)</td>
</tr>
<tr>
<td>Composite foam (After normalization)</td>
<td>53.4</td>
<td>401</td>
<td>2.6</td>
</tr>
</tbody>
</table>

$^a$ The numbers in the parenthesis denote standard deviations.

Figure 1. Stress-strain curves for tensile and compressive responses of neat and composite foams.
6.3 Preparation and characterization of the wall panels

6.3.1 Materials

Small scale panels were constructed using materials that are typically utilized in construction of wood-frame wall panels. The panels were constructed using 5.1×10.2 cm² (2 inches by 4 inches) Spruce-Pine-Fir studs, 1 cm (3/8 inch) thick Spruce plywood sheathing, 5.1 cm (2 inches) 6d common nails and 7.6 cm (3 inches) screws.

6.3.2 Construction of small scale wall panels

The wooden panels were each 61 cm (24 inches) high and 45.7 cm (18 inches) wide framed by 5.1 cm (2 inches) ×10.2 cm (4 inches) timber and sheathed with 1 cm (3/8 inch) thick plywood on both sides. Each of the top and bottom (shorter) studs was fastened to the side (longer) studs using four screws. Each plywood sheathing was fastened to the frame using sixteen 6d common nails spaced 15.2 cm (6 inches) apart on the sides and 10.2 cm (4 inches) apart on the top and bottom studs. The nails were placed 2.5 cm (1 inch) from the edges in all studs.

In case of panels including neat or composite PU foams, one sheathing was fastened to each frame in the beginning. Neat or composite PU foams were prepared according to the method described in Section 2.2 based on 1100 g of soy based polyol. After the addition of isocyanate part and mixing for 20 seconds, the mixture was transferred into the constructed panel and the foam was left to rise freely in the direction of the thickness of panels, as shown in Figure 2. The excess foam was then cut after 24 hours and the second sheathing was fastened to complete the panels. Both polyurethane foams were observed to have complete adhesion with the wood panel. This is due to the creation of chemical bonds between isocyanate groups from the foam and to a greater extent with the hydroxyl groups of cellulose and to a lesser extent to hemi-cellulose and lignin on the surface of the wood [14].
Four empty panels, four panels with neat foam, and four panels with composite foam were constructed and stored indoors at least one month before conducting the tests.

![Image of wooden panels](image)

Figure 2. Wooden panels before cutting the excess foam and fastening the second sheathing.

6.3.3 Characterization of small scale wall panels

6.3.3.1 Testing equipment

The tests were conducted by applying unidirectional displacement using a tri-axial loading apparatus available in Structures Testing Facility at University of Toronto. Specimens were mounted between reaction beam at the top of the specimen and load transfer beam at the bottom of the specimen. The connection between the beams and the specimen were made with two bolts through the timber frame. The reaction beam was a stiff element connected to the reaction column to provide a fixed support boundary condition at the top of the specimen. Between the load transfer beam and the mounting table, a low friction pad was used to minimize force transfer through friction. A pancake-type load cell was attached at the end of the load transfer beam. The load path from the actuator to the specimen is as: actuator, mounting table, load cell, load
transfer beam, and specimen. The load transfer beam provided flanges which were used to restrict uplift of the beam. The selected load cell was an F141 fatigue rated 5kip capacity load cell. The output from the load cell was fed to a Futek IPM650 signal conditioner and indicator, sampling at 1200 samples per second. Displacement of the loading apparatus was recorded using the LVDT in the actuator. The experimental setup is illustrated in Figure 3, an image of the actual experimental setup is also provided in Figure 4.

Figure 3. The experimental apparatus used to characterize the panels with the component labels.

Figure 4. Front view of the actual experimental set up.
6.3.3.2 Testing procedures

Two tests, namely monotonic and static cyclic shear tests, were conducted to study the behavior of the lightweight wooden panels under shear loads. Three types of specimens were used: control specimens without foam, specimens with neat foam, and specimens with composite foam. For each type of specimens, a total of four specimens were tested. One specimen was tested in monotonic pushover and the remaining three specimens were tested under cyclic load. The monotonic test was designed to study the behavior of the frame in monotonic loading. The static cyclic test was a quasi-static test designed to study the hysteretic behavior of the frames in cyclic loading. Because the objective of the study was to investigate the lateral force capacity of the wood panels under static load, the cyclic load was applied at slow rate such that the rate-dependent effects, such as viscosity of materials, would not influence the measured force. The procedures for each test were developed based on ASTM E2126 and are outlined in detail below:

In pushover tests, displacement was applied at the base of the specimen in push or pull along its strong axis at a rate of 3mm/min (0.5% shear strain per minute), up to a maximum stroke of 76.2mm (12.5% shear strain). Specimen was sheared until the maximum stroke or 6mm beyond observed failure or significant loss of strength.

In static cyclic tests:

1. Displacement was applied at the base of the specimen in push along its strong axis up to a predetermined stroke. The stroke was selected according to the cycle number and the strain observed for the First Major Event (FME) during the pushover test. Refer to ASTM E2126 for the dependency of stroke to cycle number. The frequency of excitation was 0.2Hz.

2. Displacement was applied as a pull of twice the predetermined stroke, to strain the specimen equivalently, in the opposite direction.
3. Steps 1 and 2 were repeated twice more, for a total of three cycles at the predetermined stroke.

4. Steps 1-3 were repeated once for each predetermined stroke, at 25%, 50%, and 75% of FME.

5. For test iterations at 100% FME and above, the displacement profile was split into a decay phase and a recovery phase (also illustrated in ASTM E2126). The first four cycles for each iteration had maximum displacements of 100%, 75%, 50%, and 25% of predetermined stroke. After the first four cycles, the recovery phase took place, where the specimen was subjected to three cycles at 100% predetermined stroke before initiating the next iteration.

6. Step 5 was repeated for increasing predetermined stroke by 50% of FME per iteration, (as suggested by ASTM E2126). This was repeated until the specimen failed.

6.3.4 Properties of wall panels

6.3.4.1 Performance of wall panels under monotonic shear load (pushover tests)

Behaviors of the panels under monotonic shear loads are shown in Figure 5. In general, the specimens behaved similarly at low shear deformations. But it is clearly shown in Figure 5 that the inclusion of both foam cores in the panels caused a significant increase in their maximum shear resistance. Initially the specimens showed similar stiffness until about two millimeters of displacement, and then experienced an increase in stiffness. This stiffness increase is presumed to be caused by the engaging of the plywood sheathings. At about four millimeters displacement, the foam filled specimens diverged from the control specimen (empty panel). The control frame experienced a significant stiffness loss as the nails holding the plywood to the frame yielded, and the specimen experienced a plateau at around 8.0kN of maximum force. It is observed that the foam-filled frames retained higher stiffness at this point due to the additional shear reinforcement provided by the foam core. Shortly after the two foam-filled specimens diverged from the control
specimen (at about 8 mm displacement), the specimen containing neat foam experienced a stiffness loss as compared to the specimen with composite foam, and both foam specimens followed a yielding plateau shape similar to the control specimen. It was shown that the panel containing the composite foam had the highest maximum strength of about 12.0 kN (50% improvement in strength over the control specimen). It was shown in Section 2.4 that neat foam had significantly higher compressive modulus and strength compared to composite foam while tensile modulus of composite foam was slightly higher than the neat foam. Figure 5, on the other hand, shows that the panel containing neat foam core supported a slightly lower maximum force (about 10.7 kN) than the panel with composite foam core. Such behavior suggests that the performance of the panels under shear loads relies mainly on the tensile properties of the foam core rather than its compressive properties.

After diverging, all of the specimens followed a similar trend and maintained a nearly constant differential between each specimen. A specimen was considered failed once it had reached a peak and lost strength or the wooden frame split and caused an immediate strength loss. Experimentation was also limited within the displacement bounds of the actuators, typically supporting a maximum displacement of 50mm. At high displacements, the force drops were observed which were believed to be caused by slippage of the nails in the specimens. Significant drops in force carried by the specimens corresponded to large slips of the plywood nails or splitting of the frame studs.
6.3.4.2 Performance of wall panels under static cyclic shear load

Figures 6 and 7 present the performances of the panels under static cyclic shear forces in comparison with their monotonic responses (adopted from Section 3.4.1). The average backbone curves of each static cyclic test were also created and analyzed as prescribed in ASTM E2126. This process involves identifying the maximum and minimum forces in each cycle of testing to define the trend the specimen experiences in cyclic excitation. The figures show that the static cyclic responses of the panels were in agreement with their monotonic responses from pushover tests. Figure 6 shows that the average backbone curves of the samples followed a similar path as their pushover curves. It is shown in Figure 7 that the backbone curves of the panels containing foam cores, either neat or composite foams were still higher than the panel without the foam core. According to Figure 7, maximum strengths of the empty panel, and the panels with neat and composite foams during the cyclic tests were 7.3, 8.6 and 8.9 kN, respectively. With the test apparatus used, frictional forces between the specimen and the supports were slightly greater when applying negative shear (left side of the diagrams in Figures 6 and 7) which may have led to the reduction of the measured force. Thus, negative shear was not used as the basis for the above discussions.
Figure 6. Static cyclic behavior of (a) empty panel, (b) panel with neat foam, and (c) panel with composite foam compared with their monotonic response.
6.3.4.3 Failure modes

The specimens exhibited two common modes of failure of the wooden frame or polyurethane foam fill. The most common failure mode observed during testing was the yielding and deforming of the nails attaching the plywood sheathing to the timber frame, typically at the shorter studs on the top and bottom of the specimens. Yielding of the nails was typically observed prior to occurrence of the plateaus in the specimen responses, but attributed significant stiffness losses over the duration of testing as more nails failed. For each specimen, control or foam filled, the plywood sheathings were responsible for carrying the majority of shear force in the specimen, due to having the greatest shear stiffness. As such, the majority of the shear forces in the frame were transferred to the plywood sheathings through the connecting nails. As shear force increased, the nails were subjected to increased shearing load and deformation, ultimately snapping most nails in two. The contribution of this failure mode to the overall behavior of the specimens is best observed in the pushover curves; large drops in the carrying capacity of the frames can be observed and coincided with abrupt snapping of the nails in most instances. The second most common failure mode observed in the specimens was the separation of polyurethane
foam from the timber frame and the sheathing plywood. This failure mode was observed in each foam specimen subjected to cyclic excitation and occasionally in monotonic loading. This failure mode was caused when the foam was subjected to significant tension and typically caused significant stiffness degradation of cyclic loaded specimens. Figure 8 shows photographs of the mentioned failure modes. The third failure after cyclic test was small diagonal cracks across the foam near the edges in both fiber and neat foam. They looked alike and no contribution was made by fiber. These failures, however, does not reflect the true behavior of actual foam insulation walls and a larger scale and more comprehensive shear tests may be performed to verify these results in the future.

Figure 8. Common failure modes in wall panels: (a) yielding and deforming of nails, (b) diagonal cracks in fiber and none fiber foams, and (c) de-bonding of the foam and wooden frame.
6.4 Conclusions

Novel bio-based PU foam cores (neat and composite foams) were proposed as reinforcement for lightweight wall panels under monotonic and static cyclic shear loads. Twelve panels were constructed (four empty panels, four panels with neat PU foam cores, and four panels with composite PU foam cores) utilizing commonly used materials and tested using a tri-axial loading apparatus. Mechanical properties of the foams were also reported along with their densities. It was shown that inclusion of wood fiber (20 php) decreased the density and compressive properties of PU foam. This was ascribed to delaying in polymerization reaction decreasing polyurethane solid structure. Tensile tests showed that the fibers caused an increase in the tensile modulus of the foam due to the reinforcing effect of fibers under tensile loads. Pushover tests revealed that both foams (neat and composite foam) increased the shear strength of the panels substantially. Interestingly, it was observed that the panels with composite foam core had the highest strength (50% higher than the control panel). It is speculated that this behavior is because the strengths of the panels were controlled by tensile strength of the foam cores rather than their compressive strength. Static cyclic responses of the panels were similar to their monotonic responses. Backbone curves of the panels with both foam cores were higher than that of the empty panel. Failures of the specimen were mainly caused by yielding of nails and also debonding of foam cores and the frames at large deformations.

This study suggests that the utilization of the proposed rigid bio-based PU foam as core layer in wall panels is a promising approach towards the enhancement of their shear strength. Main applications of such structures are in residential buildings and low-rise commercial buildings. The enhancement in the walls properties is expected to increase the resistance of the buildings against lateral forces from winds and earthquake loads. Further larger scale experiments (and
also dynamic experiments) are required to fully validate the performance of a wall panel with composite foam core.
References


CHAPTER 7.0

Conclusions and Recommendations
7.1 Conclusions and recommendations

Water-blown spray polyurethane foam (SPF) insulation was successfully produced via a free rise method, using sustainable soy-based polyol. Two types of fiber, wood fiber and cellulose fiber were incorporated in foaming in three stages, 13php, 26php, and 40php. The impact of fiber in each composite foam system was investigated in comparison with control foam (no fiber), in terms of thermal and mechanical properties as well as morphological characterization.

The following conclusions were drawn from the study:

1. The control or neat biofoam prepared by the formulation (Table 2, Chapter 1) had comparable properties; same or even better than commercially available foams. The amount of water added as blowing agent in foaming, affected the cell structure or cell size.

2. As fiber was embedded in spray foam the amount of fiber had significant effect on foam quality. At lower fiber content (below 26php) composite foam quality was mostly improved whereas at high fiber concentration (40php), the fiber mostly functioned as filler.

3. Fiber highly hydrophilic in nature and tends to agglomerate at higher fiber concentration.

4. It was demonstrated that presence of fiber in foaming increased the density of both composite foam systems due to nucleation process and fiber mass. SEM images indicated that these nucleating sites generated smaller and more homogeneous cells, increasing cell density.

5. Compatibility of resin with fiber is the most important factor affecting composite foam properties. Natural fibers are highly hydrophilic and resins are highly hydrophobic. The analysis indicated that, although there was a fairly good compatibility between them,
wood fiber was less compatible with matrix as compared to cellulose fiber. The cause was unclear, perhaps due to less accessibility of lignin hydroxyl groups.

6. The compressive strength of cellulose fiber composites was improved while that of wood fiber composites was slightly reduced.

7. SEM images revealed that cellulose fiber was efficiently embedded in cell walls. The -OH groups of cellulose, just like polyol –OH, reacted with isocyanate and generated additional urethane linkages that increased cross-linking within the composite foam network and enhanced the foam. FTIR experiments showed that more urea linkages were produced in wood fiber foam which led to phase separation within the polymer producing foam with lower compressive strength. Good balanced urea-urethane linkages are the requirement of a strong and stable network.

8. Thermal Resistance of wood fiber foam was slightly decreased due to higher viscosity and lesser adhesion between fiber and matrix in which allowed more diffused gas to escape from the material during foaming process. However, it slightly improved in the case of cellulose fiber foam at lower fiber content. As per thermal degradation, addition of fiber made no differences in delaying the degradation temperatures of both composite foams.

9. The moisture permeability through the composite materials was significantly reduced with respect to non-fiber reinforced foam. This may be attributed to moisture absorption of fiber due to swelling effect as well as the cell density increase in which delayed the passage of water vapor through voids.

10. As more fiber was introduced into the foaming, viscosity increased resulting delay in ease of flow and foam expansion during foaming process. The viscosity increase due to incorporation of fiber in polyol was found to be below 20% as long as fiber content
remains under 26php, and mixture could still be sprayed with conventional spray device. Incorporation of higher fiber content than 26php requires improvement to present spray foam equipment system.

11. High viscosity of resin also reduced the rising height of the composite foam systems due to less ease of flow and increased the gel time during foaming process. This led to reduction in composite foam volume which was proportionate to the fiber content.

12. The reinforcing quality of fiber in foaming was affected by fiber size and dispersion of fiber within the matrix. Fibers were grinded to an optimum size to reach a compromise between the viscosity increase and reinforcing effectiveness. In general, short fibers disperse better than long fibers and increase wetting between interfaces, improving adhesion. The confocal microscopy image of wood fiber foam showed that although fiber was distributed fairly within the foam matrix, the dispersion was not uniform throughout. Fiber agglomeration could be detected within the image.

13. Structural integrity performance demonstrated that application of Soy-based spray foam insulation could increase the shear resistance of wall panels against lateral forces.

14. The reinforcement of spray foam insulation with wood fiber enhanced shear resistance against wind forces due to fiber strength. The performance of monotonic test revealed that the shear strength of composite foam panels was increased by 18% as compared to non-fiber foam panels. It is assumed that this behavior was because the strength of panels was mostly controlled by tensile strength of the composite foam.

15. Wall panels under static cyclic test responded similar behavior as compared to monotonic or pushover but to a lesser extent. The shear strength of the composite foam panels was increased by 5% only with respect to none fiber foam panels. In this kind of test the specimen was subjected to alternating compression and tension forces for several times.
during the test just like seismic loads and weakened the fiber-matrix adhesion. The analysis indicated that incorporation of fiber did not improve the shear resistance against seismic loads.

**Scientific and engineering significance of the work:**

To the best of my knowledge it is the first attempt to a systematic study of the effect of natural fiber as a reinforcement substrate in bio-based insulation foam. Scientific knowledge derived from this work is original and makes a novel contribution to the better understanding of the underlying theory and practices of wood and cellulosic fibre dispersion in a bio-based liquid resin system that renders to spray under a controlled viscosity condition.

An improved understanding of the spray foam structure in relation to resin chemistry, fibre type and foaming reactions also generated new knowledge to this field.

Engineering significance of the work is in the development of formulation that can be practiced in a prototype form and enable to study the engineering principal of structure stability of such bio-foam under real life cyclic stress condition. No such work has been published earlier and it generated a significant knowledge base in terms of applicability of such foam in future building applications.

**Future work recommendation:**

- A good adhesion between the matrix and the fiber, which is vital to the performance of the composite foam insulation, can be achieved by surface modification of natural fibers such as plasma or corona treatment and graft copolymerization of polymers onto the fiber surface [1, 2]. Pre-treatment of fiber would help to separate fibers from each other and eliminate hydrogen bonds holding them together.

- Although it was possible to achieve high fiber content foam insulation of up to 40php without major impact on foaming reactions, the analysis demonstrated that the fiber content as reinforcement may not exceed more than 26php in order to achieve optimum
viscosity to be able to spray it with conventional spray gun system. However, the spraying technology could be improved to accommodate more fiber content in foaming.

- Larger scale experiments are to be conducted to validate the performances of composite foam filled panels against shear loads in structural integrity. As the results were promising in case of shear strength, dynamic experiments may also be conducted in the future.

- It is also recommended that flame spread test (ASTM-E84), fungi resistance test (ASTM-C1338), and air permeability test (ASTM-E283) are to be performed in the future.
References


### Thermal Degradation Temperatures of Cellulose Composite Foam System

Table 1. Thermal degradation temperatures of neat and cellulose composite foam system.

<table>
<thead>
<tr>
<th>Foam Type</th>
<th>Degradation Temperature (°C)</th>
<th>Residue in % @ 600 °C</th>
</tr>
</thead>
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<tr>
<td></td>
<td>T5</td>
<td>T50</td>
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<tr>
<td>Neat Foam</td>
<td>272</td>
<td>390</td>
</tr>
<tr>
<td>Cellulose fiber foam 13php</td>
<td>271</td>
<td>395</td>
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<tr>
<td>Cellulose fiber foam 26php</td>
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<td>390</td>
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<td>Cellulose fiber foam 40php</td>
<td>267</td>
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<tr>
<td>Cellulose fiber only</td>
<td>318</td>
<td>354</td>
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</table>

T5 = Degradation temperature at 5% weight loss  
T50 = Degradation temperature at 50% weight loss  
T75 = Degradation temperature at 75% weight loss
Appendix - II

Statistical Analysis for Density and Compressive Strength of Biofoam Insulation

Regression Analysis

Properties of bio foam insulation would vary with fiber content. To establish a relationship between these two variables and to assess the strength of that relationship the regression analysis has been performed.

Regression analysis

Excel Software Regression Analysis was utilized to establish a relationship between the variable Y (property) and variable X (fiber content). For that matter, six samples from each bio foam scenario containing 0 php, 13 php, 26 php, and 40 php of wood or cellulose fiber were tested and property values were tabulated below. Regression analysis was performed on each set of data to obtain $R^2$ value, average and standard deviation of each scenario samples. The observed data were plotted with their fitted trend lines and standard deviations bar diagrams.

$R^2$ - Value

When the observations are scattered quiet randomly around the trend line or far from it, the $R^2$ value is Low and the relationship between two variables get weaker. When the observations are closer to the trend line, the value of $R^2$ is high and the relationship gets stronger. $R^2$ value varies between 1 and 0 indicating the proportion of variable to each other. As $R^2$ decreases the actual relationship gets weaker, and X explaining less of Y and the relationship become weaker. At $R^2$ =0 there is no relationship between the variables.

<table>
<thead>
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<th>$R^2$- Value</th>
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<td>Density – WF</td>
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<tr>
<td>Density – CF</td>
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<td>Modulus of Elasticity – CF</td>
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Note: WF = Wood fiber CF = Cellulose fiber

Discussion

$R^2$ values of density of WF and CF are 0.78 and 0.92 respectively. These values are statistically significant at 95% confidence level ($\alpha=0.05$) representing there is inter dependence between the variables Y (density) and X (fiber content). The regression fitted line indicates that density would increase with addition of fiber in foaming. On the other hand, the $R^2$ values of compressive strength for both types of fiber contents are statistically insignificant and could not be explained.
by the model. However, the polynomial trendline shows that addition of wood fiber make no
difference but addition of cellulose fiber of up to 10% may improve the compressive strength of
the composite foam.

**WF Density regression analysis**

Observed data

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Note: S = Sample

Fitted line plot

```
Density - WF
```

Averages and standard deviations

```
Density WF
```

\[ R^2 = 0.7913 \]
CF Density regression analysis

Observed data

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Fitted line plot

Averages and standard deviations
WF Compressive Strength regression analysis

Observed data

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Fitted line plot

Averages and standard deviations
CF Compressive Strength regression analysis

Observed data

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Fitted line plot

Averages and standard deviations
Background data

Summary output (Density-WF)

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Summary output (Density - CF)

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<th>Upper 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>39.23</td>
<td>1.75</td>
<td>22.42</td>
<td>&lt; 0.001</td>
<td>35.59</td>
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</tbody>
</table>

Summary output (Comp. Strength WF)

<table>
<thead>
<tr>
<th>Regression Statistics</th>
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</thead>
<tbody>
<tr>
<td>Multiple R</td>
</tr>
<tr>
<td>R Square</td>
</tr>
<tr>
<td>Adjusted R Square</td>
</tr>
<tr>
<td>Standard Error</td>
</tr>
<tr>
<td>Observations</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Standard Error</th>
<th>t Stat</th>
<th>P-value</th>
<th>Lower 95%</th>
<th>Upper 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
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<td>0.96</td>
<td>21.54</td>
<td>&lt; 0.001</td>
<td>18.77</td>
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| 0.01 | 0.04 | 0.38 | 0.70 | -0.06 | 0.09 |
Summary output (Comp. Strength - CF)

**Regression Statistics**

<p>| | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
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<tr>
<td>R Square</td>
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</tr>
<tr>
<td>Adjusted R Square</td>
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</tr>
<tr>
<td>Standard Error</td>
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<tr>
<td>Observations</td>
<td>23</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
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<th>Standard Error</th>
<th>t Stat</th>
<th>P-value</th>
<th>Lower 95%</th>
<th>Upper 95%</th>
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</thead>
<tbody>
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<td>17.53</td>
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<td>1.46</td>
<td>0.16</td>
<td>-0.06</td>
<td>0.37</td>
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Summary output

**Regression Statistics**

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<table>
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<tr>
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</thead>
<tbody>
<tr>
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<tr>
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<tr>
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<td>Observations</td>
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<table>
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<th>Standard Error</th>
<th>t Stat</th>
<th>P-value</th>
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<th>Upper 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
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<td>66.76</td>
<td>11.82</td>
<td>0.00</td>
<td>650.50</td>
<td>928.16</td>
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<td>0.39</td>
<td>-3.16</td>
<td>7.83</td>
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