A Study of Cellulose Based Biodegradable Foams and Sponges

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A Study of Cellulose Based Biodegradable Foams and Sponges

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SUMMARY

Environmental concerns have brought about a push to replace non-biodegradable products that are made from non-renewable resources. Investigations regarding use of wood fibers and other biomass as a raw material for biodegradable foams and sponges are an example of such a replacement. Foams made at least partially of biomass can be created using cellulose from wood fibers once the cellulose is converted into a fluid form. Polyurethane foams can be made from polyols containing as much as 50% biomass by combined dissolution of wood and starch. Sponges can be made completely from cellulose regenerated from a viscose rayon solution, and the effect of using wood fibers as reinforcement material within the cellulose matrix of such sponges was studied. The effect of fiber content and fiber length on absorbance, swelling, density, air to cellulose ratios, bound water, and tensile was determined.

CHAPTER 1

INTRODUCTION

Environmental concerns are driving the effort to find new
methods for producing many common items using renewable and
biodegradable resources as opposed to the synthetic and
often petrol-based materials commonly used. Cellular
plastic, or plastic foam, is an example of such a product
which can potentially be produced completely, or at least
partially, with biomass such as lignocellulosics. These
foams can be rigid, semi-rigid, or flexible depending on
the structure of the polymer used for synthesis. They can
be absorbent or non-absorbent. The absorbent types are
typically called sponges. The pore size and arrangement,
and, therefore, the density, of these foams can be
manipulated to suit nearly any need. The great versatility
of foam/sponge materials makes them very important in our
everyday lives, with applications ranging from packaging to
furniture cushioning to insulation to household cleaning
and much more.

The major downfall of the majority of today's foams is that
they are typically produced from non-renewable, non-

recyclable, and non-biodegradable materials, such as polyurethane. The large abundance of natural cellulose from wood pulp, along with its excellent mechanical and thermal properties and biodegradability, make it an attractive alternative to such environmentally harmful materials. Cellulose must first be converted into fluid form with the appropriate properties necessary as a starting material, which is no trivial task.

It is widely known that cellulose does not melt, but it will undergo thermal degradation at high temperature [1]. Cellulose must therefore be converted into a liquid form by either direct dissolution or by derivitization and subsequent dissolution of the derivative. The strong inter-chain and intra-chain hydrogen bonding involved in the crystalline regions make reactions and dissolution of cellulose difficult. There are a number of liquefaction methods available, however, and some of these result in products that can be, at least to some extent, incorporated into foam.

CHAPTER 2

LITERATURE REVIEW

2.1 Cellulose Liquefaction Methods

There are a variety of methods used to convert cellulose into a fluid form, whether they be direct dissolution or derivitization followed by dissolution of the derivative. Some of these methods will be described below. The use of the resulting liquid for foam production will be discussed for two of these methods in section 2.2.

2.1.1 Dissolution in polyhydric alcohols

The use of polyhydric alcohols as a solvent for cellulose is potentially a very useful dissolution method for the production of polyurethane foam. A liquefied mixture of biomass and a polyhydric alcohol of appropriate molecular weight can be used directly as a polyol for polyurethane foam production [2].

The strong hydrogen bonding involved in cellulose is a result of the large number of hydroxyl groups present in the molecular chains. Polyhydric alcohols, along with a sulfuric acid catalyst, are capable of disrupting this

hydrogen bonding by providing additional hydroxyl groups to compete with the cellulose inter-chain and inter-chain hydrogen bonding and their large size forces the chains apart. This process is not very efficient, however, and the wood undergoes a recondensation reaction once wood concentrations of greater than approximately 33% are reached [3].

2.1.2 Dissolution in N-methylmorpholine-N-oxide (NMMO)

Recently, tertiary amine oxides have drawn attention as powerful cellulose solvents, with N-methylmorpholine-N-oxide (NMMO) being the most common [11]. Figure 1 is a representation of the molecular structure of NMMO. The strong polarity of the NMMO molecule again helps to break up the strong hydrogen bond network of cellulose. A mixture of water and NMMO is generally used as the solvent in this system. The ratio of NMMO to water is typically about 87/13 wt% [11],[12]. This ratio is based on the fact that hydration of NMMO with one water molecule per NMMO molecule, which is a water content of 13.3%, leads to the formation of NMMO monohydrate. Pure NMMO has melting point of 170°C, but NMMO monohydrate has a melting point of 74°C as well as improved dissolution strength [12]. NMMO dissolution of cellulose is also revered as a more

environmentally friendly method for producing cellulose

textile fibers than is the viscose rayon dissolution method

to be described later. The textile fibers that are

produced from cellulose regenerated from the NMMO

dissolution method are called Lyocell.
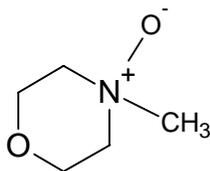
Figure 1: Structure of N-methylmorpholine-N-oxide (NMMO).

2.1.3 Dissolution in ionic liquids

The use of ionic liquids as a solvent for cellulose is a

relatively new and unexplored idea. Ionic liquids are

salt-like compounds that are above their melting

temperature. Such liquids can also solvate cellulose by

using hydrogen bond accepting ions to disrupt and break

apart the intramolecular hydrogen bonding networks that

typically inhibit solvation. Swatloski et al [4] conducted

a study using 1-butyl-3-methylimidazolium cations ($[C_4mim]^+$)

along with a range of anions, including Cl^-, PF_6^-, Br^-, SCN^-,

and BF_4^-. The $[C_4mim]Cl$ liquid, along with microwave

heating pulses, provided the highest degree of solubility.

Even this method only obtained a solubility of 25% by weight, however.

2.1.4 Dissolution in LiCl/DMAC system

Solutions of LiCl/N,N'-dimethylacetamide (DMAC) are another common dissolution system for cellulose. This system breaks up the cellulose hydrogen bonds in a similar way to ionic liquids, with the DMAC forming a complex with the lithium ions and liberating the chloride ions, which interact with the cellulose hydroxyl groups [4].

2.1.5 Viscose rayon method

The viscose method is, in fact, a very old method of dissolving cellulose by first derivatizing. A process for the preparation of dissolved cellulose solutions by treating alkali cellulose with carbon disulfide was patented as early as 1892 by Cross, Bevan, and Beadle [5]. This reaction forms cellulose xanthate, which is soluble in a dilute sodium hydroxide solution. Figure 2 is a representation of the structure of cellulose xanthate. The resulting solution is very viscous, which is why it is commonly referred to as *viscose*. The viscose solution then undergoes a procedure which regenerates solid cellulose.
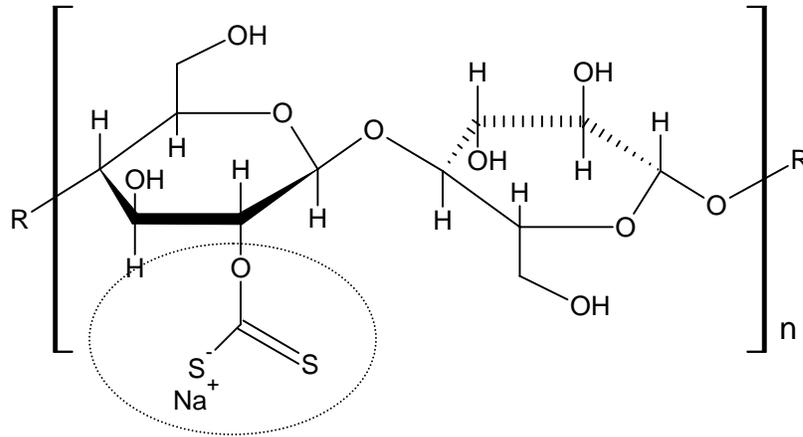
Figure 2: Cellulose xanthate representation. The actual structure of cellulose xanthate may vary since the xanthate group can attach to any number of hydroxyl groups.

There are a number of important steps in the production of viscose described below: steeping, pressing, shredding, aging, xanthation, dissolving, and ripening. The specific details of each step may vary slightly. Table I contains some examples of detailed procedures described by Laskiewicz et al [6], Mobarak et al [7], and Qunhui Sun et al [8].

   Steeping: Sheets of pulp are soaked in a 15-20% solution of NaOH. This results in the production of alkali cellulose. Alkali cellulose is more susceptible to reaction than pure cellulose and, thus, is the starting point for many different cellulose derivatives.

   Pressing: After steeping, the residual NaOH is pressed out until a specified press ratio (wet mass:mass of dry pulp) is reached.

Shredding: The pressed sheets are shredded until a bread-
crumb-like appearance is obtained. The shredding results
in a greater surface area in contact with ambient oxygen.

Aging: This stage typically last anywhere from 48-72
hours, depending on the desired end properties. During
aging, cellulose is oxidized, which results in a decrease
in the degree of polymerization (DP). The viscosity of the
final viscose will decrease with decreased DP [9]. This
step is also referred to as *mercerization*.

Xanthation: The aged alkali cellulose is treated with
carbon disulfide (CS_2) to produce cellulose xanthate. The
crystalline regions of the cellulose are not easily
penetrated by the CS_2, so the resulting compound may more
accurately be described as a block copolymer of cellulose
and cellulose xanthate.

Dissolving: The cellulose xanthate is dissolved in a
dilute NaOH solution. Dissolution is possible since the
bulky xanthate groups push the cellulose chains apart and
thereby weaken the interchain hydrogen bonds.

Ripening: Due to the initial inaccessibility of much of
the crystalline regions of the cellulose, not all of the
cellulose xanthate is initially soluble. However, the
xanthation reaction is reversible, meaning some of the
xanthate groups revert back to hydroxyl groups and release
free CS_2. This free CS_2 can then combine with another
hydroxyl group and gradually break down the cellulose

interchain bonding [10]. Essentially, the CS$_2$ forms a

xanthate group, which pushes the chains apart. The

reaction then reverses, and the liberated CS$_2$ can attack the

next hydroxyl group along the chain, which is now more

accessible since the chain is slightly pushed apart. This

process is repeated until the cellulose is fully dissolved

and viscose is formed.

Once the viscose is formed, the cellulose can be

regenerated into solid form. Regeneration is generally

accomplished by using a combination of heat and a weak H$_2$SO$_4$

acid bath, which often contains metal salts. The metal

Table I: Sample viscose production details.

	Laszkiewicz et al	Mobarak et al	Sun et al
Steeping	19% aqueous NaOH at 55ºC for 0.5 hours	19.6% aqueous NaOH at 30ºC for 1 hour	18% aqueous NaOH at room temp. for 3 hours
Pressing	pick up ratio of 2.6-1	press ratio of 2.9	press ratio of 4.8
Shredding	to 180 g/dm^3	2 hours	2 hours at room temp.
Aging	120 minutes at 55ºC	overnight at 10ºC	65 hours at room temp
Xanthation	32% CS$_2$ relative to wt. of cellulose	35% CS$_2$ at 30ºC for 150 minutes and reduced pressure (40 mmHg)	1 mL CS$_2$ per gram of pulp at room temp. for 2 hours
Dissolving	4% aqueous NaOH at 4-5ºC	dilute NaOH so as to result in 8% cellulose, 6.2% NaOH, and 2.2% CS$_2$	6% NaOH at room temp. for 2 hours
Ripening	to complete dissolution	to complete dissolution	to complete dissolution

cations form complexes with the xanthate groups, which draw

the chains back together and causes coagulation of the

fiber. The acid causes the cellulose xanthate to liberate

9

CS_2 molecules, which can easily leave in gaseous form as a result of the elevated temperature. The heat also causes water to diffuse away, which increases the concentration of dissolved cellulose. The increased concentration causes cellulose to precipitate out of solution as the solubility limits are reached [10]. Regeneration is generally completed in two phases: 1) initial coagulation and 2) complete regeneration of the coagulated cellulose.

2.2 Foams/Sponges From Dissolved Cellulose

Once wood cellulose is in a liquid form, it can be more easily manipulated to form products such as foam and sponge material. The production of polyurethane foam from wood liquefied in polyhydric alcohols and sponge material produced from viscose rayon are two common methods for biomass-based foam and sponge production. Sponge production from NMMO is also gaining some attention, but this science is still relatively new and will not be discussed in this particular study.

2.2.1 Polyurethane foam from dissolved cellulose

As previously discussed, cellulose can be dissolved in polyhydric alcohols. The resulting solution can be directly used as a polyol in the production of polyurethane foam, increasing the biodegradability of such foam. Biomass-based polyurethane foams can be produced with comparable compressive strengths, as tested by ASTM 1621, to those produced by conventional polyols [13].

Polyurethanes are produced by the reaction of a diisocyanate and a polyol. Figure 3 shows this reaction in its non-polymeric form for simplicity. Another important reaction, which is seen in Figure 4, is the side reaction between the isocyanate and water, which liberates CO_2. It is this CO_2 that is responsible for the void cells in polyurethane foam. Polyurethane foam production will generally also involve a surfactant, which can be used for cell stabilization and to control the cell size. A catalyst may also be used.

$$R_1-N{=}C{=}O \quad + \quad R_2-OH \quad \longrightarrow \quad R_1-NH-\underset{O}{\overset{O}{C}}-O-R_2$$
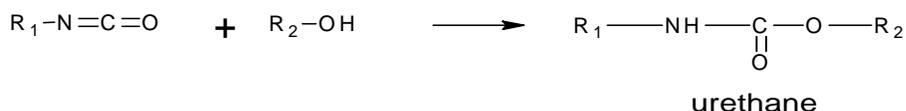
urethane

Figure 3: Reaction between isocyanate and alcohol.

11

The first step in biomass-based polyurethane foam
production is dissolution of the wood or other biomass. Of
the many polyhydric solvents available for dissolution,
polyethylene glycol (PEG) is generally used due to its
large liquefaction capacity, its desirable properties when
reacted to form foam, and its inexpensive prices [2], [3].
However, once the wood concentration in the solvent reaches
~33% by weight, recondensation begins, thus limiting the
total biomass loading. Figure 5, from Kurimoto et al [15],
shows an extensive recondensation reaction occurring after
90 minutes for a wood concentration of only 25%.

$$R-N=C=O \;+\; H_2O \longrightarrow R-NH-\underset{\underset{O}{\|}}{C}-OH \longrightarrow R-NH_2 \;+\; CO_2$$

carbamic acid
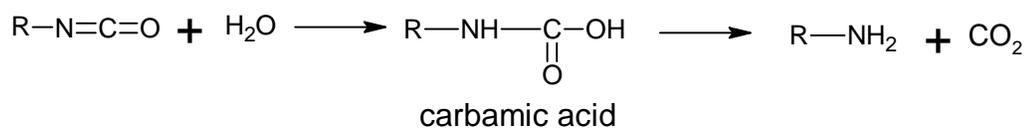
Figure 4: Reaction between isocyanate and water.

It has been shown by Yao et al that using glycerol as a
cosolvent can speed up the liquefaction of starch as well

12

as retard the recondensation reaction [2]. A PEG/glycerol

cosolvent also has the same affect on dissolution of wood,

but the addition of the glycerol results in the need for
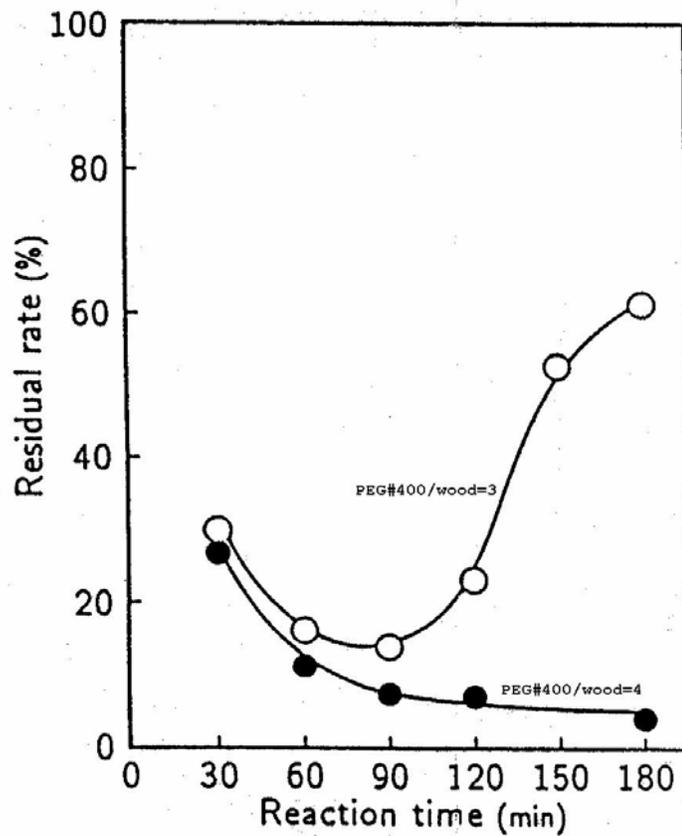
Figure 5: Change of residual rate with reaction time. The reaction temperature was 150° C [15].

larger amounts of expensive isocyanate for foam production. A glycerol content of 10% has been found satisfactory for wood dissolution [14]. The increased dissolution with glycerol is thought to occur due to the larger number of molecules and available hydroxyl groups for a given weight of glycerol. The use of glycerol in small amounts does not have much affect on the total amount of wood that can be dissolved; it mainly speeds up the dissolution and impedes the recondensation reaction that generally occurs with increased reaction time. Figure 6 shows how glycerol (glycerin) content affects recondensation in a 2:1 polyol to wood ratio. A similar, but less dramatic, effect can be achieved by using lower molecular weight PEG [15]. Low molecular weight solvents will result in foams that are rigid and brittle and will also increase the isocyanate requirements, however, so a balance must be obtained. The rigidity is a result of the decreased flexibility of short chain molecules as compared to longer chain molecules of higher molecular weight.
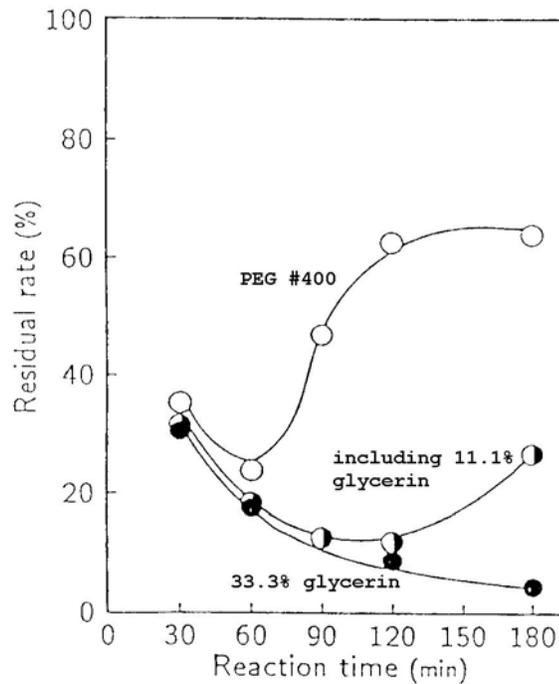
Figure 6: Effect of glycerin content on residual rate. Graph obtained from Kurimoto et al [15]. Reaction was at polyol:wood = 2 and temp = 150°C.

Another factor to be considered during the liquefaction is the hydroxyl number of the resulting polyol, where the hydroxyl number is defined as "the number of milligrams of potassium hydroxide equivalent to the phthalic anhydride consumed in the phthalification of 1 gram of sample" [2] and is determined by the procedure stated by Yao et al [16]. The hydroxyl number is important to polyurethane production as the NCO:OH ratio must be carefully controlled since this ratio contributes to the formation of the three

15

dimensional network in the polymer matrix and, thus,

influences the mechanical properties [17]. This ratio

generally ranges from 0.8 to 1.6 [15], [17], [18].

Shrinkage tends to occur with NCO:OH ratios less than one

[18].

Polyurethane foams are typically made from polyols with

hydroxyl numbers ranging from 300-500 while biomass

typically has hydroxyl numbers around 1500 [2]. Therefore,

biomass concentrations need to be kept low, even if more

could be dissolved. Yao et al have produced rigid foams

from polyols containing as much as 50% total biomass,

however, by combined liquefaction of wood and starch [16].

The resulting polyols had hydroxyl numbers from 300 to 400.

The polyols used by Yao et al were obtained by first

dissolving wood in a solvent of PEG #400 (average molecular

weight of 400), glycerol, and a sulfuric acid catalyst.

The desired amount of wood was liquefied with a reaction

time sufficient to obtain a constant amount of residual

(unliquefied wood). The starch was then added and the

reaction again continued until a constant residual amount

remained. Figure 7, from Yao et al [16], shows the

residual content and viscosity of a solution of equal parts

wood and starch so as to result in a final total biomass

concentration of 50%, where the timescale begins at the

time of starch addition. The equilibrium value of 5.5%

residual corresponds to the amount of undissolved wood

prior to starch addition. Therefore, it can be seen that

starch is completely dissolved in 20 minutes.
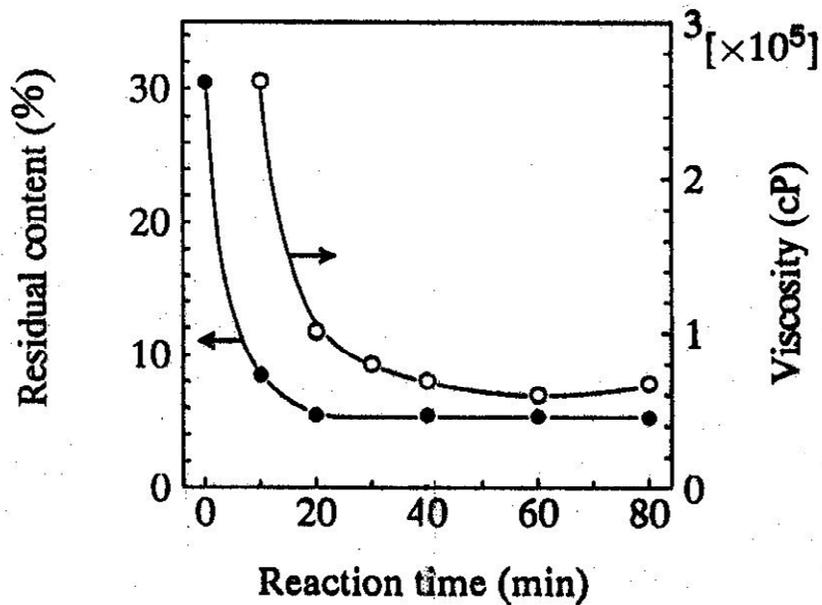
Figure 7: Residual content after starch addition. Wood/starch/solvent = 1/1/2.
Starch addition occurred after wood had been liquefied. This addition corresponds
to 0 minutes on the timescale [16].

The experiment by Yao et al was repeated for various

compositions of wood and starch so as to maintain a

17

constant total biomass concentration of 50%. Details can

be found in Table II. While the hydroxyl number remained

relatively constant regardless of the wood:starch ratio,

the viscosity increased rapidly with increasing wood

content, resulting in fluids that were very difficult to

work with.

Table II: Composition and properties of liquefied biomass polyols. Data from Yao et al [16]. The solvent was PEG #400/glycerin/sulfuric acid (80/20/3 by weight).

Compositions (wt %)			Apparent Viscosity	Residual Content	Hydroxyl Value
Wood	Starch	Solvent	(cP)	(%)	(mg KOH/g)
0	50	50	9000	0	400.4
10	40	50	14900	1	393.3
20	30	50	34420	2.8	388.9
25	25	50	80000	5.5	380.5
30	20	50	209700	7.5	340.7

The wood:starch ratio also had an affect on the physical

properties of the resulting foams. Foam produced from

liquefied starch alone was very brittle, but had a high

compressive strength and elastic modulus. Foams with

higher levels of wood demonstrated lower compressive

strengths and elastic moduli, but had higher resilience.

More details can be found in Table III.

Table III: Biomass composition influence on mechanical properties. Data from Yao et al [16].

Properties	Biomass Compositions (wood/starch ratios)				
	0/50	10/40	20/30	25/25	30/20
Density (g/cm^3)	0.028	0.028	0.028	0.028	0.028
Compressive Strength (KPa)	130.9	121.6	91.4	88.0	84.0
Elastic Modulus (MPa)	9.549	8.034	6.376	3.82	3.700
Permanent Deformation (%)	6.5	3.9	1.9	0.8	0.8

Biomass based foams are not only environmentally friendly in that they utilize renewable resources as opposed to the nonrenewable resources typically used for foam production, but they can also potentially reduce landfill space. The results of biodegradability studies by Ge et al [19] and Lee et al [20] can be seen in Figures 8 and 9. Ge et al used foam from a polyol containing 30% liquefied bark from *Acacia mearnsii*, as well as foam from a polyol containing 15% liquefied bark and 15% liquefied cornstarch. The foams were buried in soil and their weight loss was monitored over a period of 6 months. Both showed weight losses of more than 15% after 6 months, with the cornstarch-containing foam losing almost 20% of its weight. Almost no change was observed in foam made from a polyol containing no biomass. Lee et al used foams produced from polyols containing 24.5% of either liquefied newsprint or box paper waste. The foams were buried in leaf mold and the weight

loss monitored for 6 months. Both biomass-based foams

showed a weight loss of approximately 20% after 6 months

while foam made without biomass showed almost no change in

weight.
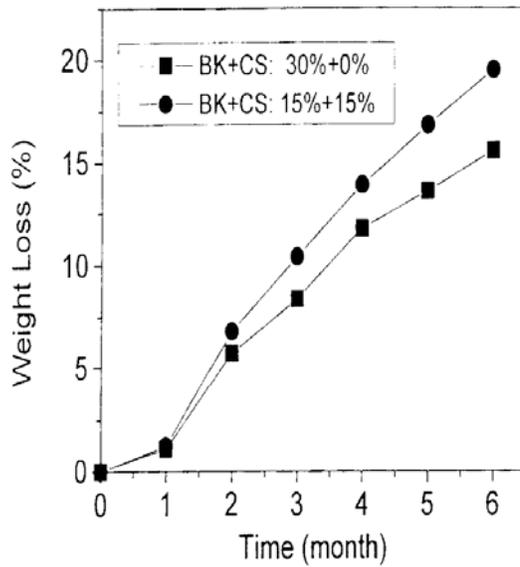
Figure 8: Weight loss of foam buried in soil. Foams contain bark (BK) or bark and cornstarch (CS). Data for non-biomass foam not shown. Graph from Ge et al [19].
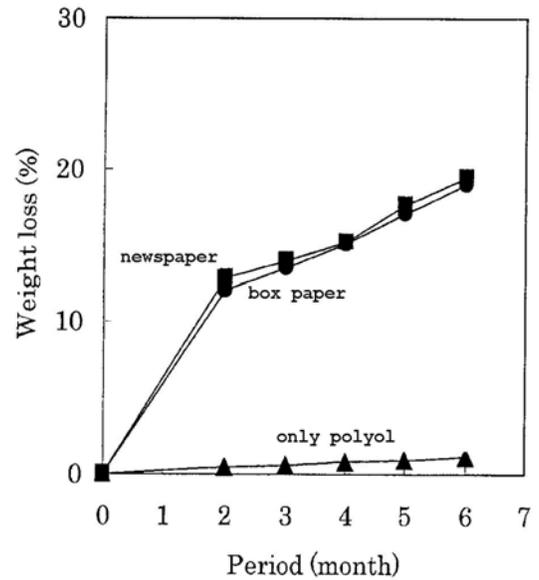
Figure 9: Weight loss of foam buried in leaf mold. The polyol only foam was produced form PEG #400 and glycerol. Graph from Lee et al [20].

The study by Lee et al also eluded to another possible way

that biomass based foams could potentially reduce landfill

space: liquefying wastepaper for polyurethane foam

production. Newspaper, box paper, and business paper were

all liquefied and the residue and hydroxyl numbers were

20

monitored for each type of wastepaper. While all 3 types

of wastepaper produced foam with satisfactory densities and

mechanical properties, the liquefaction kinetics were much

different for each wastepaper type depending on the amount

of liqnin present. The high lignin content newspaper

liquefied faster and had lower hydroxyl values than the

lower lignin content box paper and business paper. This

difference in kinetics and hydroxyl values would make it

difficult to control the polyol properties when using mixed

wastepaper. Yao et al [3] also discussed the role of

lignin in liquefaction by showing that the recondensation

reaction took place earlier in high lignin content wood

compared with dissolving pulp. This phenomenon, which was

also noticed by Kurimoto et al [14], can make it difficult

to produce foam from mixed wood waste as well due the

difference in lignin content between hardwoods and

softwoods.

While satisfactory polyurethane foams can obviously be

produced from biomass, the potential for using wood and

wastepaper in foam production is severely limited. Wood

and wastepaper both exhibit recondensation reactions when

liquefied. Also, polyols with appropriate properties are

21

difficult to produce from mixtures of wood or wastepaper containing different concentrations of lignin.

2.2.2 Cellulose sponges from viscose rayon solutions

Cellulose is a very attractive material for sponge production due to its hydrophillic nature, its renewability, and its biodegradability. Such sponges have a wide variety of applications from household cleaning to medical applications such as tissue cultures and wound healing [26], [27]. All-cellulose sponges can be readily produced from a viscose rayon solution, the manufacture of which has already been discussed. Viscose is more commonly used for textile manufacture. Unlike the textile application, however, cellulose regeneration into sponge form does not necessarily involve the use of sulfuric acid baths. The acid baths involved in rayon fiber formation serve the purpose of rapid decomposition of the cellulose xanthate at the surface of the fiber. This rapid regeneration forms a cellulose skin that helps support the fiber during spinning. This supporting skin is not necessary for sponge formation, and the application of heat alone to a viscose paste containing crystals of sodium sulfate decahydrate is enough to regenerate the cellulose

from the cellulose xanthate present in the viscose. While
other salts, such as trisodium phosphate [21], [22], [23],
can be used, sodium sulfate is the most common for sponge
formation. The choice between sodium sulfate and trisodium
phosphate mainly depends on the desired pore size, with
trisodium phosphate crystals being smaller than sodium
sulfate crystals. Also, a paste made with sodium sulfate
will be acidic in nature whereas a paste made with
trisodium phosphate will be alkaline. Therefore, sodium
sulfate pastes would need to be used shortly after they are
made up. The heat required for regeneration of cellulose
from trisodium phosphate containing pastes is slightly
lower than that of sodium sulfate containing pastes [21].

The inclusion of salt crystals in the viscose serves a dual
purpose in cellulose sponge production. First, the
crystals form void spaces within the resulting cellulose
matrix after they dissolve during the cellulose
regeneration process. To ensure a satisfactory structure
and uniformity of the final sponge, an amount of crystals
must be added so that they are in intimate contact with
each other and the liquid portion of the paste will fill in
the very small spaces between the crystals. Generally,
this means the initial paste will contain in excess of 50%

by weight of salt crystals [22]. The other purpose of the salt crystals is to coagulate the viscose by providing a high salt content in the solution. The sodium sulfate also helps retard the rate of cellulose regeneration to impart a higher degree of crystallinity in the regenerated cellulose [24]. In textile fiber formation, zinc sulfate is often used in the regeneration bath since the zinc ions help form complexes with the xanthate groups, pulling the cellulose chains together and crosslinking them. Since zinc is known to be a highly toxic chemical and can form a crust on the spinning equipment, the use of aluminum sulfate (alum) has been investigated as an environmentally friendly alternative to zinc sulfate for fiber spinning [25]. Alum was determined to be a satisfactory alternative to zinc sulfate. No literature was found, however, regarding whether aluminum sulfate could be an economically favorable replacement for the sodium sulfate involved in sponge formation.

Cellulose regeneration into sponge form from a viscose rayon solution generally occurs in two stages. During the first stage, the viscose is heated to approximately 55°-75° C for approximately 15-60 minutes, depending on the thickness of the sponge to be made [22]. This moderate

heat is sufficient to coagulate the cellulose into a gel-like form. This initial coagulation retards the dissolution and migration of the salt crystals within the paste [22]. The heat necessary for this coagulation is often provide by infrared lamps or by passing an alternating electric current through the paste to raise the temperature. A high frequency electric field may also be used [28]. These methods provide rapid, even heating to the viscose paste. The second stage of regeneration involves the complete regeneration of the cellulose from the gel-like mass by increasing the heat to approximately 90°-95° C. During this stage, the salt crystals completely dissolve in the water present in the paste. The complete regeneration also results in the release of gases, such as carbon disulfide or other sulfur compounds, and these gases displace the salt solution leaving behind gas-filled pores [22]. The paste undergoes shrinkage during regeneration, which makes it difficult to use a mold to form sponges of specific dimensions.

Cellulose sponges may also incorporate comminuted cellulose or reinforcing fibers within the regenerated cellulose matrix. Little literature was found regarding the technical aspects of including reinforcing fibers in

cellulose sponges, however, which was a driving force
behind the laboratory study to be discussed later. The
comminuted cellulose may consist of 50% or more by weight
of the overall cellulose in the final sponge. Fred Stieg
investigated the effect of comminuted cellulose by varying
the amounts and by comparing mercerized comminuted
cellulose with unmercerized comminuted cellulose within the
resulting sponge [21]. Stieg concluded that adding greater
amounts of comminuted cellulose will decrease the tensile
strength and absorbency as well as decrease the amount of
swelling upon wetting. Although the total absorbency is
decreased with increasing amounts of comminuted cellulose,
the rate of absorption increases. These effects are
further magnified for mercerized comminuted cellulose than
for the unmercerized variety [22]. The use of mercerized
comminuted cellulose also decreases the amount of shrinkage
that occurs during regeneration, making it easier to
control the final geometry with a mold during regeneration
[22].

Another method for controlling the final tensile and
absorbency properties of cellulose sponges involves the
degree of polymerization of the cellulose in the wood pulp
initially used to create the viscose rayon solution. Using

the viscosity of a solution of pulp dissolved in cuprammonium hydroxide as an indicator of the degree of polymerization, Stieg was able to conclude that a higher DP resulted in more structural stability and tensile strength but less absorbency and swelling upon wetting [22].

2.3 Fiber Reinforcement

Fibers of various types are often used to reinforce composite materials. Since foams and sponges are essentially composite materials containing void spaces, inclusion of reinforcement fibers into foams and sponges may also be advantageous in regards to mechanical properties. In the case of cellulose sponges, the length of the reinforcing fibers is typically in the range of 0.5 mm to 50 mm [29], [30].

In short fiber reinforced composites, the fibers reinforce the matrix by allowing some of the applied load to transfer to the fibers through the shearing action at the fiber-matrix interface [32]. This reinforcing mechanism obviously requires good interfacial bonding for enhanced reinforcing effects. This makes cellulose fibers an excellent choice of reinforcing fibers for cellulose sponges due to the hydrogen bonding that will occur between

the fibers and the regenerated cellulose matrix. The viscose may even attack the cellulose on the outside of the fibers ensuring good interfacial bonding [30]. Fiber surface treatments could also be used to increase interfacial bonding of cellulose fibers to a polyurethane matrix if necessary. Such surface treatments have been found beneficial for cellulose fibers in a polyethylene matrix [32].

The lengths and amounts of the fibers present as reinforcing material are also important. Both Kalaprasad et al and Yang et al have shown an initial increase in tensile strength as reinforcing fiber length increases and a subsequent decrease after a certain critical fiber length is reached [32],[33]. The critical fiber length is dependent on the strength of the individual fibers, their aspect ratio, and the interfacial bond between the fibers and the surrounding matrix. Yang et al have also shown that as the amount of fibers of a given length increases, the tensile strength increases up to a maximum point and then declines. This decrease is likely due to conglomeration of fibers. The concentration of the matrix material is low in these areas, and a weak spot is formed [33]. A similar phenomenon can occur with long fibers,

which have a tendency to exhibit large amounts of curl. This may further explain why tensile strengths begin to decrease when longer fiber lengths are used.

Fibers may also aid as tensile reinforcement by bridging across cracks that propagate when stress is applied. The result of this mechanism would be an increased importance of the number of fibers present over the total mass or volume of the fibers since a larger number of fibers would increase the probability that a bridge would be present across a propagating crack.

CHAPTER 3

EXPERIMENTAL

The objective of this study was to characterize the effect
of wood fiber reinforcement material on the absorbency,
tensile index, density, air to cellulose ratio, entrapment
of bound water (water which can not be removed by
pressing), and swelling upon wetting of the resulting
sponges formed from cellulose regenerated from a viscose
rayon solution. Sodium sulfate decahydrate crystals were
used as the pore forming media. Various amounts of
softwood fibers and hardwood fibers were incorporated into
the sponge matrix and the final properties were recorded as
a function of fiber content. Unrefined bleached softwood
Kraft pulp from James River Corporation was used to produce
the viscose solution as well as to provide the softwood
reinforcement fibers. Unrefined bleached hardwood Kraft
pulp, also from James River, was used as the hardwood
reinforcement fiber.

3.1 Preparation and Properties of Pulps

The degree of polymerization (DP) of the softwood pulp used
for viscose production was determined for reference in

future studies and so that it could be compared to the DP

of the final regenerated cellulose. After determining the

air dry moisture content of the pulp using a Metler Toledo

Moisture Balance, the cupriethylenediamine (CED) viscosity

of the pulp was determined according to TAPPI Standard T

230 om-99. The following equation, developed by J.H.

Morton of the Buckeye Cellulose Corporation [31], was then

used to determine the weight average degree of

polymerization:

$$DP_w = 118.019 * \ln^2(\eta) + 598.404 * \ln(\eta) - 449.61$$

Equation 1: Weight average degree of polymerization where η is the cupriethylenediamine viscosity. Equation from J.H. Morton of the Buckeye Cellulose Corporation where η is the CED viscosity in cP [31].

Hardwood and softwood pulp slurries were made for

reinforcement fiber supply by disintegrating dry lap pulp

for 30,000 revolutions in a disintegrator as described in

TAPPI Standard T 205 om-02. The dry lap was presoaked in

water for one hour prior to disintegration. The resulting

consistency of the softwood pulp was 1.80% air dry pulp and

the hardwood consistency was 1.82% air dry pulp. These

particular consistencies were chosen so that equal amounts

of slurry could be added for hardwood as for softwood for a given oven dry fiber content in the final sponge after accounting for the residual moisture in the air dry pulp. Small portions of each slurry were further diluted to proper conditions for a measurement of the length weighted average fiber length using a Fiber Quality Analyzer.

3.2 Viscose Preparation

The procedure that follows was developed based on the procedures described in Table I. The aforementioned softwood dry lap was used for the viscose preparation.

3.2.1 Steeping

Sheets of softwood dry lap pulp were soaked in 19.0 wt% aqueous sodium hydroxide for 3 hours at room temperature to form alkali cellulose. The total air dry mass of the pulp was 20.1 grams.

3.2.2 Pressing and shredding

The soaked sheets of dry lap were pressed between numerous sheets of blotter paper until a press ratio of 4.25 was obtained, where the press ratio is defined as the ratio of alkali cellulose mass to the original mass of the dry pulp.

The pressed alkali cellulose was then shredded in an IKA M20 Universal Grinder until a breadcrumb-like appearance was obtained.

3.2.3 Aging (Mercerization)

The breadcrumb-like alkali cellulose was exposed to room temperature air for 50 hours.

3.2.4 Xanthation

Carbon disulfide was added to the mercerized pulp at a ratio of 1 mL CS_2 per gram of oven dry pulp. The resulting mixture was shaken by hand for 30 seconds to ensure some CS_2 was absorbed by all the mercerized cellulose. Nearly all the CS_2 liquid was absorbed. The container was then shaken for 3 hours at room temperature using Lab-Line Orbit Shaker at 250 rpm. This agitation ensured continuous diffusion of the CS_2 through the mercerized cellulose.

3.2.5 Dissolving and ripening

A dilute sodium hydroxide solution was added to the xanthated cellulose such that the final solution concentration would be 8 wt% cellulose and ~8 wt% sodium hydroxide accounting for the sodium hydroxide already present from the preparation of the mercerized pulp. The

lignin content of the wood pulp was disregarded and the pulp was considered to be 100% cellulose. The resulting mixture was 8.0 wt% cellulose, 8.3 wt% NaOH, 10.1 wt% CS_2 (amount initially present, not the unreacted amount), and 73.6 wt% water. This mixture was then shaken on the Lab-Line Orbit Shaker for 1 hour at room temperature and subsequently stirred with an IKA RW20 mixer until a homogeneous mixture existed. The mixture was left at room temperature overnight to ripen to complete dissolution. The solution was then stored in a freezer for until ready for use.

3.3 Viscose Viscosity

In order to obtain some sort of characterization of the viscose viscosity for future reference, a Grace M3500 Viscometer was used. Only a small amount of viscose was available for viscosity testing after foam production, so it was necessary to dilute the viscose to a ratio of 8:1 water:viscose to meet the minimum volume requirements for the viscometer. The viscosity test took place at 72° F and a shear rate of 100 s^{-1}.

3.4 Sodium Sulfate Crystallization

To obtain the necessary crystals of sodium sulfate decahydrate, anhydrous sodium sulfate powder was dissolved in water at 90° C under agitation until the solubility limit was reached. The heat was then turned off and the solution was allowed to cool to room temperature under constant agitation. Once room temperature was reached, an ice batch was used to further reduce the temperature of this supersaturated solution. Agitation was continued until the solution became cloudy. Once the crystals reached an appropriate size, the agitation was stopped and the solution was immediately filtered using vacuum filtration. The resulting crystals were stored in a sealed container in a refrigerator to prevent reversion to the anhydrous form.

3.5 Cellulose Sponge Formation

The paste necessary for cellulose sponge formation was produced based on the formulation described by Stieg for the production of a regenerated cellulose sponge containing no filler [23]. Sponges were made such that the final dry cellulose content of the sponge was either 0% fiber, 10% hardwood fiber, 20% hardwood fiber, 10% softwood fiber, or 20% softwood fiber with the remainder of the cellulose in

each case being the cellulose regenerated from viscose. Experimentation determined that fiber amounts greater than this would require more extensive mixing techniques due to the high viscose viscosity. The addition of greater amounts of water could aid in mixing, but an unsatisfactory viscosity of the resulting paste would result as well as unknown effects on the regeneration kinetics. The ratio of sodium sulfate decahydrate crystals to cellulose was kept constant for all sponges regardless of fiber content. Constant amounts of water and total cellulose were also used for each sponge regardless of fiber content. In order to keep the water amount constant, some water had to be drained from the pulp slurries when sponges with 20% fiber content were produced. Table IV contains the details of the paste formulations.

Table IV: Compositions of pastes for sponge production. Each formulation results in a paste with cellulose composition of 2.1% by weight and a salt:cellulose ratio = 29.9.

Sponge Filler	No Filler	10% Fiber	20% Fiber
Viscose[*]	26.0%	23.9%	21.7%
Fiber	0.0%	0.2%	0.4%
Water	12.0%	12.3%	12.5%
Na_2SO_4	62.0%	63.6%	65.4%

[*]Viscose is 8% cellulose.

For each sample, the pure water or pulp slurry was first
mixed with the viscose until thoroughly mixed. The salt
crystals were then added and the mixture was again
thoroughly mixed. The resulting paste was then placed onto
the center of a dinner plate on a level surface and allowed
to flow until a uniform layer was obtained. This plate was
then placed in a level oven (not preheated) and exposed to
the temperature profile shown in Figure 10. Numerous
practice trials determined this temperature profile to be
optimum. After 180 minutes of heating according to this
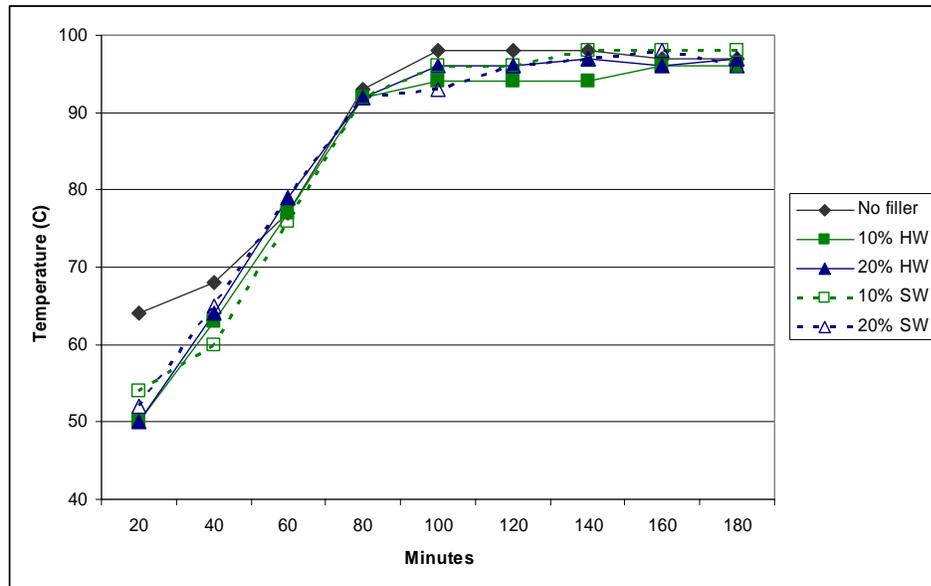profile, each sponge was washed in a series of 95°C water
baths.

Figure 10: Oven temperatures during cellulose regeneration.

37

3.6 Sponge testing

After the sponges were air-dried to a constant weight, they underwent a series of tests to characterize their absorbency, tensile index, density, air to cellulose ratio, entrapment of bound water, and swelling upon wetting. The air to cellulose ratio and the tensile index were tested with sponge material in the "bound water state" in order to obtain test samples of similar moisture content for each type of sponge. Bound water is defined as the water within the sponge that can not be removed from pressing alone. Evaporation is the only way to remove the water that is bound into the sponge. This state was chosen over the dry state since most, if not all, sponge applications will involve moisture in the sponge. The bound water state was obtained by wetting the samples to saturation, pressing the wet samples by hand, and then further pressing between blotter paper using a handsheet press at 15 psi for one minute. Experimentation determined this pressure and duration to be adequate for removal of all unbound water without any permanent deformation of the sample.

3.6.1 Air to cellulose ratio

The air to cellulose ratio was determined for the sponge material in the bound water state. One square inch of each

sponge type was scanned into a monochrome bitmap file where all open space was represented by black pixels and the cellulose area was represented by white pixels. The resulting bitmap was converted into a JPEG file format which had a pixel array of 1050 x 1050. A computer program was then developed in the Jython programming language in order to count the number of black pixels present in the image. The program returned the total number of black pixels present in the 1050 x 1050 pixel array and the ratio of black pixels to white pixels was calculated as a measure of the air to cellulose ratio. This test was completed for both sides of each sponge, and the average was assumed to be representative of the interior. The values were later verified by the 'count black/white pixels' function in the UTHSCSA Image Tool 3.00 image analysis program. The air to cellulose ratio found in this manner is not necessarily an absolute number since variation may occur when converting the image to black and white. The value may in fact be dependent on the scanner and computer used. This method is adequate for comparison purposes, however, as long as the same scanner, computer, and system settings are used for each sample. Examples of the images can be seen in Figures 11-20. These images are shown at 200% magnification.
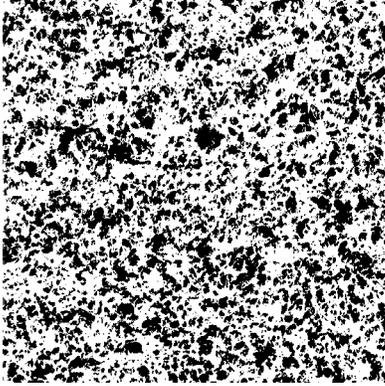
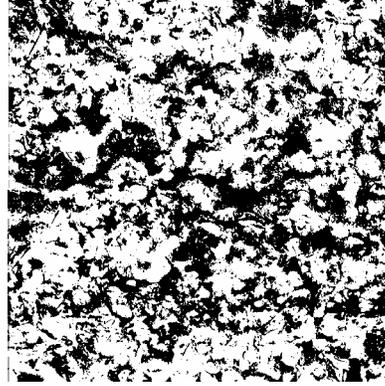**Figure 11: No filler sponge (bottom).** Magnification is 2x.

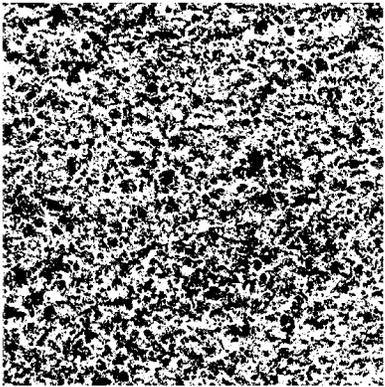**Figure 12: No filler sponge (top).** Magnification is 2x.

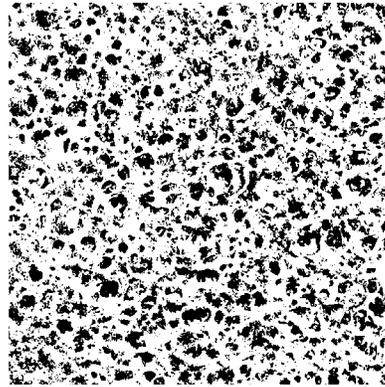**Figure 13: 10% HW sponge (bottom).** Magnification is 2x.

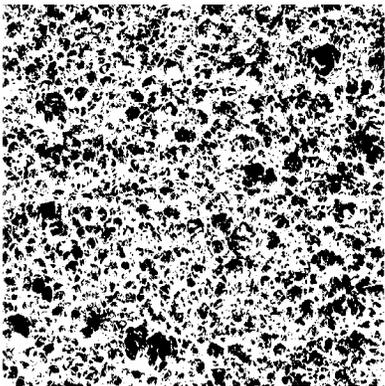**Figure 14: 10% HW sponge (top).** Magnification is 2x.

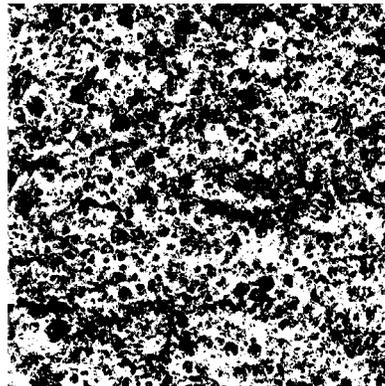**Figure 15: 20% HW sponge (bottom).** Magnification is 2x.

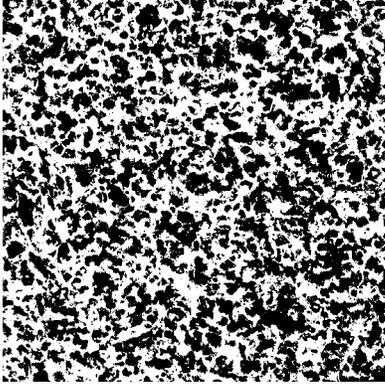**Figure 16: 20% HW sponge (top).** Magnification is 2x.

Figure 17: 10% SW sponge (bottom).
Magnification is 2x.
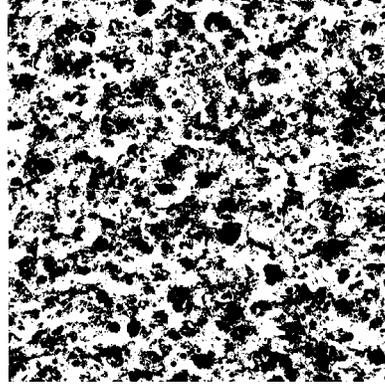
Figure 18: 10% SW sponge (top).
Magnification is 2x.
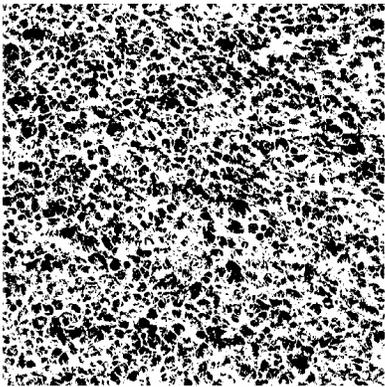
Figure 19: 20% SW sponge (bottom).
Magnification is 2x.

Figure 20: 20% SW sponge (top).
Magnification is 2x.

3.6.2 Density, absorbency, bound water, and swelling

The sponges were cut into strips while in the bound water
state. Three strips with dimensions of 15 mm x 3.5 inches
were cut out of each sponge type. This is the maximum
number of strips that could be cut out of each sponge given
the limited amount of material. The strips were cut to

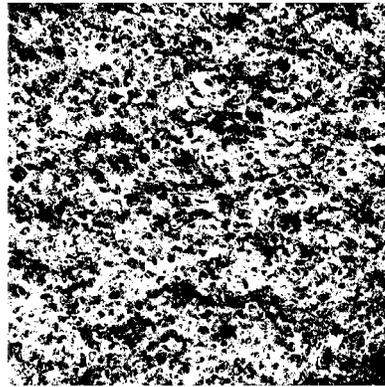these particular dimensions while in the bound water state so that the same strips could later be used for tensile testing. The mass of each strip was recorded so that the mass of bound water could be determined by comparing this mass to the dry mass. The strips were then allowed to air dry between flat surfaces of minimal weight to prevent curling upon drying. Once dry, the caliper was determined using a hand-held manual micrometer to prevent compression, which returned a value in thousandths of an inch. The length and width data were also recorded along with the mass for dry volume and density determination.

After the dry state data was collected, the strips were submerged into a graduated cylinder for 15 seconds each and then removed. The volume change in the graduated cylinder was then used as an indicator of absorbance rate. The strips were then submerged in water for 5 minutes. Once removed, the mass and dimensions were measured for determination of absorbency and swelling. The strips were then pressed back to their bound water state for tensile testing.

3.6.3 Tensile testing

Tensile tests were conducted using the 15 mm wide strips in their bound water state. An Instron 4400R was used with an initial jaw separation of 2 inches and a crosshead speed of 0.5000 inches per minute. The tensile index was calculated using the maximum load and the grammage of the sponge material in its bound water state.

3.6.4 Regenerated cellulose DP

A small portion of the sponge containing no filler was used to determine the degree of polymerization (DP) of the regenerated cellulose so that it could be compared to DP of the original softwood pulp. The cupriethylenediamine (CED) viscosity method described in TAPPI Standard T 230 om-99 was again used along with Equation 1, on page 31, to determine the DP.

CHAPTER 4

RESULTS, DISCUSSION, AND CONCLUSIONS

4.1 Raw Materials

The viscose used in the preparation of the cellulose foam was produced with a softwood pulp with a weight average degree of polymerization of approximately 2750. Dissolution of the cellulose was very nearly complete. Very few undissolved fiber fragments could be seen under 10x magnification. The longest fragment that was seen was only ~75 μm in length as determined by the UTHSCSA Image Tool 3.00 image analysis program. An image of this particular fiber can be seen in Figure 21. The viscosity of the viscose diluted to 8:1 water:viscose was 19.0 cP at a shear rate of 100 s^{-1}. The regenerated cellulose had a degree of polymerization of ~700. This decrease in DP from the DP of the cellulose in the original pulp was expected due to the cellulose chain cleavage that occurs during the preparation of viscose. The hardwood and softwood fibers used had length-weighted mean lengths of 1.02 mm and 2.24 mm respectively. The mean length of the hardwood fibers was slightly larger than expected.
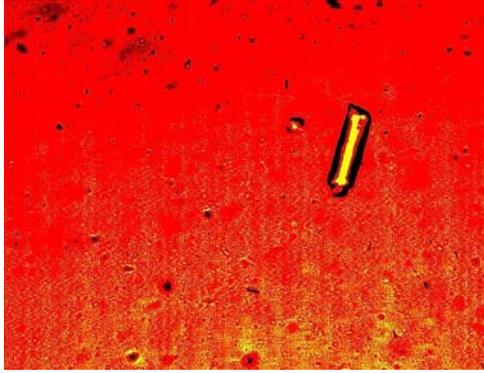
Figure 21: Photo of undissolved fiber fragment at 10x magnification.
Picture is 415 μm wide and the undissolved fiber is ~75 μm in length.

4.2 Sponge Results

Tables V and VI contain summaries of the average results for the hardwood reinforced and softwood reinforced sponges respectively. Statistical analysis of the data was done at a 5% significance level. This significance level means that if that if two means are determined to be statistically different, there is only a 5% chance that they are actually equal, and that the difference actual comes from experimental error.

4.2.1 Air to cellulose ratio and dry density

The air to cellulose ratio average was determined by averaging the result of the two sides of the sponges. The top sides generally had a greater air to cellulose ratio than the bottom sides, which was initially unexpected since

Table V: Average results for hardwood reinforced sponges (including the 0% filler sponge)

Filler (%)	Density (g/cm^3)		Grammage (g/m^2)	Absorbency			Swelling	Bound Water		Tensile		Air to Cellulose
	Dry	Wet	Pressed	15 sec. (mL)	Total (g)	Total (%)	Wet (%)	Total (g)	Total (%)	Strength (N/mm)	Index	Ratio
0	0.27	0.75	320.7	1.7	2.92	1534	582	0.24	125	0.385	1.20	0.67
10	0.28	0.79	358.5	2.5	3.23	1341	520	0.24	98	0.640	1.79	0.64
20	0.24	0.74	270.2	2.5	2.62	1565	534	0.19	116	0.632	2.34	0.89

Table VI: Average results for softwood reinforced sponges (including the 0% filler sponge)

Filler (%)	Density (g/cm^3)		Grammage (g/m^2)	Absorbency			Swelling	Bound Water		Tensile		Air to Cellulose
	Dry	Wet	Pressed	15 sec. (mL)	Total (g)	Total (%)	Wet (%)	Total (g)	Total (%)	Strength (N/mm)	Index	Ratio
0	0.27	0.75	320.7	1.7	2.92	1534	582	0.24	125	0.385	1.20	0.67
10	0.20	0.69	237.7	2.5	2.14	1480	471	0.13	90	0.402	1.71	0.90
20	0.20	0.67	256.5	2.5	2.70	1548	502	0.17	96	0.523	2.04	0.83

some pore forming crystals typically settled towards the bottom before the initial coagulation of the cellulose. After further examination, however, the top surfaces appear to have larger, more irregular pores, as can be seen in Figures 11-20. This phenomenon makes sense since the gases released during regeneration escape from the top causing these large pores. The air to cellulose ratios of the fiber-containing sponges were about 20-35% greater than that of the sponge with no filler. The 10% hardwood specimen did not follow this trend, but that is likely due to the fact that a low porosity cellulose skin formed on the top layer of this sponge resulting in a very low air to cellulose ratio. This skin layer is evident in Figure 13 and also explains why this specimen does not fit some other trends.

The dry density results also correlate with the air to cellulose ratios. The densities of the fiber-containing sponges are statistically lower than the no-filler sponge, except in the case of the 10% hardwood sponge, due to the skin on the top layer. The hardwood fiber sponges have statistically higher densities at a given fiber content than the softwood fiber sponges. The amount of fiber only affects the density in the hardwood sponges according to

the statistical analysis. This difference is most likely

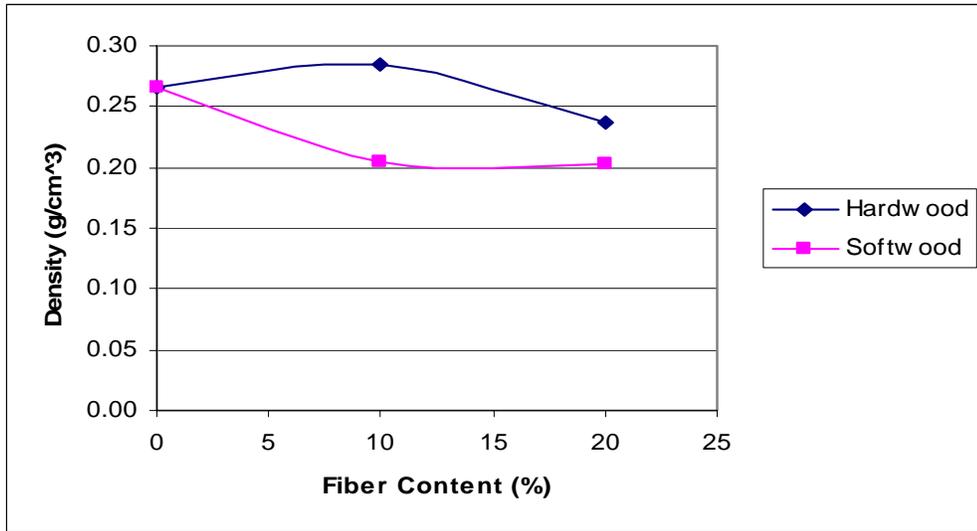due to the skin formed on the 10% content sample, however.

Figure 22: Dry density as a function of fiber content. The 10% hardwood data is
artificially high due to formation of a cellulose skin on the sponge's top surface.

A possible explanation for the decrease in dry density with

the inclusion of fibers is that the fibers are forming a

support through the middle of the pores preventing them

from shrinking as much from the wet state to the bound

water state and the dry state. The density differences

between fiber types may be a result of softwood fibers

holding the pores farther open than hardwood fibers.

Figures 23 and 24 show photos of one such pore at 10x

magnification in the 20% hardwood sponge and one in the 20%

softwood sponge respectively. This theory is also

supported by the absorbency, swelling, and bound water

results.

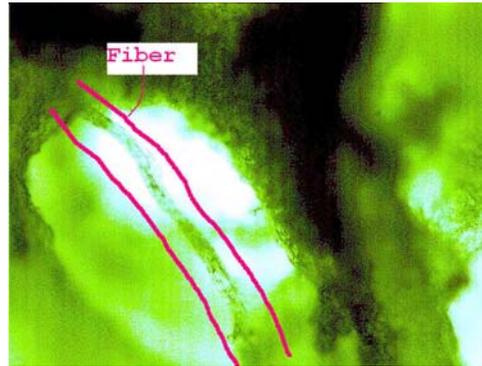**Figure 23: Hardwood fiber across pore.** Fiber content = 20% HW.

Figure 24: Softwood fiber across pore. Fiber content = 20% SW.

4.2.2 Absorbency, swelling, and bound water

The total water absorbency, expressed as a percentage of

dry cellulose, was essentially unaffected by the presence

of fibers, as can be seen in Figure 25. Again, the 10%

hardwood sponge data is skewed due to the skin forming on

the surface. The absorbance rate, however, was strongly

affected by the presence of fibers. The length or amount

of fibers did not seem to matter. This dependence on

49

fibers is evident from the fact that sponges containing

fibers soaked up almost 50% more water mass during the 15

second soaking period. This result again supports the

theory that the fibers prevent the pores from closing as

far upon drying as does the fact that the swelling upon

wetting appears to decrease in the sponges containing

fibers. The swelling results can be seen in Figure 26. The

amount of swelling in the softwood samples was

statistically lower than that of the no-filler sponge.

These swelling results are somewhat inconclusive, however,

since only the softwood-containing samples showed swelling

values that were statistically lower than the no-filler

samples. Even though the swelling of the hardwood samples

was not statistically different than that of the softwood

sponges, the hardwood samples were calculated to be

statistically equal to the no-filler samples. The amount

of fiber did not affect the swelling when fiber was

present.

The amount of bound water, expressed as percent of dry

cellulose, is also statistically lower in the fiber-

containing sponges. The bound water trends can be seen in

Figure 27. Again, the lower amounts of bound water in the

fiber-containing samples may possibly be attributed to more

open pores in these sponges. The pores in the no-fiber
sponge may close enough during compression that water is
held within the matrix by capillary forces within these
small pores. It should also be noted that the bound water
percentage is statistically higher for the hardwood-
containing sponge than the softwood-containing sponge at
20% content. This difference is likely due to the amount
of bound water within the fibers themselves. The 10%
hardwood samples did not contain statistically different
amounts of bound water than the 10% softwood samples, but
the hardwood results were artificially lowered due to the
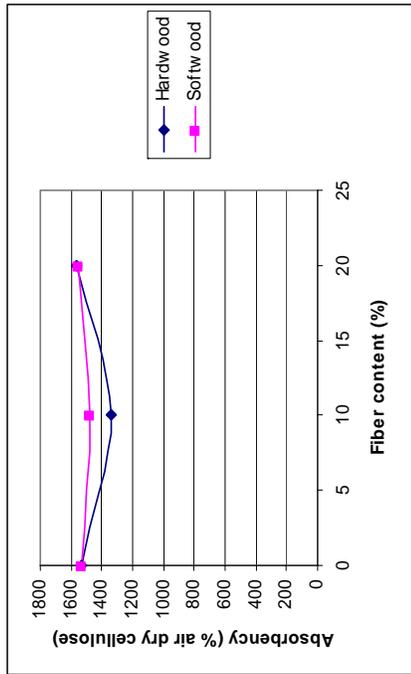skin effect.
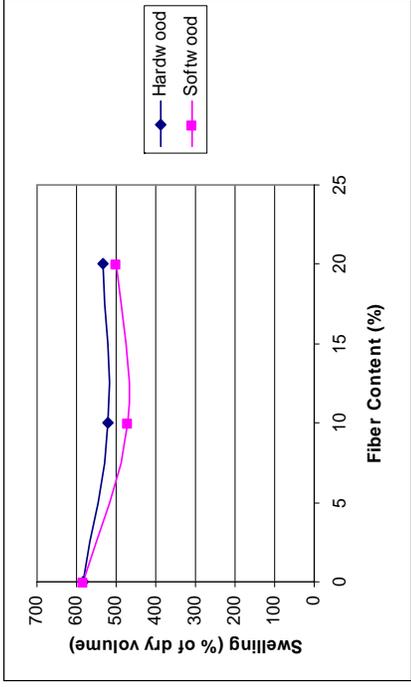
Figure 25: Sponge absorbency.
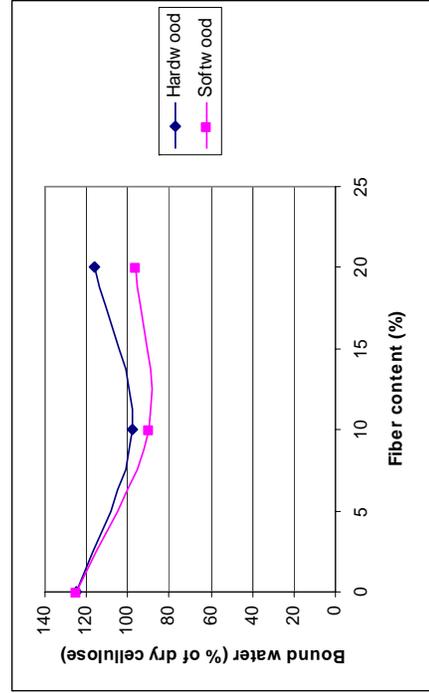
Figure 26: Sponge swelling upon wetting.

Figure 27: Bound water in sponge.

52

4.2.3 Tensile index

The tensile index results can be seen in Figure 28. The inclusion of fibers as reinforcement material has an obvious affect on the tensile index. The tensile index increases at a statistical level with increasing fiber content, except from 10% softwood to 20% softwood. The index of the 20% hardwood sponge is statistically higher than that of the 20% softwood sponge, indicating that the shorter hardwood fibers may have a greater affect on the tensile properties than the longer softwood fibers. The skin on the 10% hardwood sponge may have affected the tensile index, but reporting the tensile index rather than the absolute tensile strength should help compensate for density differences and limit the skewing of these results.

The greater tensile index with the short hardwood fibers as compared to the longer softwood fibers was initially unexpected. However, as supported in the literature [32], [33], tensile strength only increases with increasing fiber length up to a certain critical fiber length. The determination of critical fiber length requires calculations that involve measurements of the strength of the individual fiber, its diameter, and the bond strength between the fiber and the surrounding matrix. These

measurements are outside the scope of this particular project, but the data suggest that the critical fiber length may fall somewhere between the hardwood fiber length and the softwood fiber length assuming similar fiber strengths, diameters, and interfacial bonding. The difference may be a result of differences in hardwood and softwood properties themselves rather than the actual length of the fibers, however. The greater tensile index for a given hardwood content may also be higher than that of the same softwood content since more hardwood fibers are present. This larger number of fibers increases the probability that cracks propagating as a result of the tensile stress would be bridged by a fiber.
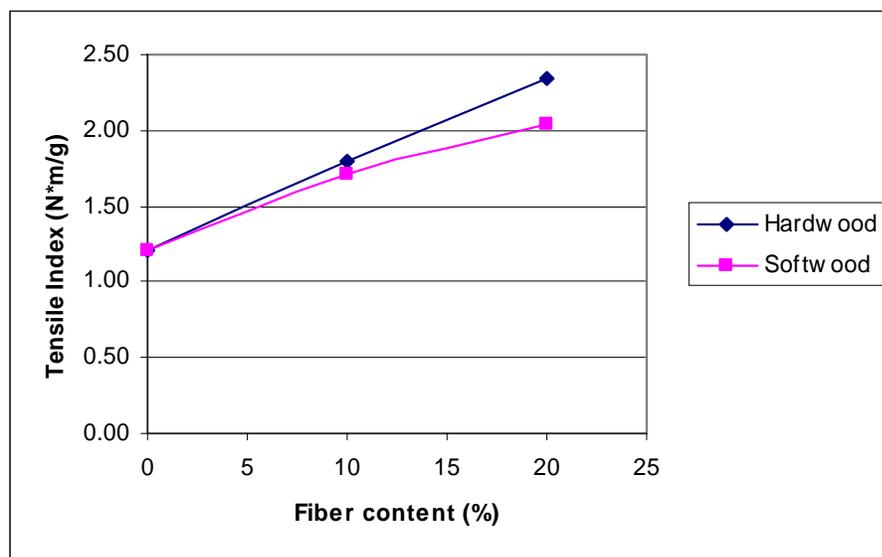
Figure 28: Sponge tensile index.

4.3 Discussion and conclusions

The initial laboratory work uncovered many roadblocks to the production of consistent foam samples. Initial practice samples of various geometries showed severe nonuniformity in the finished sponge due to settling of the pore forming crystals before adequate coagulation took place. A large number of practice trials were completed before a suitable method and sample geometry were developed for final foam preparation. The thin, flat geometry used in the final foam preparation, along with the heating profile that was used, minimized pore settling and uneven heating of the paste during regeneration. Once this roadblock was overcome, samples of suitable uniformity could be produced. The low porosity skin that developed on the top of the 10% hardwood sponge sample did not initially seem like it was severe enough to have much affect on the results. In retrospect, this sample should have been redone. The data from this sample initially seemed to fit into the trends, however, so the data were kept. During final preparation of the data, a formula error was noticed in the spreadsheet used to calculate many of the final properties, and it then became obvious that the 10% hardwood data was quite skewed. However, it is still reasonable to conclude from these results that:

- Inclusion of fibers in cellulose sponge materials has little affect on total water absorbance. The absorbance rate of a dry sponge is increased, however, likely due to fibers preventing pores from closing upon drying. Lower dry density of fiber-containing sponges also supports this theory. Absorbance rate and dry density do not appear to be dependent on the fiber content when fiber is present.

- Swelling upon wetting appears to be reduced by fiber inclusion for the same reason. The fiber type or amount does not have much affect, if any, on swelling. Statistical analysis showed the swelling results to be somewhat inconclusive, however, since only the softwood samples showed statistically lower swelling values compared to the no-filler sponge even though the hardwood and softwood samples were statistically the same.

- Fiber reinforced sponges contain lower amounts of bound water than sponges with no filler. This is likely due to increased capillary forces holding water in the smaller pores of sponges containing no fiber. Hardwood containing sponges appear to contain more bound water than softwood containing sponges, and the

amount of fiber does not appear to affect the bound
water content when fiber is present.

- Inclusion of reinforcement fiber increases the tensile index of the resulting sponge. The index increases with increasing fiber content, and hardwood fibers appear to provide more reinforcement.

CHAPTER 5

FUTURE

There are many aspects of cellulose sponges that can be investigated in future work. The inclusion of comminuted cellulose in the sponge matrix along with reinforcing fibers could result in great control over the final properties of the sponge. Also, the alternate methods mentioned like infrared heating and electric currents may minimize the problem of crystal migration in the paste. These methods allow for quicker coagulation time while still maintaining even heating of the sample. More work should be done to determine if the apparent increase in tensile strength for hardwood fibers over softwood fibers is a result of the properties of the fibers themselves, or if it due to the fiber length or number of fibers.

There is also much more work to be done involving biomass-based polyurethane foams. While only low concentrations of dissolved wood can be achieved, biomass concentrations of 50% have been successfully used for polyurethane foam production by dissolving wood and starch together. A biomass loading of 50% will still have a large affect on

biodegradability and landfill space. Polyurethane foam

production does not seem to have much potential as a use

for wastepaper or wood wastes, however.

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