

ABSTRACT

HAYDEN, KRISTIN ANNLEATHA. Water Absorption Behavior of Bio-Based Polymeric Materials. (Under the direction of Richard A. Venditti and Joel J. Pawlak.)

Absorbent hygienic materials are an important part of our society, fulfilling serious health and safety needs. Typically, these products are derived from non-renewable petroleum-based acrylic acid, making sustainability, disposal and biodegradability in landfills a concern. Superabsorbents derived from renewable plant- and animal-based sources may be a viable alternative. Due to the increased cost of petroleum-based feed stocks for absorbent materials, renewable absorbents have become more cost-competitive. Previous studies have shown the performance of renewable-based absorbents to be acceptable. The objective of this research was to understand the absorbent properties of renewable carbohydrate-based materials as a function of composition.

A method for evaluating the dynamic water absorption of absorbent materials including carbohydrate-based powders was developed, termed a dynamic wetting apparatus (DWA). The system gravimetrically measures the water uptake of a sample positioned on a filter paper in contact with a water reservoir. The DWA results were observed to be reproducible and in agreement with a standard commercially-available wetting tester, the Gravimetric Absorption Testing System (GATS, MK Systems, Inc). The DWA results were sensitive to the loading density (grams of sample per unit area of filter paper) and distribution of the sample across the sample holder. A mathematical model was developed to quantify the amount of water that was absorbed by the sample, evaporated, and trapped at the interface between the sample and the filter paper. The model could be used to determine the actual

water uptake of the sample alone for samples that were saturated within the timeframe of the experiment.

The DWA was used to investigate the dynamic water absorption behavior for several bio-based powders, sand, clay and their blends. Samples that were expected to have gel blocking, the swelling of particles that blocks capillary flow, showed a much slower water uptake rate. A non-linear synergistic effect was observed for blends of swellable and non-swellable particles. In some cases, a maximum in water uptake was observed for low levels of the swellable material. For carboxymethyl starches, gel blocking, as affected by degree of substitution and crosslinking, was the dominant factor to determine water uptake.

Static swelling and mass loss behavior were also evaluated for films cast from starch, carboxymethyl starch, chitosan, hemicellulose and selected blends. Chitosan was found to have significantly higher water swellability than starch and hemicellulose. Strong ionic interactions exist between xylan and chitosan, creating a strong gel network that is more absorbent and resistant to dissolution in water than xylan-starch blends. The carboxymethyl starches have water uptake values greater than starch as a result of crosslinking and an increased degree of substitution.

Water Absorption Behavior of Bio-Based Polymeric Materials

by
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Dedication

I would like to dedicate this thesis to my husband and my family. Their love, encouragement and patience have enabled me to complete this work.

Biography

Kristin Hayden grew up in Stewartstown, Pennsylvania. She received her Bachelor's Degrees in Chemistry and Environmental Studies from Washington College in Chestertown, Maryland in 2005. While at Washington College, Kristin researched the prescribed burning of restored prairie grasslands and the effects of the fires on soil chemistry. In 2005, Kristin entered graduate school at North Carolina State University in the Wood and Paper Science Department. Her research has focused on the use of natural polymeric materials as absorbents.

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Chapter 1

Introduction

Objective

The objective of this research was to understand the absorbent properties of renewable carbohydrate-based materials as a function of composition and structure.

Absorbency

Absorbency is both a physical (macroscopic) and a chemical (molecular) phenomenon.

Physical absorbency is termed macroscopic, because “the fluid wets the surface of the absorbent material and is physically transported into and throughout a porous medium as a moving front of continuous liquid threads or columns. If fluid input ceases before the system reaches saturation, the liquid front will, for a time, continue to move into the capillary structure” (Gross 1990). Both the behavior and characteristics of the absorbent and fluid play a role in absorbency as well. The main factors which affect the physical absorbency are gravity, pore radius, pore length, surface tension, viscosity and contact angle (Gross 1990).

The smaller the pore radius, the higher the fluid will rise. The largest pores tend to dominate capillary pressure, but small pores can drain large ones and leave dense concentrated areas of small pores which retain their fluid and interfere with the wicking of the material (Gross 1990). Uniformity of the fiber structure is also important for absorbency. A non-uniform web of material will wick in random directions whereas a uniform web will wick in the direction of the absorbent orientation (Gross 1990).

The second major type of absorption, chemical absorption, is deemed ‘chemical’ because it occurs on the molecular level. Chemical absorbency is governed by diffusion, hydration, salivation, osmotic pressure, porosity of the network, and electrostatic considerations (Gross 1990). Chemically absorbed water is categorized as either freezing or non-freezing. For cellulose-based absorbents, chemical absorption only accounts for a small portion of the total absorbent capability. The inclusion of a superabsorbent polymer can significantly improve absorption.

It is often the characteristics of water that determine which materials will be able to transport, absorb and retain aqueous liquids. Because of the high surface tension of water, an effective absorbent material must have a high surface energy. Hydrophilic groups are almost always necessary and can be imparted onto the absorbent through chemical treatment. Such hydrophilic groups include hydroxyls and carboxyls which can be added to the absorbent to improve water-loving characteristics (Gross 1990). Different degrees of hydrophilicity are important for personal care products. In a diaper for example, the lining closest to the skin is responsible for receiving and transmitting the fluid. These materials are less hydrophilic than the absorbent itself. This difference helps to effectively pull the fluid away from the skin and leave a dry feeling (Gross 1990).

There are two major classes of traditional absorbents: fiber masses and foams (Buchholz 1998a). Fiber masses include woven cloth, cotton wadding, cellulose batting, and paper. Although the structures may differ, traditional absorbents have similar features which give

rise to absorbent behavior. The actual level of absorbency depends on the relative volume of open space, connectedness of the pores, size of the pores, and the overall mechanical strength of the material (Buchholz 1998a). Traditional absorbent materials contain open spaces or pores which vary in size from about 0.5 μm to several hundred micrometers. Beyond the presence of pores, absorbency is also dependent upon the total amount of open space along with the size of the openings (Buchholz 1998a). Void fraction is closely related to the absolute open volume of the material and is defined as the volume weighted density of the material and it depends on the amount and density of the absorbent substance. It can be modified and controlled during processing to produce specific densities and therefore absorbencies (Buchholz 1998a). In general, the amount of water absorbed increases as the void fraction decreases.

The transportation of liquid into and through a porous material requires not only open space but also a force or pressure applied to the liquid (Buchholz 1998a). Three main forces help move fluid into and through open spaces including gravity, capillary pressure, and hydrostatic pressure. The general relationship for steady slow flow in one direction through a porous medium is governed by Darcy's Law given by:

$$\frac{dv}{dt} = - \frac{\kappa_D A \Delta P}{\mu L} \quad (1-1)$$

where the volumetric flow, dv/dt , is given in terms of sample cross-sectional area, A , sample length, L , fluid viscosity, μ , specific sample permeability, κ_D , and the pressure difference driving the flow, ΔP .

Capillary pressure is responsible for initially wicking the fluid into the dry material (Buchholz 1998a). Capillary pressure, p_c can be defined as where R is the radius of the capillary, σ is the surface tension of the fluid, g is gravity, h is the height of the rise of the liquid, and ρ is the density of the liquid (Equation 1-2).

$$p_c = \rho gh = \frac{2\sigma}{R} \quad (1-2)$$

The Lucas-Washburn equation gives the rate of wicking for a liquid in a capillary:

$$\frac{dh}{dt} = \frac{R^2}{8\mu h} \left[\frac{2\sigma \cos\theta}{r} - \rho gh \right] \quad (1-3)$$

The wicking rate, dh/dt equals the change in height, h , of the liquid with viscosity, μ , versus time, t , in a vertical tube with radius, R , under the influence of gravity and capillary pressure. The first term inside the brackets is the capillary pressure given by surface tension, σ , radius of curvature at the pore's air-liquid interface, r , and the cosine of the contact angle, θ (Konopka 2001, Buchholz 1998a). The effect of gravity on wicking rate is defined by the

second term in the brackets, liquid density, ρ , gravitational force, g , and the height the liquid has traveled, h .

When the interfacial tension is balanced by the weight of the liquid, the liquid will stop rising in the capillary. The force behind wicking is the spreading of liquid with a high interfacial tension along a surface of absorbent material (Buchholz 1998a). In order to obtain maximum wicking, the absorbent should have a large capillary radius and the liquid should be of low viscosity. Unfortunately, absorbent materials often have irregular pores with radii that vary and change along the fluid flow path (Buchholz 1998a).

Hydrostatic pressure, the third driving force, is the difference in pressure between the faces of the absorbent material. Liquid flow in a pore under hydrostatic pressure can be maintained even after saturation. Unlike capillary flow, hydrostatic pressure pushes the fluid into the pore (Buchholz 1998a).

The tendency of an absorbent material to be dewatered by external forces such as compression is dependent upon the mechanical rigidity and structure. A material's compressibility is based on the modulus of the pore structure and is calculated using Young's modulus:

$$E_f/E_0 = \Phi(2 + 7\Phi + 3\Phi^2)/12 \quad (1-4)$$

The Young's modulus, E_f , for the porous material is determined by the modulus of the solid structural material, E_0 , and the solid's volume fraction within the absorbent material, Φ .

Traditional absorbents have a propensity to be dewatered even if the structure is sufficiently rigid to prevent compressive collapse (Buchholz 1998a). The rigidity can be overcome by gravitational force or capillary pressure, resulting in structural collapse.

Absorbency is directly related to the volume of open space, connectedness and size of the pores and the mechanical strength of the material (Buchholz 1998a). These characteristics can be controlled by choosing a traditional absorbent's structural material, manufacturing process, and fiber and pore dimensions. These parameters allow it to be possible to design an absorbent for a specific purpose.

Superabsorbency

A superabsorbent is loosely defined as a crosslinked network of flexible polymer chains.

Many synthetic water-absorbing materials were developed in the first half of the 20th century.

Most were based on acrylic acid. One of the first synthetic water-absorbing polymers known by the public was hydrolyzed acrylonitrile-grafted starch (H-SPAN), which was developed in

the 1970's (Gross 1990). It was described as a material which could absorb up to 5,000 grams of water per gram and was termed "Super slurper". The term "superabsorbent" was first used at the First International Absorbent Products Conference: INSIGHT 80, in 1980.

Later, R. E. Erickson of Dow Chemical qualified a superabsorbent as a dry material which could “spontaneously imbibe about twenty times its own weight of aqueous fluid. The hydrogel, resulting from the transformation of the dry superabsorbent, must have sufficient physical integrity to resist flow and fusion with neighboring particles. When exposed to an excess of water, true superabsorbent hydrogel particles swell to their equilibrium volume and do not dissolve.” (Gross 1990). During this extreme volume change, the superabsorbent must retain its identity and be recognizable in its own form. The mechanisms which control swelling are the same ones which control dissolution. Therefore, in order to prevent the material from dissolving, a network connection, or crosslink, must be present (Gross 1990, Buchholz 1998a).

The simplest type of crosslink is the covalent bond. These bonds form an infinite three-dimensional network between the polymer chains. Crosslinking has great influence over the swelling behavior of a material. Crosslink density is defined as the average number of monomer repeat units between crosslinks. In general, as the crosslink density increases the swelling usually decreases significantly (Figure 1-1, Castel, Ricard and Audebert 1990). Another result of crosslinking is a more rigid polymer in the swollen state. For diaper applications, this enables the superabsorbent to push aside the fibers in the absorbent core to maintain permeability (Buchholz 1998b).

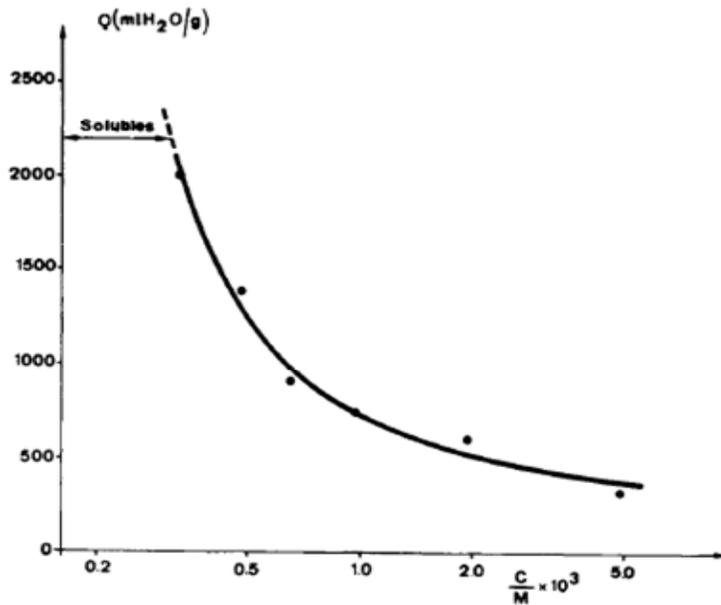


Figure 1-1: Absorbency (g/g) as a function of crosslink density (C/M). As the crosslink density increases, the water uptake decreases rapidly. The y-axis is the water swelling (grams of water/gram sample) and the x-axis is the crosslinking density (number of monomer repeat units between crosslinks) (Castel, Ricard and Audebert 1990).

The preparation of superabsorbent polymers is done in a step-wise fashion, beginning with the preparation of the monomers (Figure 1-2, Graham and Wilson 1998, Buchholz 1994).

The monomers typically used are a mixture of acrylic acid and the crosslinking monomer. A free-radical initiator is added to the aqueous system to begin the polymerization of the monomer. Examples of the free-radical initiators include sodium persulfate and the combination of hydrogen peroxide and ascorbic acid. A gel is formed soon after the reaction is started. During polymerization, the gel is often broken up to produce a rubbery material which will be easier to dry. The dryers can be through-circulation conveyors or rotating drum dryers. Grinding and screening the dried polymer provides the desired particle size. The fines

recovered during screening are recycled or converted into other sealable products (Graham and Wilson 1998).

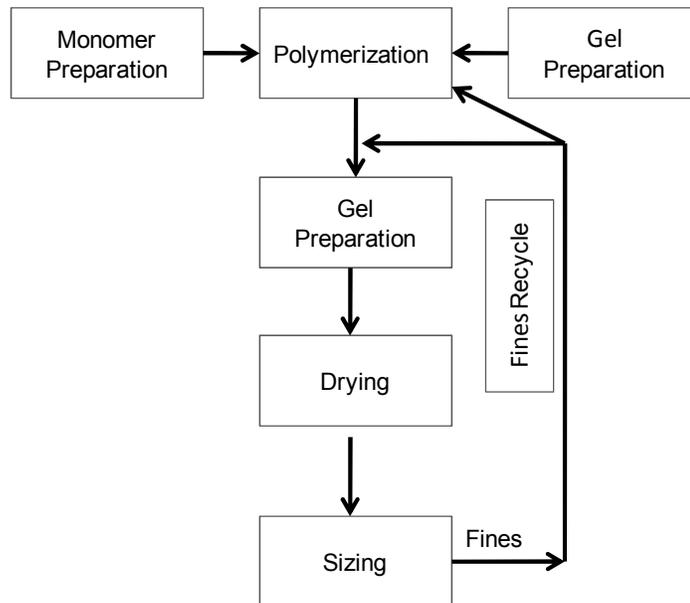


Figure 1-2: Stepwise schematic for the production of superabsorbent polymers (adapted from Graham and Wilson 1998).

Superabsorbents take up water by diffusion and osmosis whereas traditional absorbents function by capillary forces. Diffusion is the molecular mechanism wherein molecules move in a random way as a result of concentration gradients enhanced typically by thermal energy. The constant random movement of the molecules results in the net movement of the molecules from high concentration to lower concentration. In the case of superabsorbents, water moves or diffuses into the absorbent because there is lower water concentration inside the absorbent. As water moves into the absorbent, the polymer expands to compensate for the

added volume (Buchholz 1998a). The rate of water diffusion is slow in superabsorbent materials because each of the polymer chains is connected together by crosslinks which restrict the polymers' movements. The law governing diffusion is Fick's law:

$$\frac{f}{A} = -D \frac{dc}{dx} \quad (1-5)$$

The concentration gradient, dc/dx of the diffusing substance is related to the diffusional flow rate, f , in the x direction. The cross-sectional area of the sample is A , and D is the diffusion coefficient. According to Fick's law, the absorption in a superabsorbent is proportional to the chemical activity and flow depends on the random motion of the individual molecules, their size and thermal energy (Buchholz 1998a).

Osmosis is the other absorption phenomenon in superabsorbent polymers. Osmosis is the spontaneous diffusion of a solvent through a semi-permeable membrane, in the direction of the concentrated solution (Osmosis 2008). The direction of the flow is based on the tendency to balance the concentrations of both sides.

Diffusion and osmosis are phenomena which seek to balance the charges and concentrations within two or more regions (Figure 1-3). This means dissociated ionic groups within the polymeric structure help create the most effective and efficient water absorbers because they spread out the structure and increase the rate of diffusion and osmotic pressure (Buchholz and Burgert 1996).

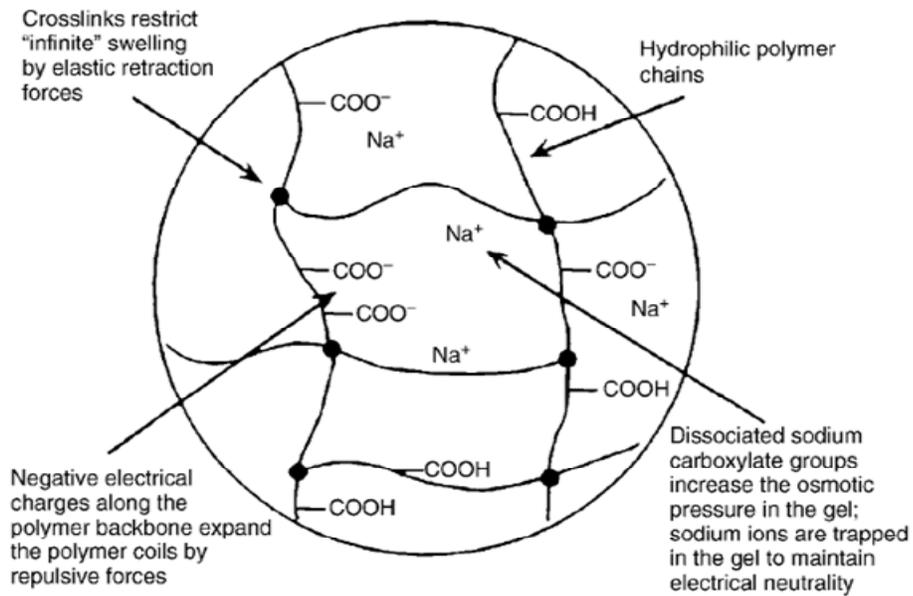


Figure 1-3: Schematic drawing of ionized crosslinked polymer network. Crosslinks between polymer chains are represented by dark dots (Buchholz and Burgert 1996).

The most common superabsorbent polymers exist in granular powder form and have an appearance similar to white sand and table sugar. These materials are also available as microspherical powders and fine fibers (Buchholz 1998a). Superabsorbent polymers can be found most frequently in infant diapers, feminine hygiene products and adult incontinence materials but they are also utilized in paper towels, medical sponges, disposable door and bathroom mats and pet litter (Buchholz 1998b). The tendency of superabsorbent polymers to release water in vapor form also allows them to be utilized in humidity-controlling and soil conditioning applications. The fact that they slowly release the water makes them ideal for controlled release situations.

The largest application for superabsorbent polymers is in personal hygiene products, with more than 90% of the total polymers used in disposable infant diapers (Buchholz 1998b). The three components of diapers are the porous top-sheet, impermeable back-sheet and absorbent core. The top sheet is next to the baby's skin and covers and contains the absorbent core because it is fragile when wet. This sheet is typically made of a hydrophobic material, often polyester or polypropylene fabric and its main purpose is to allow the urine to pass away from the baby's skin into the absorbent core. The back-sheet is also a hydrophobic material, usually polyethylene, and it helps keep the baby's clothing dry. The absorbent core receives the liquid, distributes it to other areas of the core and holds in the liquid under the pressure of the baby's weight. Early absorbent cores were layers of creped tissue. Without a polymer network to hold the water in place, the core could only keep water in the void spaces between the tissue fibers. The greater the void space, the greater the absorption capacity. This produced a thick core with many small pores and a low crosslink density. Gels with light crosslinking have a low modulus when swollen and are easily deformed. These deformed particles adhere to one another and greatly reduce the porosity of the gel. This decreases the diffusion rate and therefore the swelling, leading to what is known as gel-blocking (Graham and Wilson 1998, Buchholz 1998b). In diapers, gel blocking equates to a higher probability of leaks. Increasing the crosslink density improved the gel modulus and reduced the gel-blocking.

Modern diaper cores utilize layering in a different way. Density gradations of the absorbent material throughout the core help reduce the overall thickness and improve wicking, liquid holding and total capacity (Buchholz 1998b). The addition of superabsorbents to the core has also helped reduce diaper bulk. Diaper superabsorbents can retain approximately thirty times their weight in urine even when under 1-5 kPa of pressure. Superabsorbents make up at least 10% of the material within the core and therefore the diaper itself is relatively thin in the dry state (Buchholz 1998b).

Gels

Hydrogels are networks of hydrophilic polymers which can absorb greater than 20% of the total weight in water without dissolving or losing structural integrity (Bajpai and Sharma 2006). A superabsorbent hydrogel typically absorbs greater than 95% of the total weight (Hydrogels 2007). Once wet, the structure is typically soft and rubbery with texture resembling living tissue. It is appropriate to use hydrogels in medical fields because the structures are often compatible with human organs and stable towards biofluids (Bajpai and Sharma 2006). Biomedical applications of hydrogels include contact lenses, wound dressings, controlled drug release systems and artificial implants (Bajpai and Sharma 2006). Hydrogels are also frequently used for molecular separation, protein isolation, fire protection, water sealing construction materials, agricultural soil additives and for superabsorbents (Hydrogels 2007).

The structure of a gel, which dictates swelling behavior, can be controlled by adjusting the ionic unit content, the crosslinking density and the graft length during synthesis (Castel, Ricard and Audebert 1990). The water absorbing behavior of hydrogels is a result of the electrostatic repulsion of ionic charges within the network. As ionic groups are introduced, the charges repel one another, opening up the network and leaving room for swelling. Increasing ionic groups eventually spreads the structure out too far. The charges become so far apart that they no longer interact with one another and the water swelling capability decreases. For example, a gel with a copolymer concentration of 35% has the highest absorbency in distilled water but as the ionic concentration from the copolymer increases beyond 35%, the swelling capability decreases (Figure 1-4, Castel, Ricard and Audebert 1990). The same behavior is present with swelling in simulated urine, a high ionic strength solution. The overall water uptake in simulated urine is lower than in distilled water because of the abundant ions already present. The ions in solution decrease the osmotic pressure difference between the gel and the solution. The ionic strength of a solution depends on the mobile ions and their charges. Only small amounts of divalent or trivalent ions are needed to dramatically decrease swelling (Castel, Ricard and Audebert 1990).

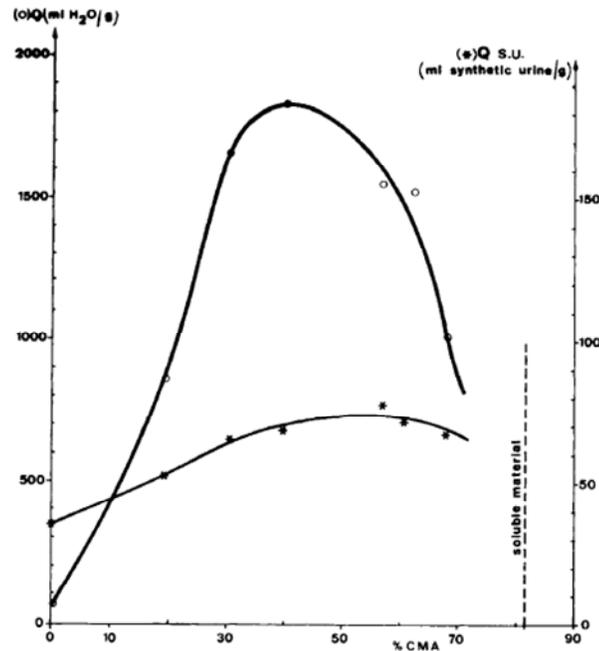


Figure 1-4: Water uptake (ml/g) for cationic absorbents as a function of copolymer content. The x-axis is the percentage of cationic copolymer trimethyl-aminoethylacrylate chloride (CMA). The primary y-axis is water uptake in distilled water. The secondary y-axis is water uptake in simulated urine (Castel, Ricard and Audebert 1990).

The level of crosslinking not only affects the overall water uptake capabilities, but it affects the way in which the water is absorbed. A major difference between gels of gelatin, natural gums and those of superabsorbent gels is the ease with which they form hydrogels.

Superabsorbents form gels spontaneously when they come in contact with water, whereas gelatin and others require assistance before a gel is formed (Gross 1990).

Natural polymers

Absorbent hygienic materials are an important part of modern society, fulfilling serious health and safety needs. The demand for these materials is greater than 40,000 metric tons

annually (Nexant, Inc. 2004). Typically these products are derived from non-renewable petroleum-based acrylic acid, making disposal and biodegradability in landfills a concern. As the price of oil rises, the price for these absorbent feedstocks also rises. Many recent research articles have focused on the preparation and utilization of bio-based absorbents.

Grafted starch-acrylonitrile absorbents were developed in the 1970's by the USDA, but were never commercialized on a large scale (Gross 1990). Yamaguchi, Watamoto and Sakamoto (1987, 1988) prepared superabsorbents from these starch-polyacrylonitrile graft copolymers. Superabsorbents with swelling values of 70-390 gram/gram were prepared by Lanthong, Nuisin and Kiatkamjornwong (2006) using cassava starch.

The grafting of acrylic acid and acrylamide onto cellulose chains greatly increases the water-loving nature of cellulose. Non-potable water from three sources in India was passed through columns filled with the absorbent polymers and the unhealthy ionic content of the water was greatly reduced (Chauhan and Lal 2003).

Other plant and animal-derived polymers used as absorbents include red seaweed or carrageenan (Pourjavadi and Amini-Fazi 2007), pullulan, a polymer produced by fungus (Dulong, Mocanu and Le Cerf 2007) and chitosan (Yao et al. 1998, Mahdavinia et al. 2004, Crescenzi et al. 1997 and Yu and Hui-min 2006), just to list a few.

Chitosan, a material derived from the shells of crustaceans like shrimp and crabs, is the linear deacetylated highly-soluble form of chitin, $\beta(1-4)$ -2-amino-2-deoxy-D-glucose (Arguelles-Monal, et al. 2003, Sanford 1989, Figure 1-5). To produce chitosan, chitin is subjected to strong NaOH to hydrolyze the N-acetyl linkage and rinsed. The pH is adjusted and the material is dewatered. At this stage, the product can be made into flaked chitosan (Sandford 1989, Roberts 1992). Milling flaked chitosan results in a finer mesh powder which can be blended with an organic acid to obtain a self-dissolving chitosan acid.

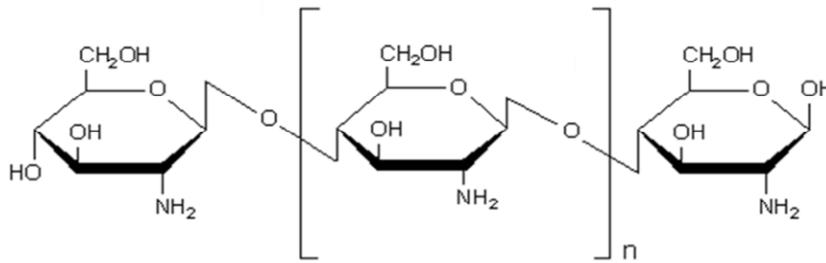


Figure 1-5: Chitosan.

Unlike chitin which is sparingly soluble, chitosan becomes water soluble after salts are formed with organic acids including formic, acetic, and ascorbic acids. Hydrochloric acid is the only mineral acid which makes chitosan water soluble. When chitosan is reacted with acids, a glucosamine residue with protonated amino groups is formed. This makes chitosan behave like a cationic polymer (Uragami and Tokura 2006). The pKa of chitosan is ~ 6.5 . Many biological materials like proteins and nucleic acids carry negative charges and therefore interact strongly with the chitosan to create electric neutrality (Sandford 1989). For

medical uses it is a superior material due to its biocompatibility, non-toxicity, ability to clot blood, and ability to absorb liquids while forming protective coatings (Arguelles-Monal, et al. 2003, Sanford 1989).

Hemicellulose is another effective absorbent. Hemicelluloses are branched, amorphous, contain more than one type of saccharide, and have multiple functional groups (Figure 1-6). This allows the molecules to act in ways different than cellulose and starch. These hemicelluloses are soluble in aqueous alkali but insoluble in almost all organic solvents (Sun, Sun and Tomkinson 2004). The organic insolubility is probably due to the high density of hydrogen bonds within xylan (Jain, Sjostedt and Glasser 2001). Solubility can therefore be induced when some of the hydroxy groups are substituted by alkoxy or acetoxy functionalities (Jain, Sjostedt and Glasser 2001). Some of the structural and behavioral disadvantages can be overcome by chemical and structural modification. The chemical modification of hemicellulose was studied as early as the 1960's, focusing on modification of xylan. Applications for hemicelluloses and other lignin polymers include adhesives, coating and foam products, engineering plastics, food additives, thickeners, emulsifiers, gelling agents and adsorbents (Gabrielii and Gatenholm 1998). The reaction of xylan with propylene oxide in aqueous alkali produces a thermoplastic hydroxypropyl xylan with a low molecular weight, branched structure, and solubility in water (Sun, Sun and Tomkinson 2004).

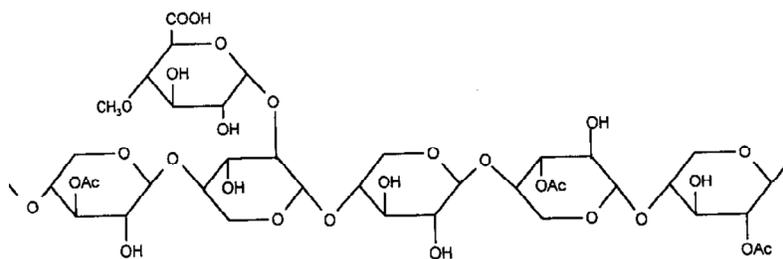


Figure 1-6: Birchwood glucuronoxylan (hemicellulose).

Gabrielii and Gatenholm (1998, 2000) have used birchwood and aspen xylan as the base for hydrogels and combined them with chitosan. Beechwood xylan, barley husk xylan and carboxymethyl xylan are also viable biobased absorbent alternatives (Tanodekaew, Channasanon and Uppanan 2006, Grondahl, Eriksson and Gatenholm 2004, Petzold, Schwikal and Heinze 2006).

Carboxymethyl starch (CMS), another material that has been utilized as a natural absorbent, is obtained as a product of the reaction of starch (St-OH) with sodium hydroxide and sodium monochloroacetate (MCA) (Figure 1-7, Stojanovic, Jeremic, and Jovanovic 2000). This is a two-step reaction, the first step being the alkalization of starch followed by etherification:



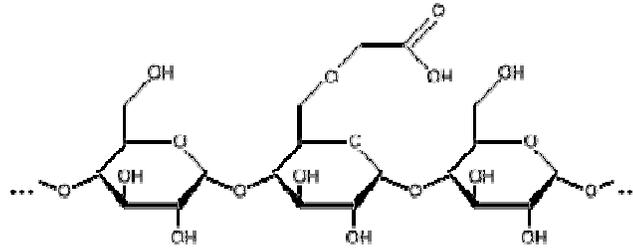


Figure 1-7: Carboxymethyl starch.

These modified starches have increased water solubility as the degree of substitution (DS) is increased. For this reason organic solvents are used for the production of granular CMS like the ones used in this study (Stojanovic, Jeremic, and Jovanovic 2000). For CMS, the degree of substitution is the average number of carboxymethyl groups on the starch repeat unit (Heinze, et al. 2004). Typically CMS is used as an additive in the paper industry, as a thickener for textile printing pastes and as a tool for enhanced oil recovery (Stojanovic, Jeremic, and Jovanovic 2000).

Unmodified corn starch (Figure 1-8), similar to the Pearl B starch from Cargill, has been utilized as a blend component along with other biobased absorbent materials.

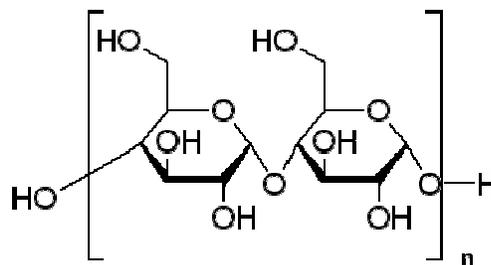


Figure 1-8: Amylose, a major component of corn starch.

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Chapter 2

DWA Description and Characterization

Introduction

The dynamic wetting apparatus (DWA) allows for the study of the behavior of fluid-absorbing materials over specific time intervals. This will help determine when and how quickly a material reaches its maximum saturation and its overall fluid uptake capability. The timing for saturation is important for determining the application of the absorbent material.

Typical water uptake measurements are static and usually only measure overall water uptake or capacity. For absorbent applications requiring fast and large absorptions, it is imperative to evaluate dynamic water uptake. Castel, Ricard and Audebert (1990) developed a capillary suction technique (Figure 2-1) to measure water uptake in a dynamic way. The concern with this setup is that it is labor-intensive and introduces human error because a person is required to read the water level from the burette periodically in order to gather the necessary kinetic data.

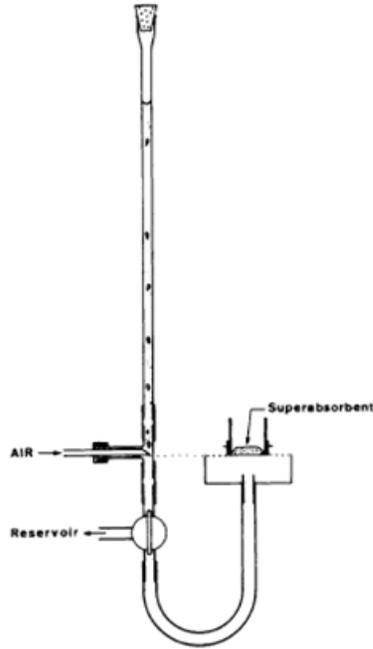


Figure 2-1: Dynamic swelling apparatus based on capillary suction (Castel, Ricard and Audebert 1990).

Another dynamic water uptake technique involves a sample cell attached to Thermomechanical Analysis (TMA) equipment (Figure 2-2, Nakamura, et al 2000). This method has been used to investigate sample deformation due to swelling under various load levels. It is reproducible and reduces the human error involved.

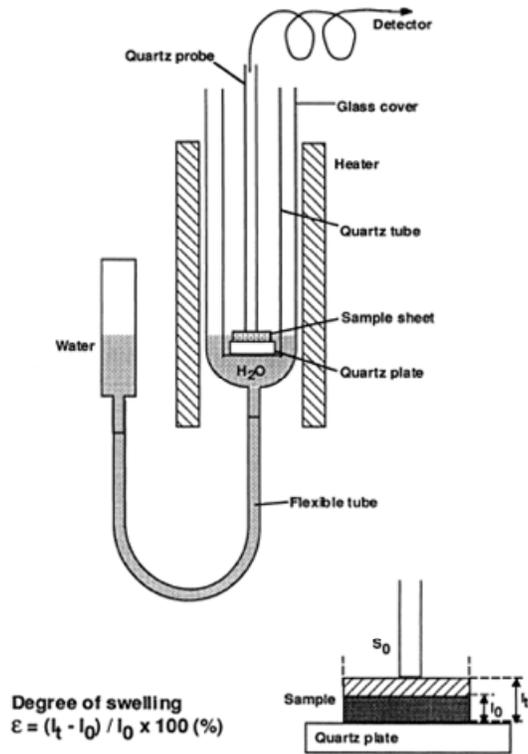


Figure 2-2: Thermomechanical Analysis (TMA) sample cell designed to measure dynamic water uptake (Nakamura, et al 2000).

In another method, utilized by Suzuki, Ikkai, and Shibayama (2007), a sample is immersed in a thermostated chamber which is filled with distilled water. The diameter of the gel is monitored by an inverted microscope coupled with an image processor. In another method, used by Budtova and Navard (1998), the dry gel was placed between two microscope slides. A solution was added and the gel radius was measured by optical microscopy as a function of time. The tea-bag method is another widely used technique for measuring swelling kinetics (Yuk, et al 1996, Chen, et al 2007). A known amount of polymer is placed in a tea bag and

sealed. The tea bag is immersed in the testing solution. At specific time intervals, the tea bag is removed, the excess water is wiped off and the bag is weighed. The amount of swelling is recorded as the weight change per unit time.

Three standard testing methods exist for measuring absorption rate and capacity (ASTM D 824, ASTM D 4250 and TAPPI T561 pm-96). For the TAPPI test method, a test plate or sample platform is connected to a water supply which is placed on a balance (Figure 2-3). A small amount of water is forced into the sample to initiate the test. Once wetted, the sample should continue to draw water from the supply chamber. The mass loss on the balance is recorded as water uptake from the sample.

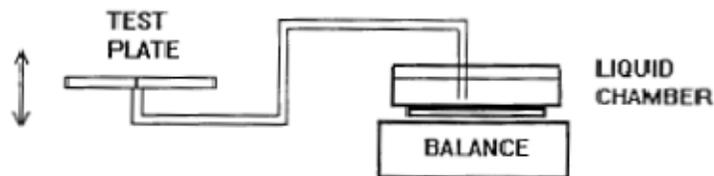


Figure 2-3: Water uptake setup for TAPPI method T 561 mp-96.

A commercially available dynamic water uptake method, Gravimetric Absorption Testing System (GATS), is sold by M/K Systems, Inc. (Bethesda, MD). For this equipment, fluid is absorbed radially along the plane of the sample and is delivered by a ¼ inch hole at the bottom of the test plate (Figure 2-4, Textile Protection 2008).

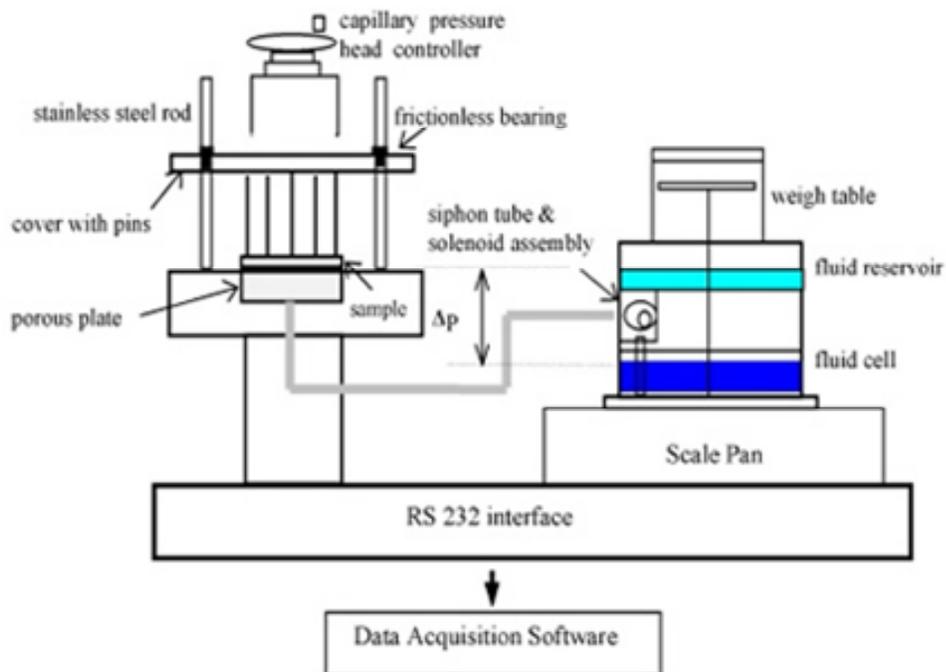
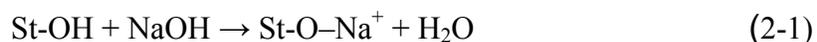


Figure 2-4: Gravimetric Absorption Testing System (GATS) setup (Textile Protection 2008).

The fluid level is adjusted in relationship to the sample height to provide zero hydrostatic pressure. This allows the water to be taken up solely on-demand. The fluid reservoir is attached to a balance and the weight of the fluid transferred from the reservoir to the sample is recorded and transmitted to data acquisition software. Results from the GATS are reproducible but the equipment itself costs more than \$28,000.

The development and characterization of a water uptake method comparable to the GATS, but more cost-effective, was one of the objectives of this study. Some of the natural polymers used to evaluate the new water uptake method include carboxymethyl starch (CMS) and hemicellulose.

Carboxymethyl starch (CMS) is obtained as a product of the reaction of starch (St-OH) with sodium hydroxide and sodium monochloroacetate (MCA) (Stojanovic, Jeremic, and Jovanovic 2000). This is a two-step reaction, the first step being the alkalization of starch followed by etherification:



These modified starches have increased water solubility as the degree of substitution (DS) is increased. For this reason organic solvents are used for the production of granular CMS like the ones used in this study (Stojanovic, Jeremic, and Jovanovic 2000). For CMS, the degree of substitution is the average number of carboxymethyl groups on the starch repeat unit (Heinze, et al. 2004). Typically CMS is used as an additive in the paper industry, as a thickener for textile printing pastes and as a tool for enhanced oil recovery (Stojanovic, Jeremic, and Jovanovic 2000).

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Materials and Methods

The materials used to evaluate and characterize the DWA include filter paper, sand, starch, carboxymethyl starch (CMS) 270ul, CMS 220ul and hemicellulose. The filter paper circles used to evaluate the GATS were 90 mm Whatman #41 quantitative filter paper circles (Whatman #1441-090) and those used to characterize the new method were 55 mm Whatman #41 quantitative filter paper circles (Whatman # 1441-055). For the 55 mm circles, the average weight per circle was 0.1976 grams and the standard deviation was 0.0083 grams. The basis weight (g/m^2) was 83.1482 g/m^2 . The average water uptake for the filter paper circles was 0.8556 grams of water/gram filter paper and the standard deviation was 0.1021 grams/gram. The evaluated sand was red craft sand from a local craft supply store. The starch was Pearl B unmodified corn starch from Cargill. Two CMS powders from Aquasol Corporation (Charlotte, North Carolina) with different degrees of substitution (DS) were utilized in this study. The high and low levels of DS are 0.70 and 0.20, respectively and are represented by CMS 270ul and CMS 220ul. The hemicellulose used was birchwood xylan (Aldrich- X0502).

Dynamic Wetting Apparatus

The Dynamic Wetting Apparatus (DWA) is designed to measure the change in mass as a sample absorbs water. The estimated cost for the DWA is \$1,500 which includes a balance, computer and data acquisition software. The balance (Mettler Toledo Model PG203-S) is connected to a computer which records the mass changes in a text file. A water reservoir

constructed out of a piece of polyvinyl chloride (pvc) pipe is placed on the balance, filled to the water line with distilled water and covered with a Petri dish lid (VWR polystyrene disposable Petri dish 100 x 15 mm catalog # 25384-088) to prevent evaporation (Figure 2-5).



Figure 2-5: Water reservoir with cover to prevent evaporation.

A second piece of pvc pipe is filled with a piece of Oasis[®] brand floral foam (Smithers-Oasis North America, Wet Foam Brick- 3 x 4 x 9 inches). The Oasis[®] floral foam is designed to saturate completely and provide a continuous supply of water to floral arrangements. In this situation the foam will supply water to the sample. This pipe piece is placed on a small adjustable lab jack (Figures 2-6 and 2-7). The two pipe sections are connected to one another using an 8.5” piece of latex rubber tubing (Figure 2-8). The water levels were adjusted to the same height (Figure 2-9). This will insure that the only water flow is due to the water uptake capability of the testing materials. As the water is flows over and is drawn up by the sample, the balance will measure a mass loss which will be recorded as water uptake.

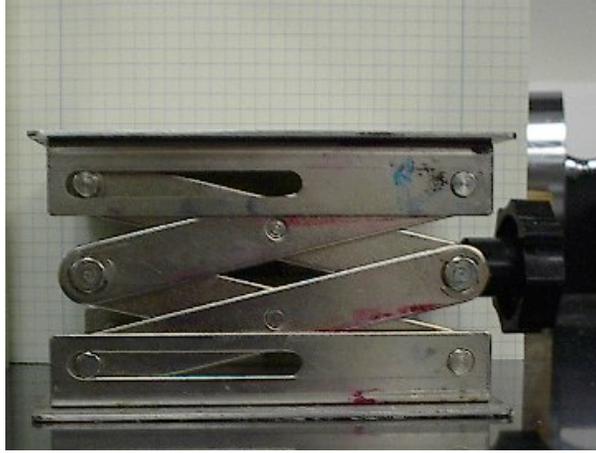


Figure 2-6: Small adjustable laboratory jack used to support floral foam-filled pvc pipe.

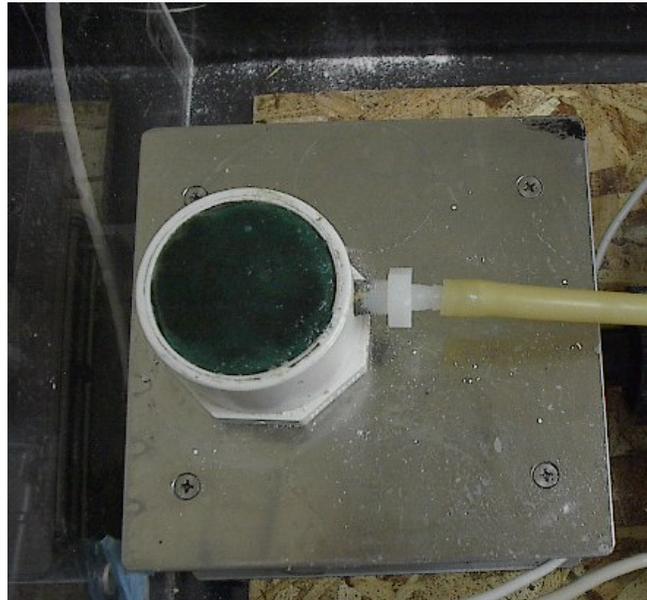


Figure 2-7: Foam-filled pvc pipe on adjustable laboratory jack.



Figure 2-8: Foam and water reservoirs connected by rubber tubing.

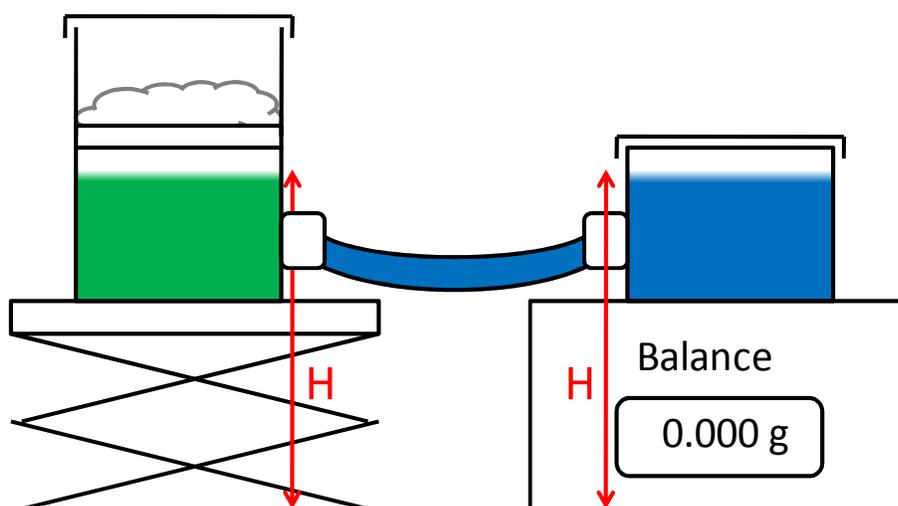


Figure 2-9: Schematic representation of DWA setup. The H denotes the height of the water in the water and foam reservoirs.

The 5.5 cm filter paper circle is placed on the flower foam. The sample holder is added next followed by the sample and the cover (Figure 2-10). Complete testing instructions are listed in Appendix A.



Figure 2-10: Foam-filled pvc with filter paper circle, sample holder and cover (*left*) and water reservoir with cover (*right*).

Evaporation Rate

The evaporation rate of the system was tested with a piece of filter paper (Whatman #41 ashless 5.5 cm circle Whatman #1441-055), the sample holder (1.5” inner-diameter, 1.75” tall PVC pipe) and the sample cover (VWR polystyrene disposable Petri dish 100 x 15 mm catalog # 25384-088). The empty system was allowed to equilibrate until a steady state was reached. The filter paper and sample holder were added and allowed to equilibrate for three minutes, after which time the filter paper absorbed, on average, 0.868 grams of water (Figure 2-11) or 4.393 grams of water/gram of filter paper. After this equilibration, data collection was begun and the sample cover added. Data was collected every 30 seconds and the system was left for several hours.

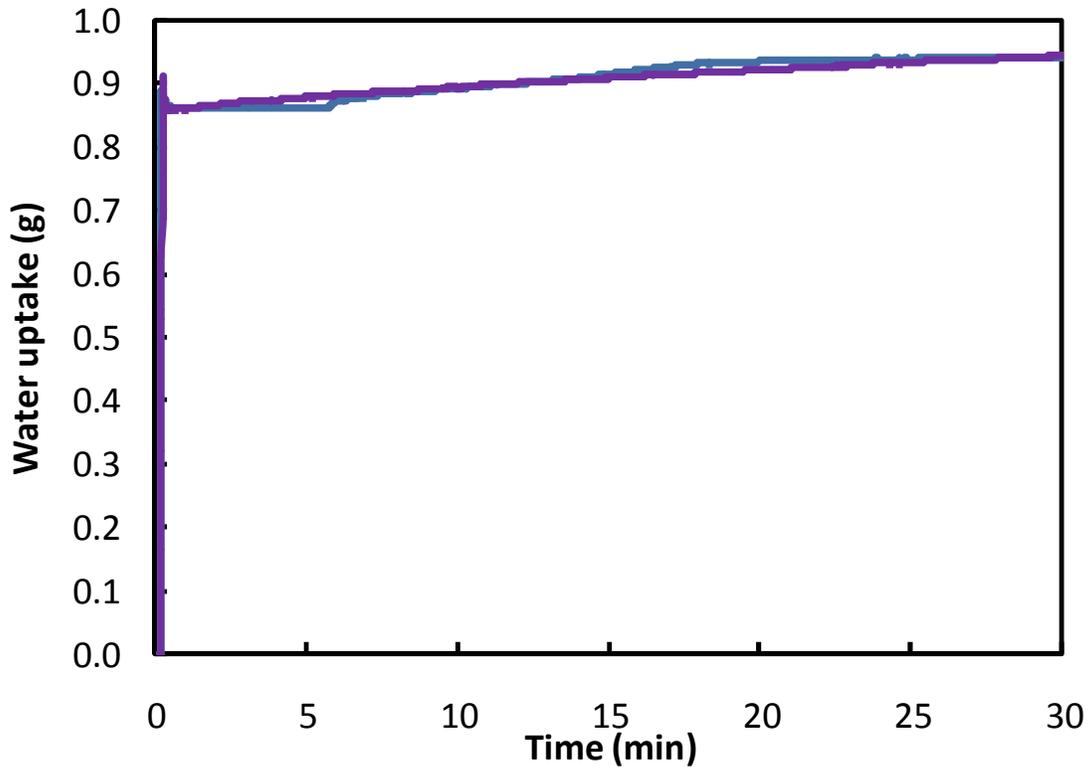


Figure 2-11: Water uptake for 5.5 cm filter paper. Note the water uptake scale is from 0.0 to 1.0 grams. Duplicate runs are plotted.

Sample Size

Sample size is known to have an effect on water uptake. Sample sizes between 0.5 grams and 6.0 grams were studied using uncooked dent starch. Another set of experiments were performed using CMS 270ul with sample sizes ranging from 0.5 grams to 4.0 grams.

Sample Coverage

Each sample was manually spread over the filter paper so it was necessary to determine whether the evenness of the sample across the filter paper had an effect on the water uptake

results. Four tests were conducted using the high DS, uncrosslinked carboxymethyl starch CMS 270ul. The material was spread manually across the filter paper in an attempt to cover 100, 75, 50 and 25% of the paper (Figure 2-12).

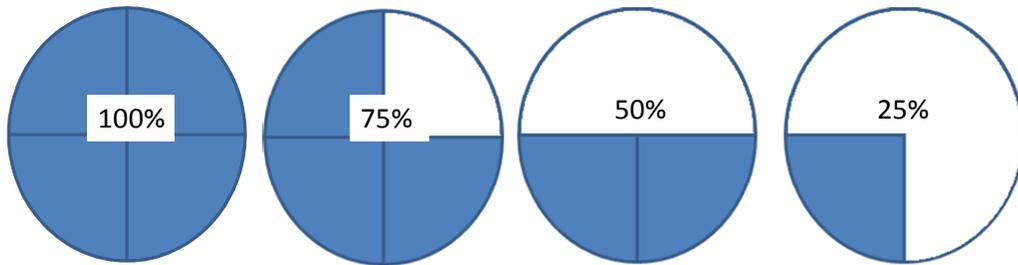


Figure 2-12: Schematic for four coverage levels.

Comparison of DWA to the GATS

One way to evaluate the performance of the DWA was to compare it with a known water uptake method- Gravimetric Absorption Testing System (GATS) (Konopka 2001, Figure 2-4). These two setups are designed to measure dynamic wetting but the DWA was considerably less expensive to build and operate.

Initial tests were performed with the GATS using 9 cm filter paper (Whatman #41 ashless 9.0 cm circle Whatman #1441-090) only. Water uptake was measured for 2.0, 4.0 and 6.0 grams of starch and for 6.0 grams of CMS 270ul and CMS 220ul with the GATS. In order to properly compare the same materials using the DWA, the sample size had to be adjusted to match the sample density of the GATS (Table 2-1).

Table 2-1: Sample density conversion for GATS and DWA.

GATS sample size (g)	2.0	4.0	6.0
Equivalent for DWA (g)	0.747	1.494	2.241

Results and Discussion

Evaporation Rate

The evaporation experiment was performed three times, with linear trend lines of $y = 0.0019x \text{ g/min} + 0.0312 \text{ g}$, $y = 0.0018x \text{ g/min} + 0.0185\text{g}$ and $y = 0.0021x \text{ g/min} + 0.0134\text{g}$ (Figure 2-13). The average water evaporation rate was therefore 1.933 mg/minute. The area of the filter paper was 0.002376 m^2 so the evaporation rate per unit area was $0.8137 \text{ g/min}\cdot\text{m}^2$. The water uptake associated with the filter paper after the initial three-minute equilibration period was only 0.0655 grams after 20 minutes. This uptake had only a small impact on the overall water uptake when powdered samples were added to the system.

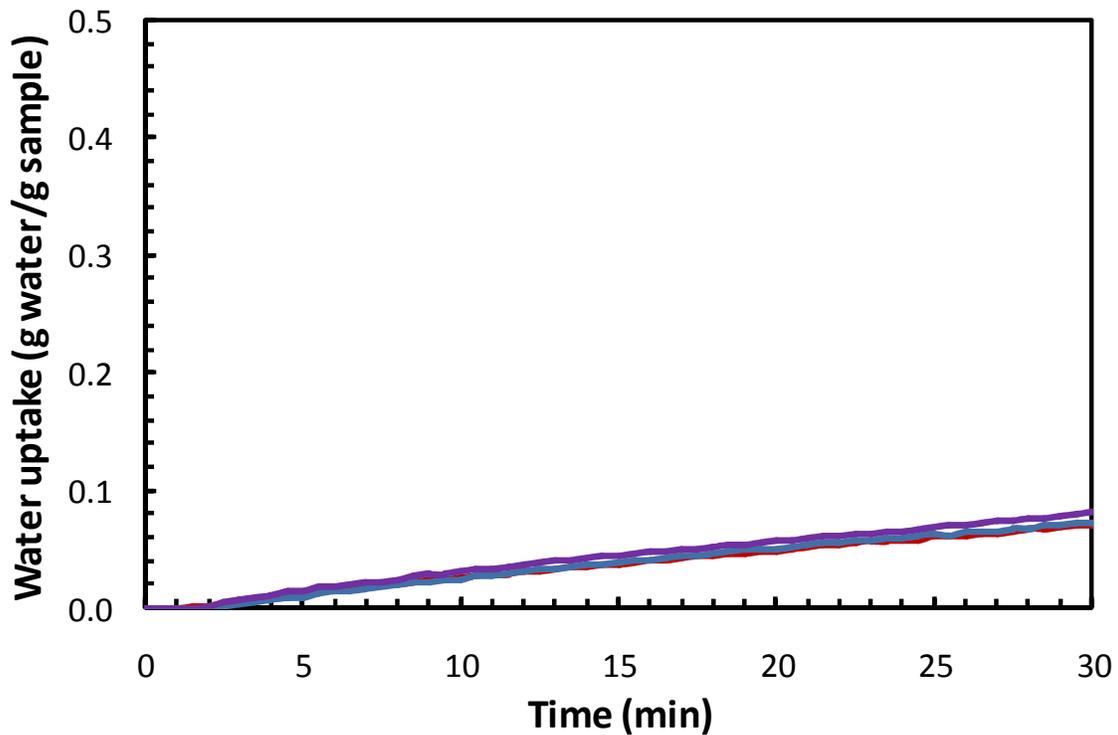


Figure 2-13: Baseline evaporation for DWA. Note the y-axis scale is 0.0-0.5 grams. Triplicate runs are plotted.

In order to put the evaporation rate into perspective, the rate was compared with the overall water uptake of sand and hemicellulose. A one gram sample of sand took up an average of 0.2469 grams of water/gram of sand in the first ten minutes. The amount of evaporation for a ten minute experiment was 0.01933 grams or 8% of the total uptake for the sand. For a one gram hemicelluloses sample, the uptake in the first ten minutes averaged 5.3154 grams of water/gram of hemicellulose. Again, the evaporation for ten minutes was 0.01933 grams which was 0.36% of the total uptake for the hemicellulose. Sand had the lowest uptake for all materials studied as it is not expected to swell with water. The hemicellulose had the highest water uptake. As a result, the effect of the evaporation rate on the uptake of all materials studied will be between 0.36% and 8% for the first ten minutes. Therefore, the effect of water loss due to evaporation will be minor in terms of overall water uptake.

Sample Size

As the sample size increased for both materials, the water uptake per gram of material decreased (Figures 2-14 and 2-15). This was probably due to a transportation delay. A small sample allows fast and easy uptake of the water into the entire sample. As the sample size increases the time it takes for the water to contact the entire sample also increases. The greatest range of water uptake due to sample size is evident with the CMS 270ul. Starch samples have a spread of approximately 0.2 g water/g sample. The water uptake for the CMS 270ul material has about a 2.1 g water/g sample range. This large difference for the CMS 270ul uptakes is consistent with gel blocking phenomenon (Figure 2-15). Although the rates

for CMS 270ul water uptake differ for each sample size, it is presumed that if the experiments were allowed to continue, the steady state values of uptake for all sample sizes would be similar to one another, like in the starch experiments. The uptake for the 0.5 gram starch sample reaches saturation the fastest but according to the graph (Figure 2-14), the uptake never levels off. This steady rate of water uptake is due to evaporation which has a large effect on such a small sample size. A sample size of 1.0 gram was chosen for the subsequent experiments because 1 gram was enough to cover the filter paper yet was not large enough to significantly decrease the water uptake per gram of material.

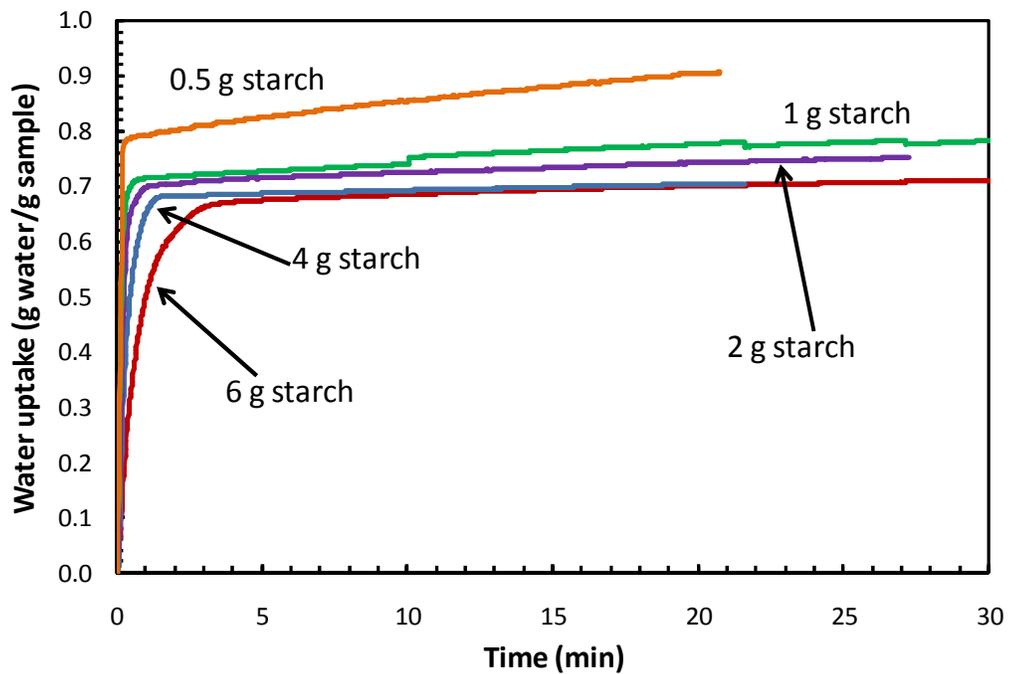


Figure 2-14: Average water uptake for starch sample sizes ranging from 0.5 grams to 6.0 grams.

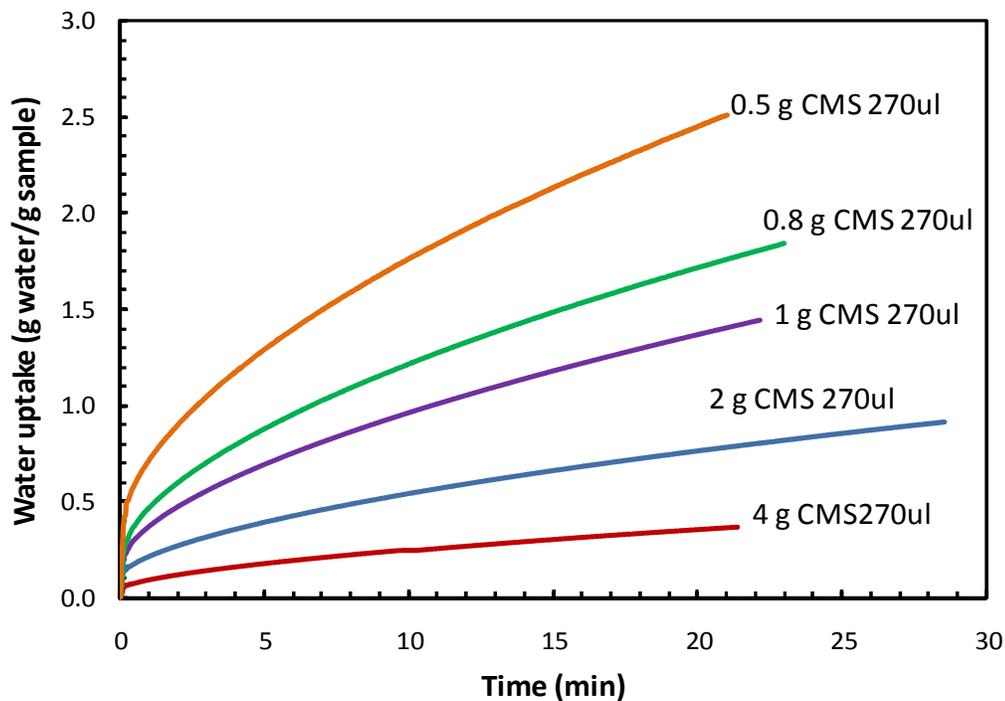


Figure 2-15: Average water uptake for CMS 270ul samples ranging from 0.5 grams to 4.0 grams.

Instrument Characterization: Partition of Water in Sample

By comparing the water uptake in a gram of water/gram of sample basis, it is noted that the smallest samples take up the largest amount of water. The purpose of this data analysis method is to determine the actual amount of water taken up by each sample and whether the smallest samples really have the highest uptakes.

The behavior of the materials in the DWA system was defined using the following equations:

$$M_W = M_K + M_E + M_S \quad (2-3)$$

$$M_W/G = (M_K + M_E + M_S)/G \quad (2-4)$$

where M_W is the total mass of water taken up in grams (Figure 2-16). The variable M_K is the mass of water in grams taken up as the interface between the sample and the filter paper fills with water (interface variable) and M_E is the mass of water in grams that has evaporated. The mass of water in grams absorbed and held by the sample is defined as M_S and G is the mass of the sample in grams. The mass of water evaporated, M_E , is a function of the evaporation rate, E , and time, t . The evaporation rate is 0.001933 g/minute and was determined with filter paper (Figure 2-13). The amount of water taken up by the sample, M_S , is equal to the water uptake rate, R , multiplied by time, t . The uptake rate, R , is a function of capillary action and diffusion.

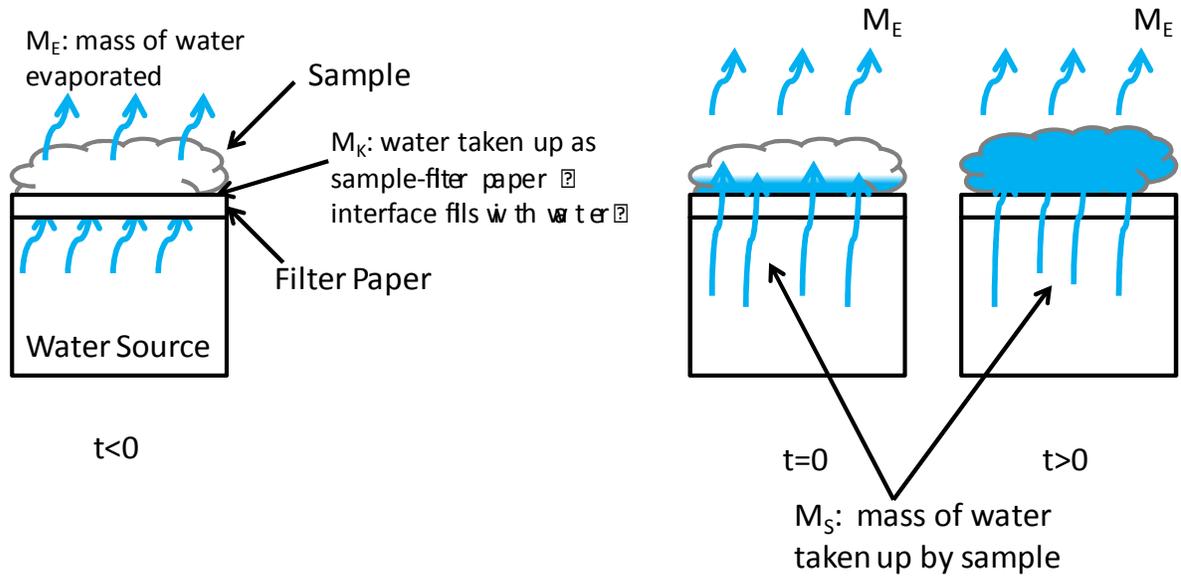


Figure 2-16: Schematic for water uptake variables. Note that the sample size is not to scale.

Several assumptions were made and used to characterize the above equation. It was assumed that M_K is proportional to the area covered by the sample and is specific to each material. If $M_K \ll G$ the effect of M_K on M_S is negligible. If $M_E \ll M_S$ the effect of evaporation on the sample's water uptake is negligible. *Another important assumption was that M_S is proportional to G and that in order to determine M_K , M_S/G must be constant for each material after saturation.*

The first step in the data analysis was to determine the contribution of evaporation to the total water uptake. The value for M_E is time-dependent, so M_E at any time was determined by

multiplying the evaporation rate, 0.001933 g/minute, by the time. By rearranging the main equation to:

$$M_W - M_E = M_K + M_S \quad (2-5)$$

it was possible to solve for $M_K + M_S$ by subtracting each value for M_E from M_W (Figure 2-17). The effect of evaporation was critical for the first few data points because of the low initial uptake. As the time for each experiment increased, the effect of evaporation became smaller and less important.

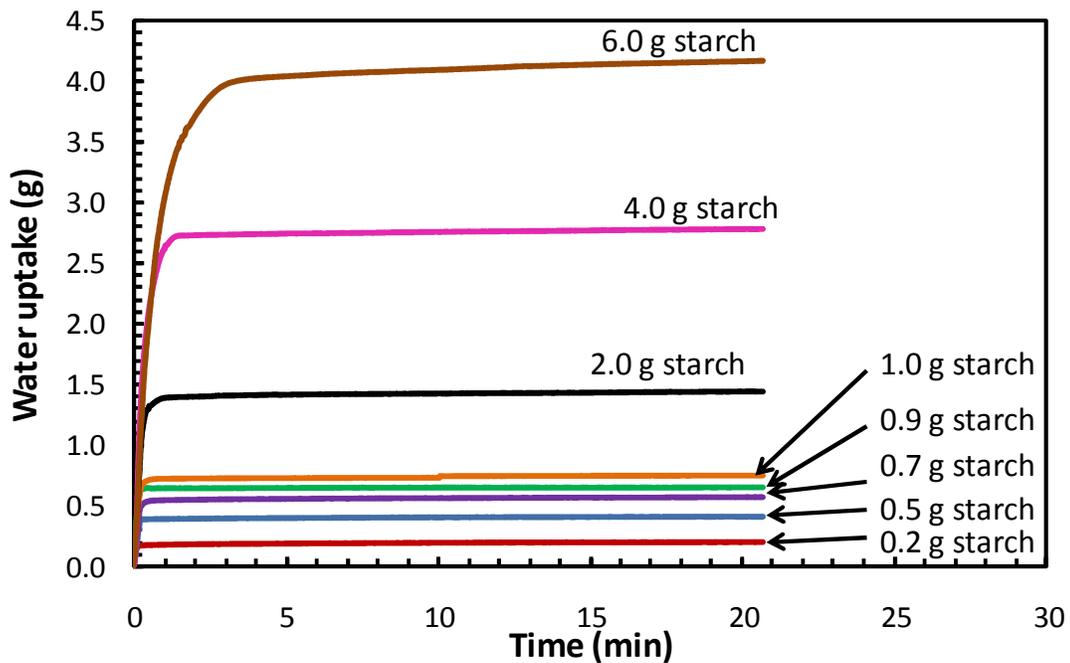


Figure 2-17: Total water uptake minus water evaporation ($M_W - M_E$) for starch at 8 different sample sizes.

The next step was to solve for M_S/G .

$$(M_W - M_E - M_K)/G = M_S/G \quad (2-6)$$

The value for M_K is a constant that had to be determined. This constant is related to the contact between the sample and the filter paper and should be the same for all sample sizes for a constant coverage area. The determination of the constant eliminates a ‘systematic error’ and results in the actual water uptake by the sample. The value for M_K was initially set to zero and systematically changed in the graphing program to converge the data sets. The value which converged the data series from $M_W - M_E$ (Figure 2-17) to $M_W - M_E - M_K$ for starch was 0.065 grams (Figure 2-18).

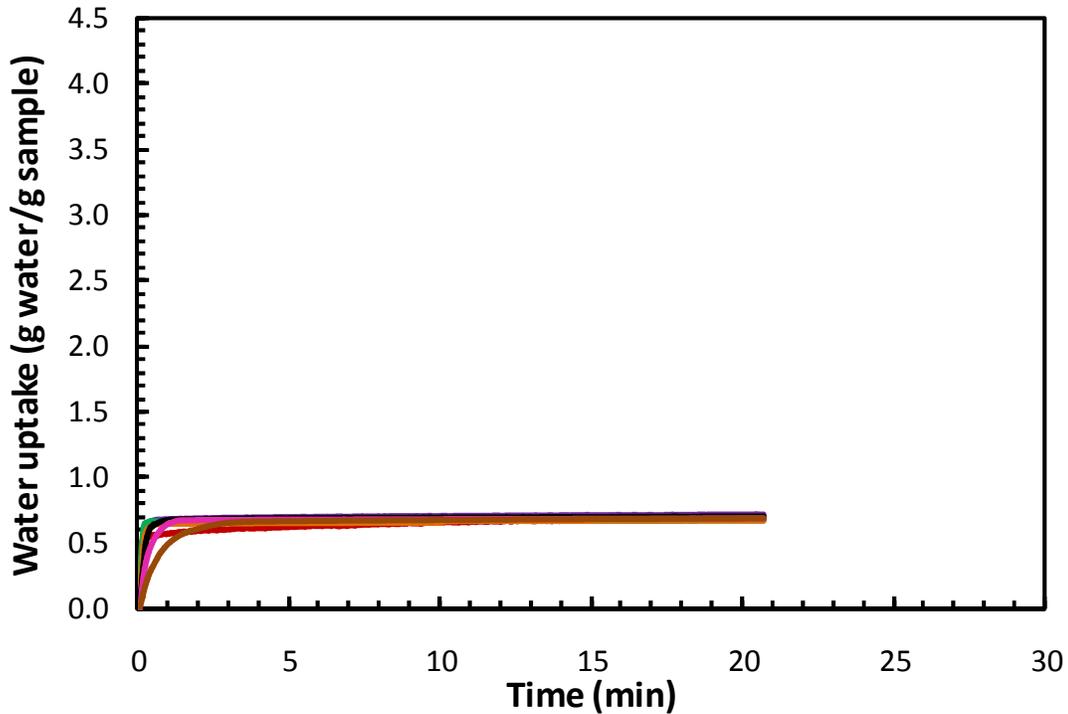


Figure 2-18: Total water uptake minus evaporation minus interface variable ($M_W - M_E - M_K$) for 8 starch sample sizes. M_K is 0.065 grams.

One value for M_K which causes the water uptake data to merge together means there is no difference in water uptake as a function of sample size. This is based on the assumption that because starch reaches a constant rate of water uptake, the value for M_S is no longer dependent on sample size. Although the uptake trends converged, there was still a 0.05 gram range between them all after 20 minutes. This is a result of the small sample sizes. The use of one constant for M_K is only applicable if the coverage area is the same for all samples. The sample sizes between 0.2 and 0.9 grams do not completely cover the filter paper surface so

they do not fit exactly with an M_K value of 0.065 grams. A sample size of 1.0 gram was chosen for subsequent experiments, because it is the smallest sample size that completely covers the filter paper.

In plots of M_W/G and M_S/G versus G at 0.5, 3 and 20 minutes, the data series essentially converge at sample sizes larger than 1.0 gram (Figures 2-19, 20, 21). At thirty seconds, the water uptake for the large samples is lower than that of the 4 smallest samples (Figure 2-19). The large samples exhibit a transport delay and therefore the water uptake rate is slower and the total uptake is lower. By three minutes, the water uptake only decreases slightly at the point of convergence, signifying that most of the starch has reached saturation (Figure 2-20). At twenty minutes, samples larger than 1 gram have no noticeable difference in water uptake (Figure 2-21). The contributions of M_K and M_E on M_W are visible in each figure as the difference between the two series. At 30 seconds, for example, the difference between M_S/G and M_W/G for the 1.0 gram sample is approximately 0.35 g/g (Figure 2-19), and the corresponding value for $(M_K/G + M_E/G)$ is also approximately 0.35 g/g. For the data at 30 seconds, the interface variable is the main difference between the total water uptake and the sample water uptake. There is only 0.0009665 grams of water evaporated after 30 seconds and the difference between M_W/G and M_S/G is about 0.35 g/g. As the sample size increases, the difference between the two uptake values decreases, but the M_E/G and M_K/G values go almost to zero, indicating those two variable have little effect on the water uptake for large samples.

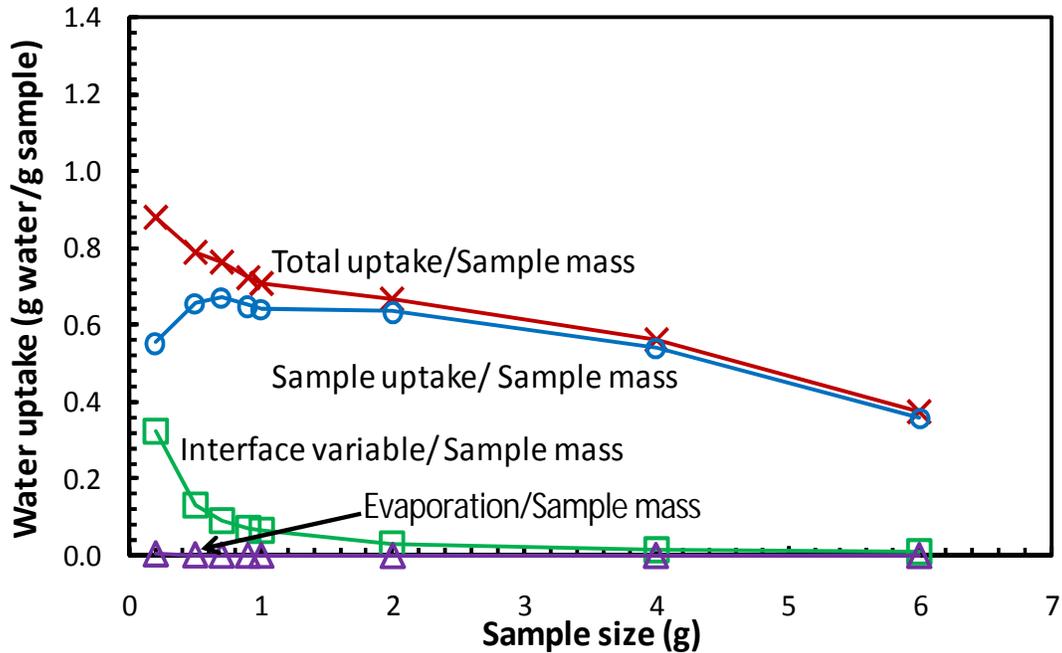


Figure 2-19: Total water uptake, M_W/G , sample water uptake, M_S/G , interface variable, M_K/G , and water evaporation, M_E/G , plotted against sample size, G , for starch at 0.5 minutes. M_K/G is 0.065 grams.

The correspondence between sample uptake, the interface variable and evaporation is also present for three and twenty minutes (Figures 2-20 and 2-21). For larger sample sizes, both the total gram/gram water uptake and sample gram/gram water uptake after equilibrium are independent of the actual sample size. With the water uptake variables properly defined and the sampling parameters chosen, it is possible to test other materials to determine the differences between water uptake levels.

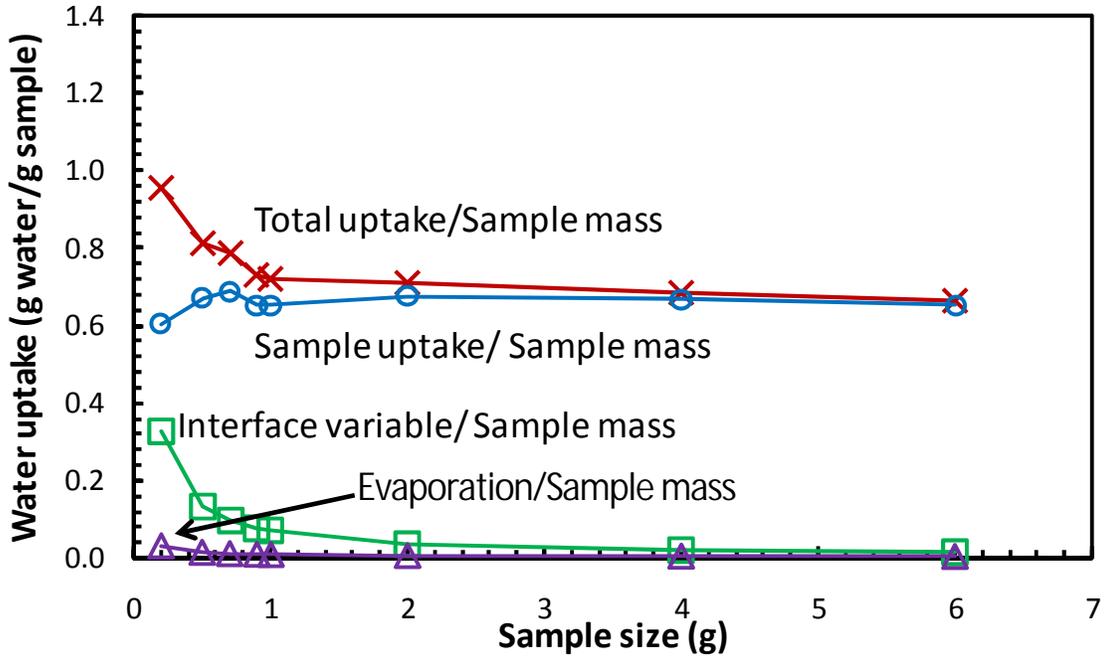


Figure 2-20: Total water uptake, M_W/G , sample water uptake, M_S/G , interface variable, M_K/G , and water evaporation, M_E/G , plotted against sample size, G , for starch at 3.0 minutes. M_K/G is 0.065 grams.

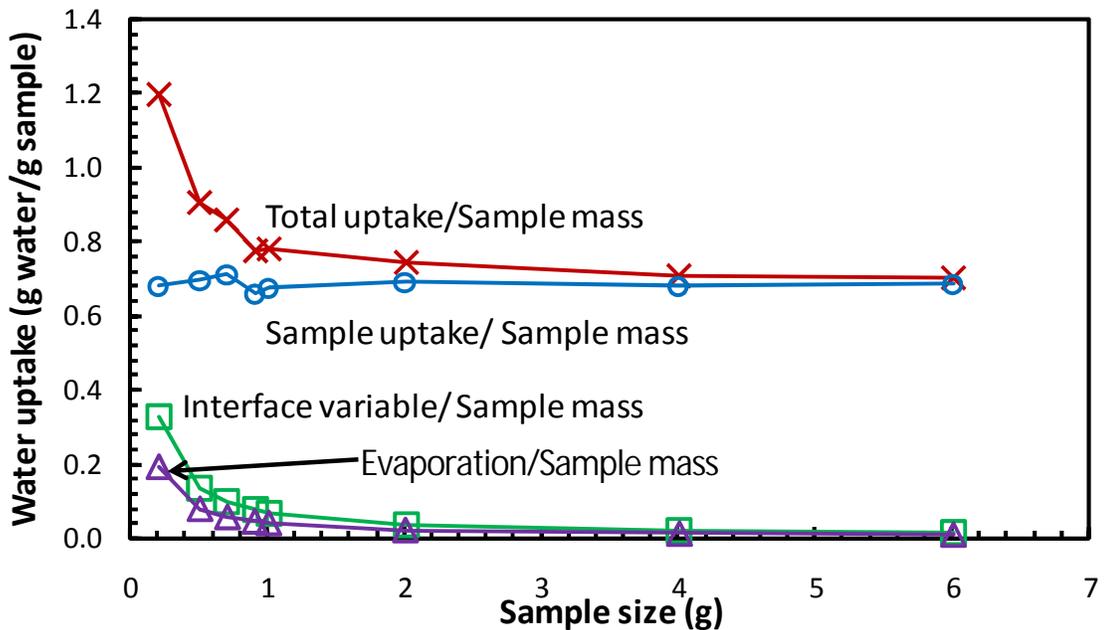


Figure 2-21: Total water uptake, M_W/G , sample water uptake, M_S/G , interface variable, M_K/G , and water evaporation, M_E/G , plotted against sample size, G , for starch at 20.0 minutes. M_K/G is 0.065 grams.

The data analysis for CMS 270ul was performed in the same way as the analysis for starch. For M_W , the plot looks similar to that of starch but the amount of uptake does not correspond to the sample size in the same way (Figure 2-22).

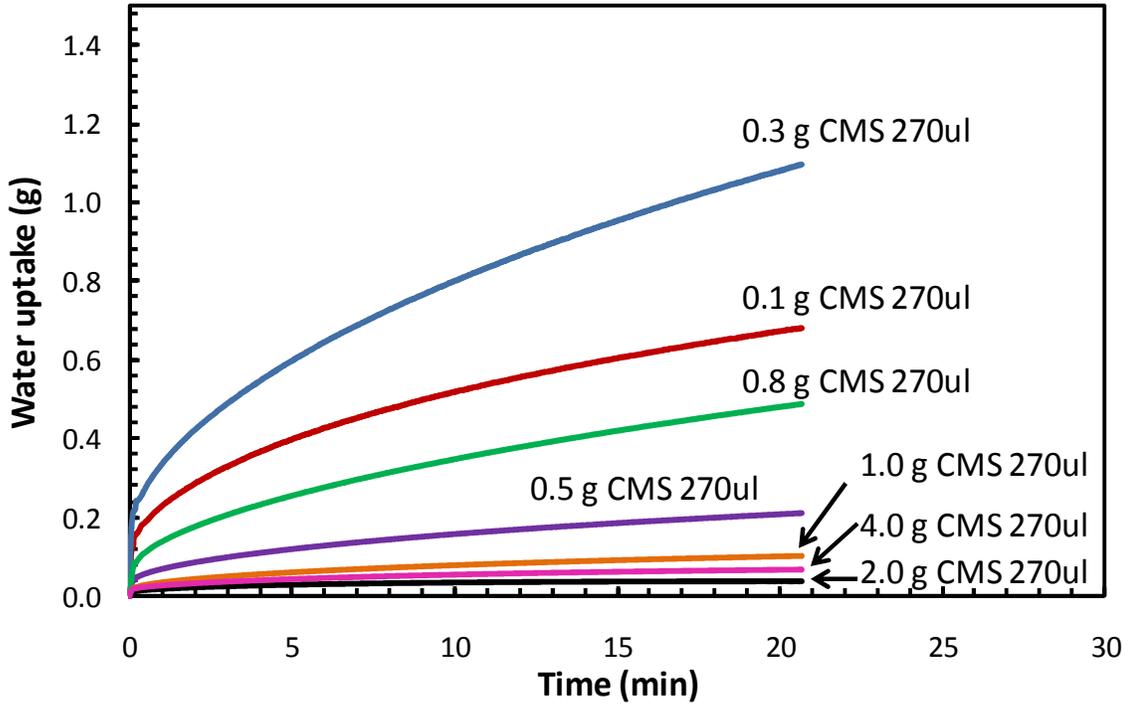


Figure 2-22: Total water uptake minus evaporation ($M_W - M_E$) for 7 sample sizes of CMS 270ul ranging from 0.1 grams to 2.0 grams.

The evaporation rate is the same as the one used with starch, 0.01933 grams/minute, because the tests were performed in the same location with the same setup. The determination of M_K was more complicated for CMS 270ul than for starch. One of the main assumptions for this data analysis method was that *in order to determine M_K , M_S/G must be constant for each material after saturation*. The problem was that CMS 270ul never reached a saturation point.

This means the previously mentioned assumption no longer holds true and there is no single value for M_K that will converge the data series. A dynamic system like CMS 270ul is very dependent upon sample size. The smallest spread in water uptake (M_K/G) is 2.2 grams water/gram sample and the associated M_K is 0.7 grams (Figure 2-23). The problem with this interface variable is that some of the water uptake values are negative. Use of the starch M_K value 0.065 grams is small enough so all sample sizes have positive water uptake but the series are not converged (Figure 2-24).

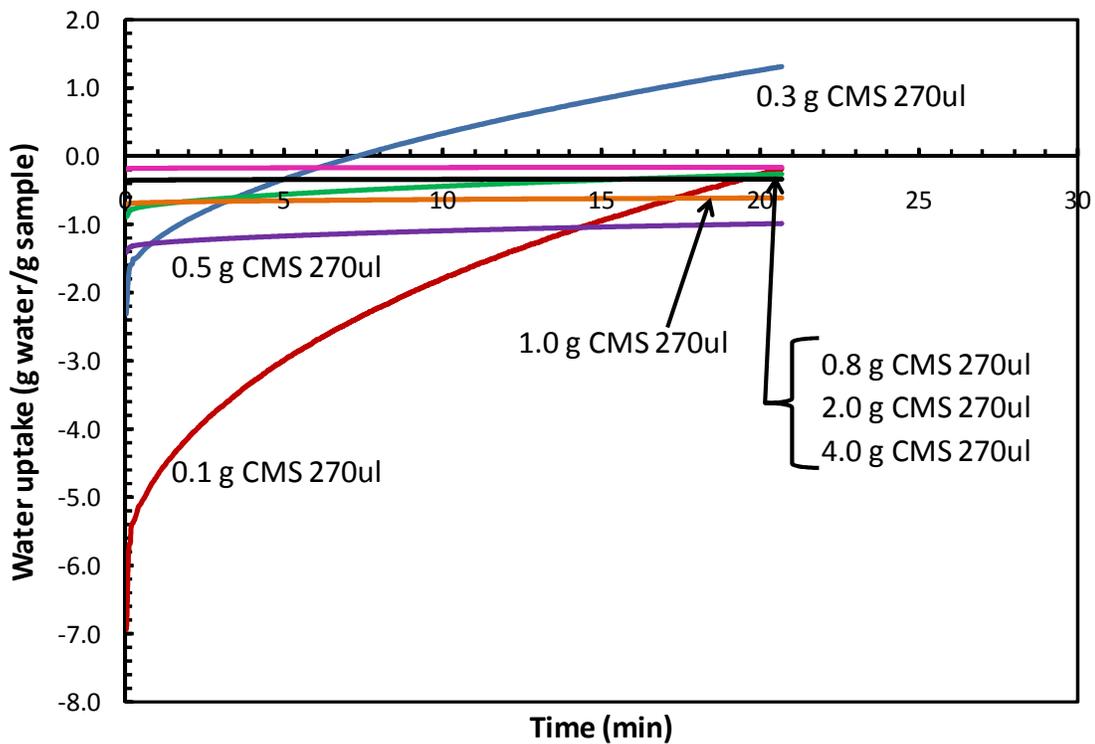


Figure 2-23: Total water uptake minus evaporation minus interface variable ($M_W - M_E - M_K$) for 7 CMS 270ul sample sizes. The associated M_K value is 0.7 grams.

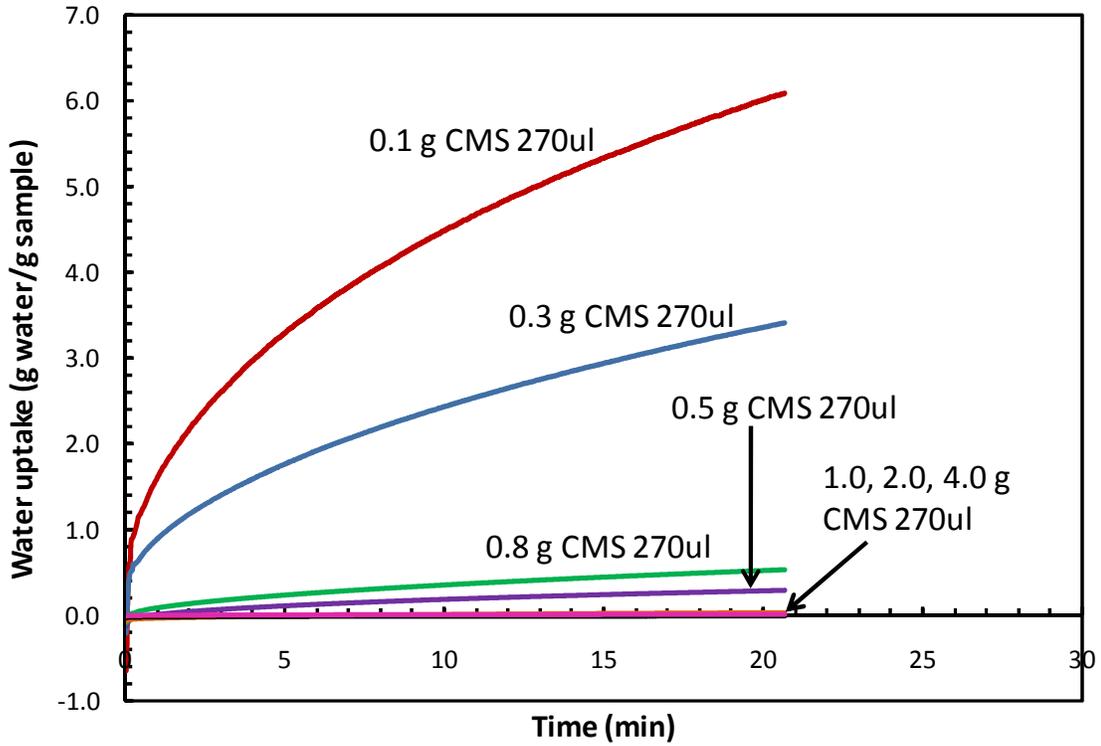


Figure 2-24: Total water uptake minus evaporation minus interface variable ($M_W - M_E - M_K$) for 7 CMS 270ul sample sizes. The associated M_K value is 0.065 grams.

Sample Coverage

As the coverage area increased, the water uptake increased (Figure 2-25). This is logical because increasing the coverage area means there was more of the water-absorbing material in direct contact with the filter paper and water reservoir.

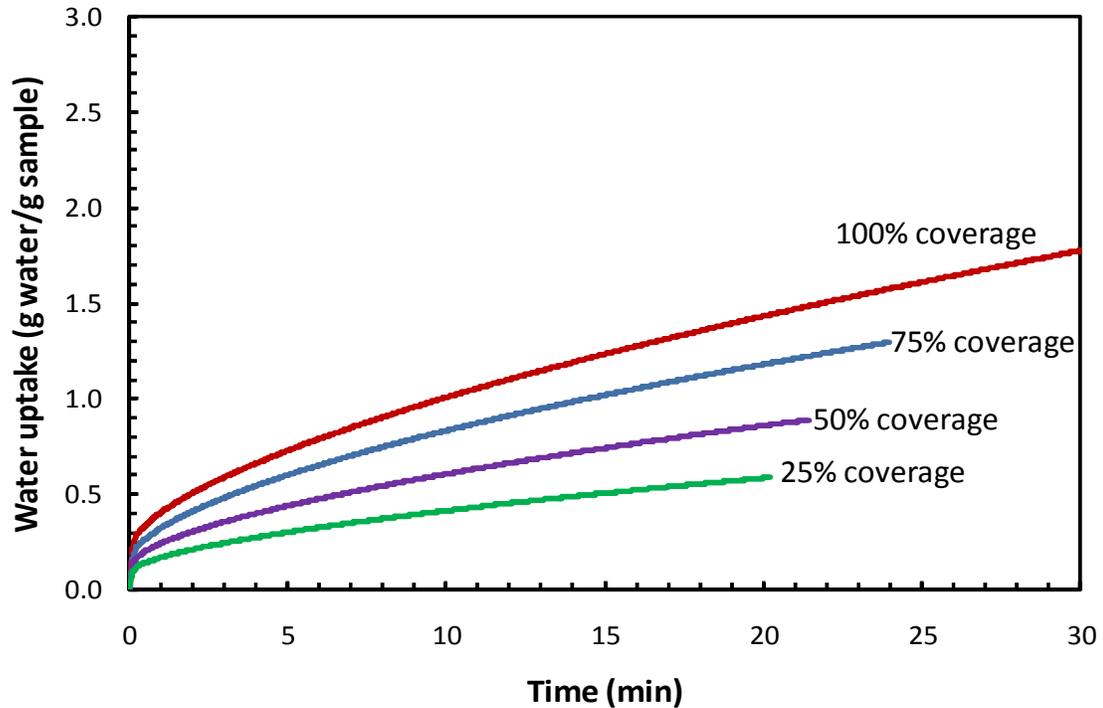


Figure 2-25: Water uptake for CMS 270ul with different percent coverage for the same 1.0 gram sample size.

The sample loading density (g/m^2) was calculated for each coverage level with a 1.0 gram sample (Table 2-2). The loading density was plotted against the water uptake levels for the four coverage levels at twenty minutes (Figure 2-26). The sample loading density, assuming 100% coverage, was calculated for sample sizes 1.0-4.0 grams (Table 2-2). The loading density was graphed with the twenty-minute uptake for the same sample sizes (Figure 2-25). The sample loading density for 100% coverage matched the loading density for a 1.0 gram sample. The same relationship existed for 50% coverage- 2.0 gram sample and 25% coverage- 1.0 gram sample. These matches made it easier to evaluate the relationship

between coverage and sample size. Both curves had the same basic shape and the values for 100% coverage and 1.0 gram sample size were very similar with uptakes of 1.4326 g/g and 1.3718 g/g respectively. This set of experiments showed that coverage area and sample mass were equally important to the water uptake levels. The results also suggest that sample delivery was a possible source for water uptake variation.

Table 2-2: Twenty-minute water uptake for CMS 270ul for 4 sample coverages and 3 sample sizes.

Coverage - CMS 270ul

	100%	75%	50%	25%
Loading density (g/m²)	421.053	561.482	841.751	1684.069
20 min water uptake (g/g)	1.433	1.179	0.858	0.585

Sample Size - CMS 270ul

	1g	2g	4g
Loading density (g/m²)	421.053	842.105	1684.211
20 min water uptake (g/g)	1.372	0.722	0.356

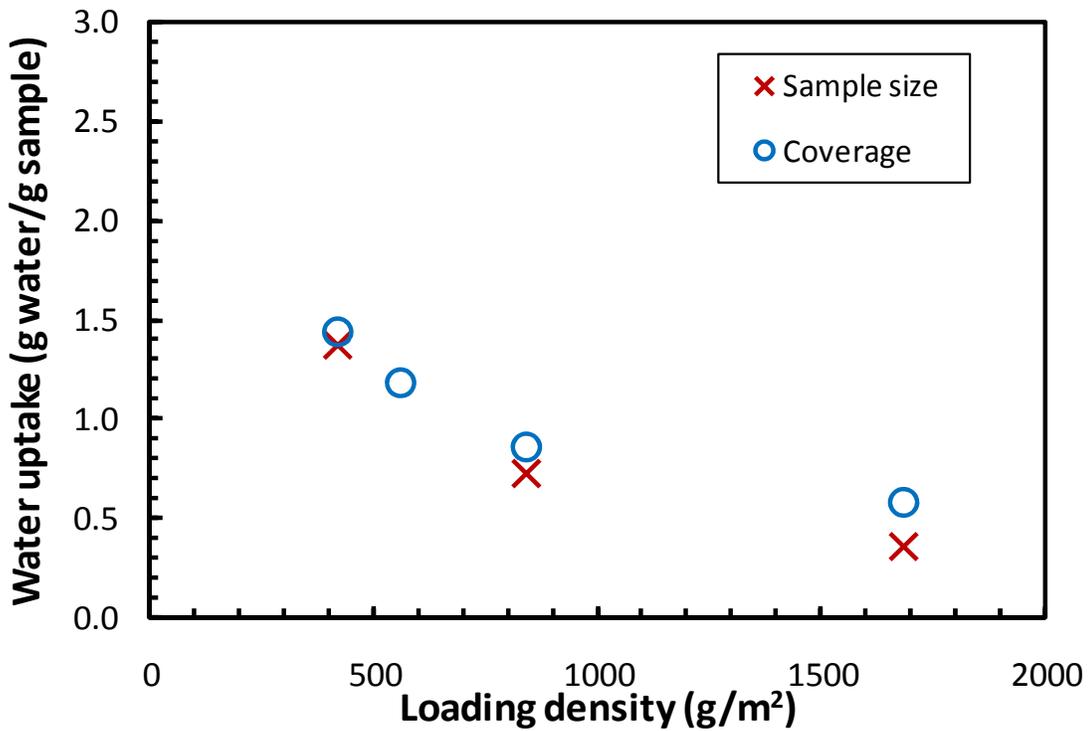


Figure 2-26: Water uptake at twenty minutes for the four coverage values and for sample sizes 1.0, 2.0 and 4.0 grams.

Repeatability

It was essential that water uptake measurements using the DWA were consistent and repeatable. The water uptake values for starch and CMS 270ul were each tested several times, over the course of several days, with fairly reproducible results (Figures 2-27 and 2-28). For the CMS 270ul tests, 4 out of 5 showed similar water uptake behaviors. Because there was only one test in the series that differed drastically, it was appropriate to consider that test to be abnormal in some way. At twenty minutes, the average water uptake was

0.7757 g/g and the standard deviation was 0.0228 grams for starch and 1.3718 g/g and 0.2060 grams for CMS 270ul.

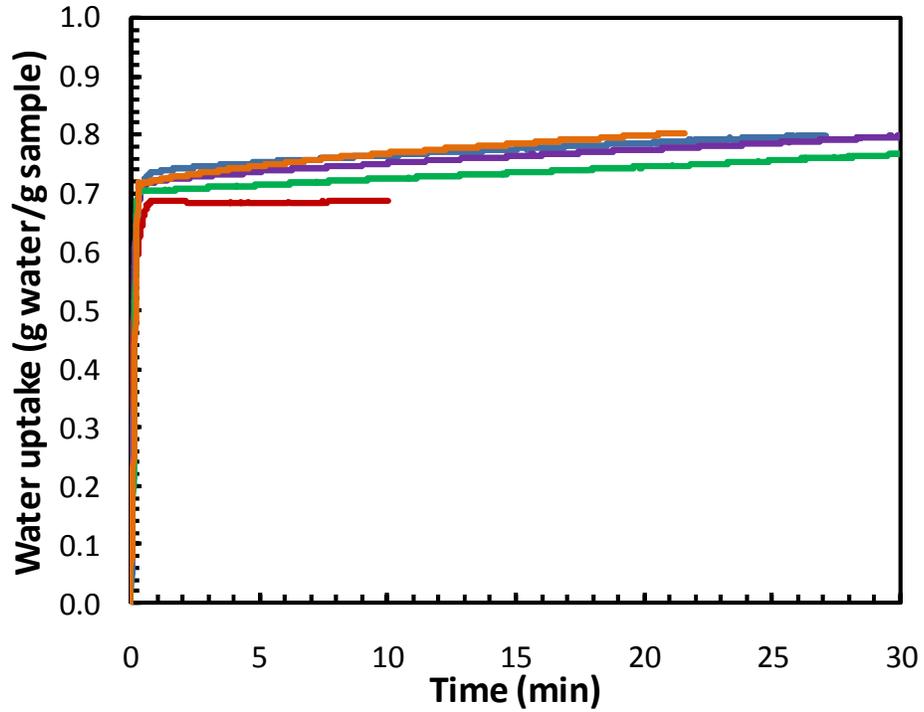


Figure 2-27: Water uptake for starch. Average uptake at twenty minutes was 0.7757 g/g and the standard deviation was 0.0228 grams.

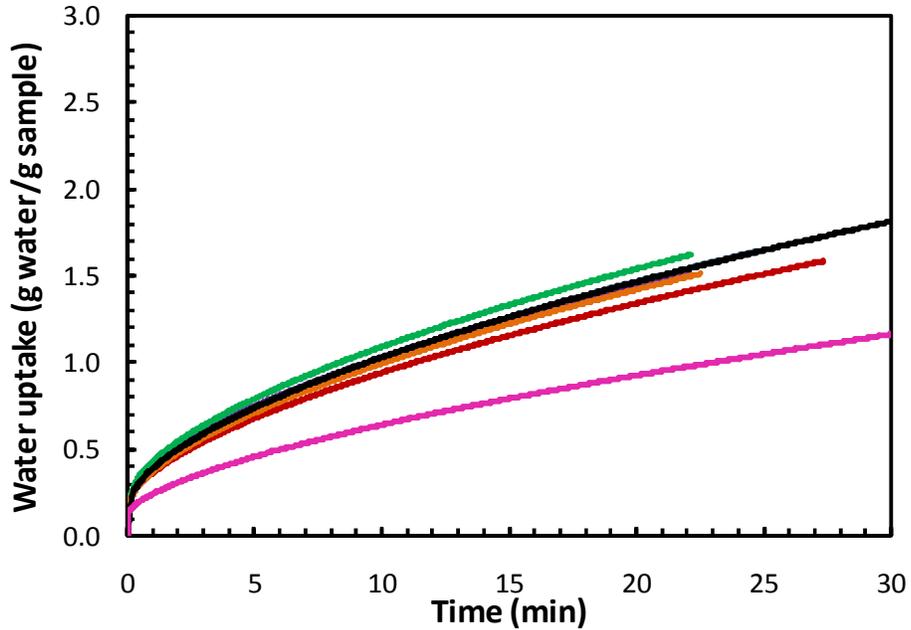


Figure 2-28: Water uptake for CMS 270ul. Average water uptake at twenty minutes was 1.3718 g/g and the standard deviation was 0.2060 grams. Note that y-axis scale is 0.0 to 3.0 grams.

Comparison of DWA to the GATS

The data for all materials tested using the GATS is located in Appendix B. The 9 cm filter paper used with the GATS had an average water uptake of 3.5317 grams in 3 minutes, compared to the small filter paper for the DWA that takes up an average of 0.868 grams in the same time period. When the uptake was normalized by area (g/m^2) the GATS filter paper averaged $555.12 \text{ g}/\text{m}^2$ and the DWA filter paper $365.32 \text{ g}/\text{m}^2$. The difference between the uptakes per unit area for the two testing systems can be attributed to differences in the physical setups for each. The sample loading densities were calculated for the different sample sizes for the materials tested using the GATS (Table 2-3). The same loading densities were used for the subsequent DWA experiments.

Table 2-3: Sample loading densities for GATS and DWA experiments.

GATS sample size (g)	2.0	4.0	6.0
Equivalent for DWA (g)	0.747	1.494	2.241

The 6.0 gram CMS 220ul sample had the highest water uptake and the 6.0 gram CMS 270ul sample had the lowest (Figure 2-29) for the GATS. The higher degree of substitution decreased the water uptake rate. The starch uptakes were similar to one another and were between that of the two modified starches at short times but are expected to be lower at equilibrium. It is suggested that the dynamic differences between starch and the modified starches are due to gel blocking.

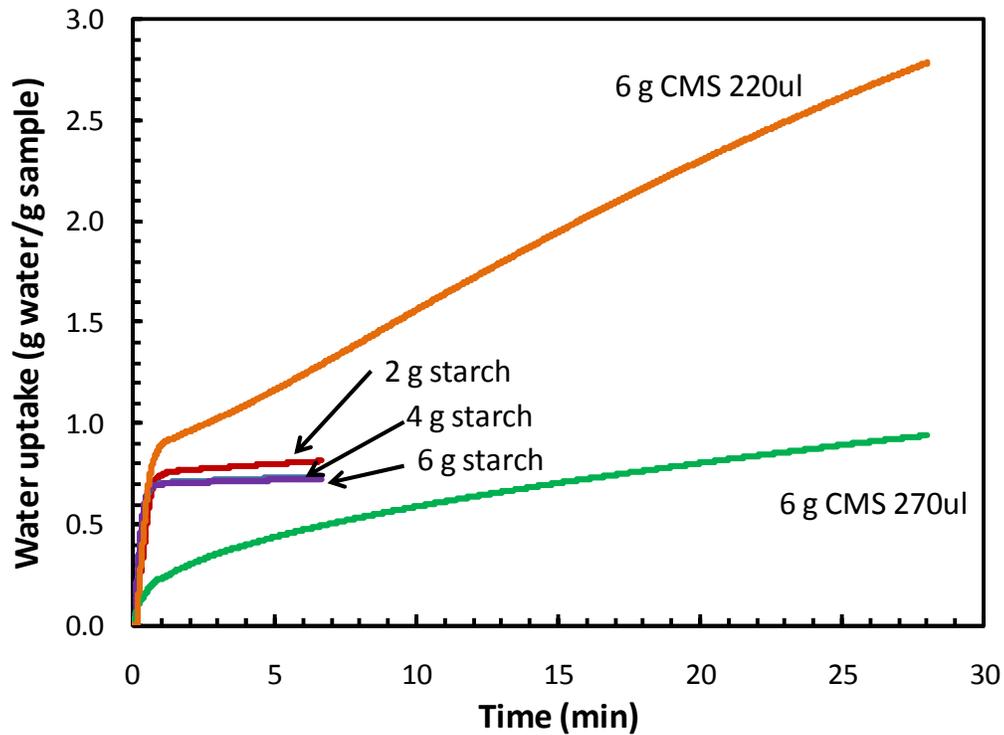


Figure 2-29: Water uptake for starch, CMS 270ul and CMS 220ul using GATS.

The DWA and GATS results for starch showed very similar behavior with a ‘shoulder’ within the first 2 minutes (Figure 2-30). The values for the starch water uptake were also similar for both methods around five minutes. For CMS 270ul and CMS 220ul, there was general agreement between the two methods (Figure 2-31). Summarizing all comparison data it can be concluded that the DWA system provides results consistent with a proven dynamic absorption tester.

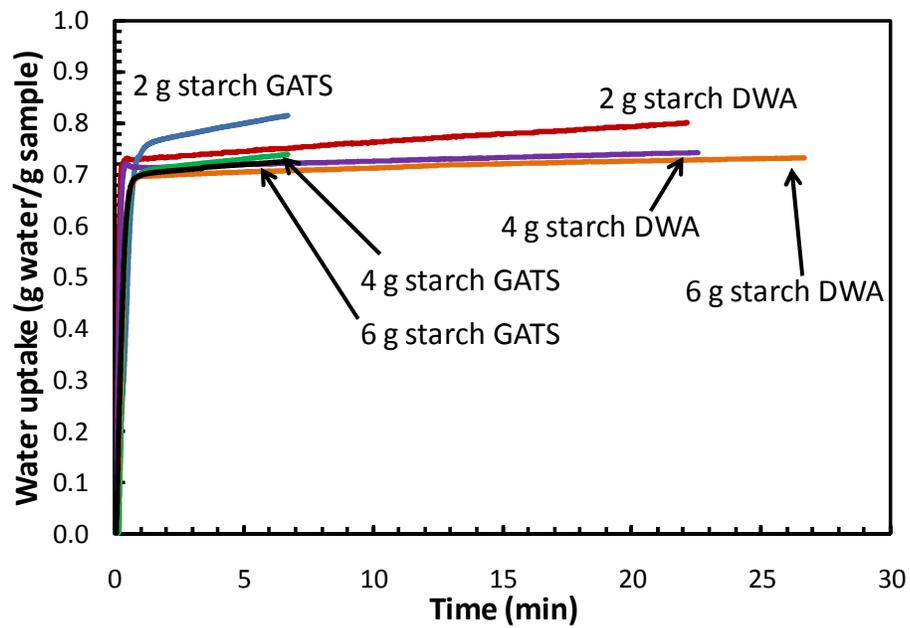


Figure 2-30: Comparison of GATS and DWA for starch.

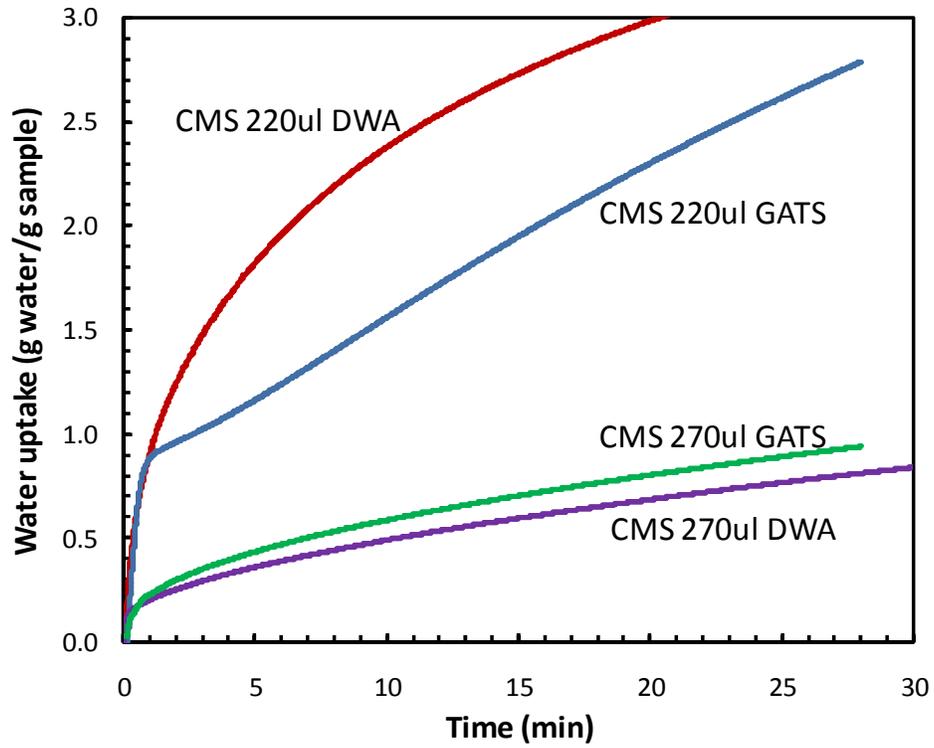


Figure 2-31: Comparison of GATS and DWA for CMS 270ul and CMS 220ul. The GATS samples were 6.0 grams. The DWA samples had the same sample density as the 6.0 gram GATS sample.

Conclusions

- The Dynamic Wetting Apparatus (DWA) is a convenient, repeatable, precise, cost-effective instrument that measures the dynamic water uptake of a variety of forms of materials.
- Several experimental factors are significant in the dynamic water uptake measured, including sample size, sample delivery method and sample coverage on the water delivery platform.
- The total water uptake measured in a DWA experiment can be divided into three categories: interface water, evaporated water, and water taken up by the sample.
- For samples that have fast uptake and equilibrate within the time frame of the experiment, the interface water amount can be identified, along with the known evaporation rate. Both are used to determine the true sample water uptake.
- For samples that are fully saturated, the equilibrium water uptake (grams of water absorbed per gram of sample) is independent of sample size. For samples that are not saturated within the experimental time frame, the sample size has significant impact on the recorded final (experimental) water uptake.

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Chapter 3

Material Characterization and DWA Analysis

Introduction

Absorbent hygienic materials are an important part of modern society, fulfilling serious health and safety needs. The demand for these materials is greater than 40,000 metric tons annually (Nexant, Inc. 2004). Typically, these products are derived from non-renewable petroleum-based acrylic acid, making disposal and biodegradability in landfills a concern. As the price of oil rises, the price for these absorbent feedstocks also rises. Many recent research articles have focused on the preparation and utilization of bio-based absorbents.

The preparation of the absorbent determines a majority of the material's uptake behavior. Crosslinking and degree of substitution (DS) define the structure of the material, how quickly fluid is absorbed and how much can be taken up overall. Gels with light crosslinking have a low modulus when swollen and are easily deformed. These deformed particles adhere to one another and greatly reduce the porosity of the gel. This decreases the diffusion rate and therefore the swelling, leading to what is known as gel-blocking (Graham and Wilson 1998, Buchholz 1998b). In diapers, for example, gel blocking equates to a higher probability of leaks. Increasing the crosslink density improved the gel modulus and reduced the gel-blocking. For the DWA it will be essential to determine whether or not gel-blocking alters the absorption rate.

Grafted starch-acrylonitrile absorbents were developed in the 1970's by the USDA, but were never commercialized on a large scale (Gross 1990). Yamaguchi, Watamoto and Sakamoto (1987, 1988) prepared superabsorbents from these starch-polyacrylonitrile graft copolymers. Superabsorbents with swelling values of 70-390 gram/gram were prepared by Lanthong, Nuisin and Kiatkamjornwong (2006) using cassava starch. The grafting of acrylic acid and acrylamide onto cellulose chains greatly increases the water-loving nature of cellulose (Chauhan and Lal 2003).

Other plant and animal-derived polymers used as absorbents include red seaweed or carrageenan (Pourjavadi and Amini-Fazi 2007), pullulan, a polymer produced by fungus (Dulong, Mocanu and Le Cerf 2007) and chitosan (Yao et al. 1998, Mahdavinia et al. 2004, Crescenzi et al. 1997 and Yu and Hui-min 2006), just to list a few.

Two additional biobased materials that have been used for absorbents are hemicellulose and carboxymethyl starch (CMS). Hemicelluloses are branched, amorphous, contain more than one type of saccharide, and have multiple functional groups. This allows the molecules to act in ways different than cellulose and starch. These hemicelluloses are soluble in aqueous alkali but insoluble in almost all organic solvents (Sun et al, 2004). The organic insolubility is probably due to the high density of hydrogen bonds within xylan (Jain, Sjostedt and Glasser 2001). Solubility can therefore be induced when some of the hydroxy groups are substituted by alkoxy or acetoxy functionalities (Jain, Sjostedt and Glasser 2001). Some of

the structural and behavioral disadvantages can be overcome by chemical and structural modification. The chemical modification of hemicellulose was studied as early as the 1960's, focusing on modification of xylan. Applications for hemicelluloses and other lignin polymers include adhesives, coating and foam products, engineering plastics, food additives, thickeners, emulsifiers, gelling agents and adsorbents (Gabrielii and Gatenholm 1998). The reaction of xylan with propylene oxide in aqueous alkali produces a thermoplastic hydroxypropyl xylan with a low molecular weight, branched structure, and solubility in water (Sun, Sun and Tomkinson 2004).

Gabrielii and Gatenholm (1998, 2000) have used birchwood and aspen xylan as the base for hydrogels and combined them with chitosan. Beechwood xylan, barley husk xylan and carboxymethyl xylan are also viable biobased absorbent alternatives (Tanodekaew, Channasanon and Uppanap 2006, Grondahl, Eriksson and Gatenholm 2004, Petzold, Schwikal and Heinze 2006).

Another biobased absorbent is carboxymethyl starch (CMS). CMS is obtained as a product of the reaction of starch (St-OH) with sodium hydroxide and sodium monochloroacetate (MCA) (Stojanovic, Jeremic, and Jovanovic 2000). This is a two-step reaction, the first step being the alkalization of starch followed by etherification:



These modified starches have increased water solubility as the degree of substitution (DS) is increased. For this reason organic solvents are used for the production of granular CMS like the ones used in this study (Stojanovic, Jeremic, and Jovanovic 2000). For CMS, the degree of substitution is the average number of carboxymethyl groups on the starch repeat unit (Heinze, et al. 2004). Typically CMS is used as an additive in the paper industry, as a thickener for textile printing pastes and as a tool for enhanced oil recovery (Stojanovic, Jeremic, and Jovanovic 2000).

The objectives of this chapter are to characterize several materials, both absorbing and non-absorbing, and evaluate the materials in terms of water uptake using the DWA.

Materials and Methods

The materials used to characterize the DWA include filter paper, sand, starch, carboxymethyl starch (CMS) 270ul, CMS 220ul, hemicellulose and clay #1. The filter paper circles used were 55 mm Whatman #41 quantitative filter paper circles (Whatman # 1441-055). The average weight per circle was 0.1976 grams and the standard deviation was 0.0083 grams. The basis weight (g/m^2) was 83.1482 g/m^2 . The evaluated sand was red craft sand from a local craft supply store. The starch was Pearl B unmodified corn starch from Cargill. The hemicellulose used was birchwood xylan (Aldrich- X0502). Clay #1 is kaolin clay used for papermaking coatings. Its equivalent spherical diameter is between 1.0 and 0.1 μm (Figure 3-1, Hagemeyer 1997).

Four carboxymethyl starch (CMS) powders from Aquasol Corporation (Charlotte, North Carolina) with varying degrees of substitution (DS) were utilized in this study to determine the effect of DS on water uptake. The high, medium and low levels of DS are list in Table 3-1. The low DS material CMS 220 is both lightly crosslinked with epichlorohydrin and uncrosslinked.

Table 3-1: Description of carboxymethyl starch (CMS) materials.

Name	DS	Presence of Crosslinking
CMS 270ul	0.70	Uncrosslinked
CMS 252 ul	0.52	Uncrosslinked
CMS 220 ul	0.20	Uncrosslinked
CMS 220x	0.20	Crosslinked

Particle Size

A direct relationship has been found between average particle radius and the swelling rate of granular polymers (Buchholz 1998a). Therefore, the average particle size for the powders was measured using an Olympus BH2-UMA light microscope at either 5 or 10x magnification.

Kaolin clay #1 has an equivalent spherical diameter is between 1.0 and 0.1 μm (Figure 3-1, Hagemeyer 1997).

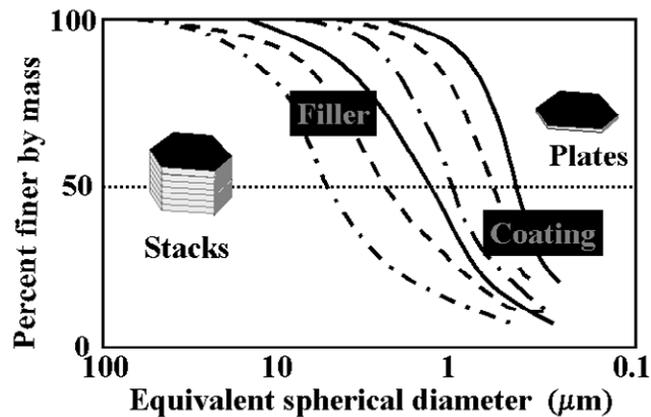


Figure 3-1: Average particle size range for kaolin clays (adapted from Hagemeyer 1997)

Particle and Packing Density

A polymer particle with a lower density will absorb water as if it had a small effective particle radius. Particles with small radii have a fast swelling rate (Buchholz 1998a). Particle

density was tested for each of the nine powdered materials based on the method described by Buchholz (1990). A 10 ml graduated cylinder was filled with a known amount of a powder (0.5 grams). Eight ml of distilled water was added by pipette into the graduated cylinder. A small wooden dowel was used to mix the contents and insure that all powder was saturated. The volume of liquid or gel was recorded 15 seconds after the water was added. The sample mass (grams) was divided by the change in water (cm^3) to obtain the particle density. Each material was tested three times and the average and standard deviation was calculated.

As void fraction decreases, the water uptake of the material increases (Buchholz 1998a). Void fraction is closely related to the absolute open volume and therefore an increased amount of open space leads to more room for water. Packing density was also calculated for each of the eight powdered materials. A 10 ml graduated cylinder was tared on a balance. A small amount (0.5-1.0 gram) of the powder was added to the graduated cylinder. The cylinder was tapped lightly 5 times against the edge of the counter to level out the powder. The volume of the powder was recorded. The cylinder was placed on the balance and the weight of the sample was recorded. Again the graduated cylinder was tared and the process was repeated for a total of six times. The sample mass (grams) was divided by the change in volume (cm^3) to obtain the packing density. The average and standard deviation were calculated.

The void fraction was also calculated for these powdered materials. The void fraction is described by the equation:

$$\text{Void Fraction} = 1 - \frac{\rho_{\text{packing}}}{\rho_{\text{particle}}} \quad (3-3)$$

Crosslinking and Degree of Substitution

The four CMS samples (Table 3-1) were used to evaluate the effect of DS and crosslinking on water absorption.

Moisture Content

The moisture content of each powder was tested to determine whether it would have an effect on the overall water uptake rate and capacity. Approximately 0.5 grams of each powder was weighed out and left open to the conditioned atmosphere (50% RH and 23°C) and weighed periodically. The materials were weighed until they reached a constant weight at which time they were placed in a 105°C oven and left overnight. After oven-drying the samples were placed in a desiccator, cooled and weighed. Moisture content was calculated using the following formula:

$$MC \% = \left(\frac{\text{conditioned weight} - \text{oven dried weight}}{\text{conditioned weight}} \right) \times 100\% \quad (3-4)$$

Powder Blends and Water Uptake

Blends were prepared with two powdered materials in six different ratios. The percentages

were 100/0, 90/10, 70/30, 50/50, 20/80 and 0/100. The blend combinations are listed in Table 3-2. The sample size was 1.0 grams. In order to reduce possible variations in sample mixing, a 10.0 gram batch of each combination was prepared. The 1.0 gram samples of each mix were taken from these batches for testing with the DWA described in Chapter 2. The testing procedure is listed in Appendix A. Each mixture was tested at least twice.

Table 3-2: Material combinations for powdered blends.

Material 1	Material 2
Starch	CMS 270ul
	CMS 252 ul
	CMS 220 ul
	CMS 220 x
Hemicellulose	CMS 270ul
Sand	CMS 270ul
Clay #1	CMS 270ul

Results and Discussion

Particle Size

Particle sizes were measured with an optical microscope and the average and standard deviation for each material are shown in Table 3-3. Sand was the only sample evaluated using 5x magnification. Microscope images for each material are in Appendix C (Figures 1-3).

Table 3-3: Average particle size for nine materials.

Sample	Average (mm)	Std Dev (mm)
Hemicellulose	0.21279667	0.52540333
Starch	0.20924667	0.24528667
CMS 220x	0.38017333	37.47679000
CMS 220ul	0.71999000	0.35980667
CMS 252ul	0.96795333	2.06922667
CMS 270ul	0.46444000	0.68143000
Clay #1	0.74190667	1.58590333
Sand	302.85363333	51.21313333
Chitosan	0.27978000	0.76530000

Particle and Packing Density

Particle density of the modified starches was difficult to analyze because some of the powders gel immediately when contacted with water. The range for particle densities was 0.98 to 3.71 g/cm³, but the higher densities are suspect (Table 3-4). Hemicellulose had the lowest particle density and the crosslinked CMS 220x had the highest.

Table 3-4: Particle density (g/cm^3) for eight powdered materials.

Sample	Density (g/cm^3)			Average (g/cm^3)	Std Dev (g/cm^3)
Hemicellulose	0.99	0.93	1.02	0.98	0.047
Starch	1.43	1.43	1.72	1.52	0.169
CMS 220x	4.92	1.26	4.95	3.71	2.122
CMS 220ul	0.83	1.24	1.03	1.04	0.205
CMS 252ul	1.60	1.66	1.09	1.45	0.312
CMS 270ul	2.50	2.50	2.49	2.50	0.007
Clay #1	1.26	1.25	0.93	1.15	0.186
Sand	2.50	2.18	2.29	2.32	0.165

The packing density measurements ranged from 0.28 g/cm^3 to 1.56 g/cm^3 (Table 3-5). A higher packing density suggests a tight grouping of particles with little inter-particle space for water. Tightly packed particle groups could limit the amount of space available for swollen particles.

Table 3-5: Packing density (g/cm^3) for eight powdered materials.

Sample	Average (g/cm^3)	Std Dev (g/cm^3)
Hemicellulose	0.28	0.028
Starch	0.40	0.019
CMS 220x	0.46	0.015
CMS 220ul	0.51	0.043
CMS 252ul	0.67	0.050
CMS 270ul	0.73	0.053
Clay #1	0.82	0.061
Sand	1.56	0.091

The void fraction for each material was calculated from the particle and packing densities (Table 3-6). The range for void fraction was 0.29 g/cm³ for clay #1 to 0.88 g/cm³ for CMS 220x.

Table 3-6: Void fraction (g/cm³) for eight powdered materials.

Sample	Average particle density (g/cm³)	Average packing density (g/cm³)	Void Fraction (g/cm³)
Hemicellulose	0.98	0.28	0.72
Starch	1.52	0.40	0.74
CMS 220x	3.71	0.46	0.88
CMS 220ul	1.04	0.51	0.50
CMS 252ul	1.45	0.67	0.54
CMS 270ul	2.50	0.73	0.71
Clay #1	1.15	0.82	0.29
Sand	2.32	1.56	0.33

Moisture Content

The initial and equilibrium moisture contents were calculated and the results are shown in Table 3-7 and Figure 3-2. Based on their initial mass, there is almost a 9% difference between the CMS 270ul and the hemicellulose. After reaching equilibrium, the range is only about 4% between the hemicelluloses and the CMS 220ul. The materials have low moisture content when they are taken directly from their sealed containers, but to insure that moisture does not affect the water uptake measurements, each material is left in a container open to a standard atmosphere (23°C, 50% RH) at least twenty-four hours prior to testing.

Table 3-7: Moisture content for six powdered materials.

Sample	% Moisture Content	
	Initial	Equilibrium
Hemicellulose	4.91%	14.62%
Corn Starch	10.87%	11.98%
CMS 270UL	13.58%	14.62%
CMS 252UL	11.27%	13.20%
CMS 220UL	9.31%	11.11%
CMS 220X	10.39%	11.79%

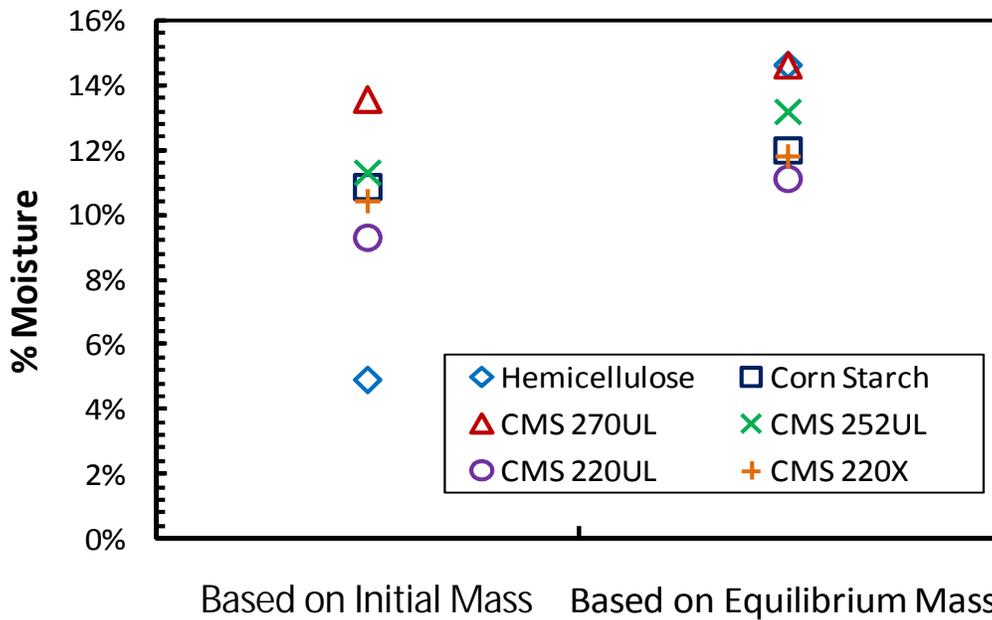


Figure 3-2: Moisture content for six powdered materials. Moisture on initial mass is calculated from the mass of powder from a closed container. Moisture on equilibrium mass is calculated from powder that has been allowed to equilibrate in a conditioned atmosphere (50% RH and 23°C).

Water Uptake for Powder Blends

The water uptake was first tested for each blend component (Figure 3-3). Sand had the lowest uptake for all materials studied as it was not expected to swell with water. Chitosan had the highest uptake. Sand, starch, clay, chitosan and hemicellulose all had a rapid water uptake within the first two minutes followed by saturation characterized by a 'shoulder'. This rapid uptake is due to capillary flow which allows the sample to uptake water quickly. The carboxymethyl starches do not reach a steady state during the testing. CMS absorbs water slowly and does not reach equilibrium as a result of gel blocking. Further, the CMS shows swelling, the diffusion of water into the particles, within the 20 minutes experiments. This slower water swelling process is far from complete after 20 minutes. The crosslinked CMS (220x) has the highest uptake for the modified starches within this experimental time.

Although crosslinking strengthens a material and makes it more resistant to heat degradation, the chemical bonds reduce the material's elasticity and therefore its ability to swell. In this case, the crosslinking is probably reducing the gel blocking and therefore increasing the water uptake. It should be noted that the level of crosslinking for this material is unknown and therefore solid conclusions regarding water uptake versus crosslinking are not reliable.

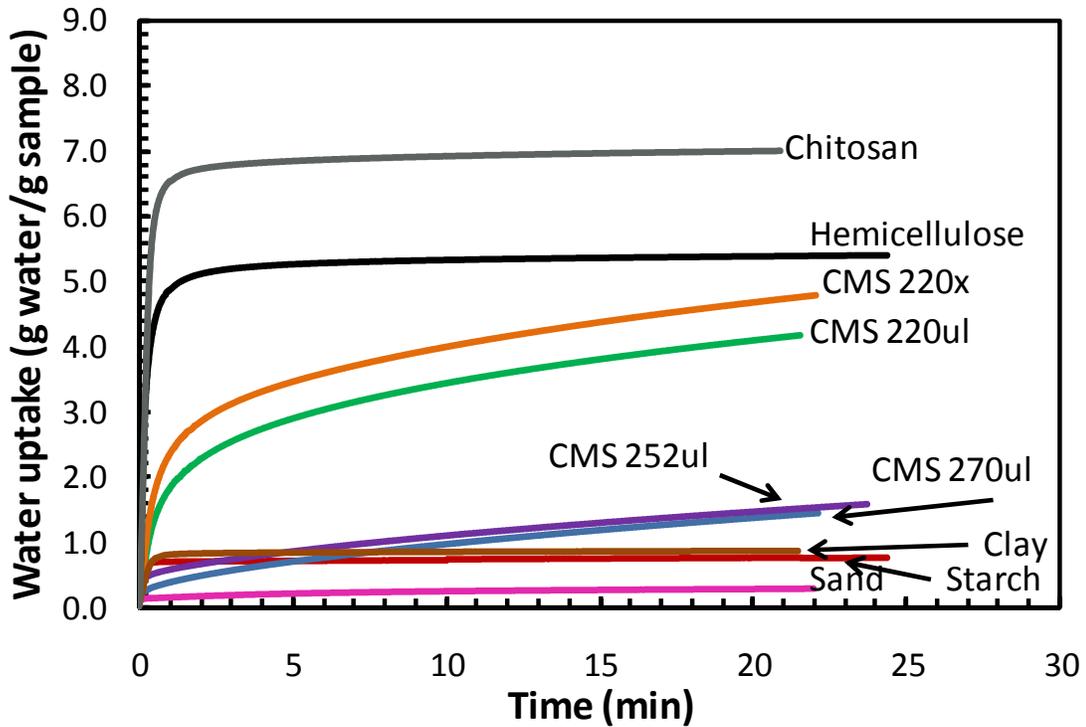


Figure 3-3: Average water uptake (grams of water/gram sample) for 100% of each material.

Starch and CMS 270ul Blends

The water uptake for starch and CMS 270ul blends at different ratios was plotted in Figure 3-4. The uptake at 1, 5, and 20 minutes is tabulated (Table 3-8) and plotted (Figure 3-5) as a function of percent starch. By comparing uptake as a function of percent composition it was possible to determine the trend for absorption and whether any synergistic effects by blending two materials exist.

Figure 3-4 shows a sharp shoulder for starch alone. This abrupt shoulder decreased with increasing CMS 270ul content, in accordance with gel blocking and slow swelling into the particle. It appears that at 90% starch 10% CMS 270ul, there was a maximum uptake for all times plotted (Figure 3-5). It might be worthwhile to explore ratios with less than 10% CMS 270ul (and other modified starches) to determine where the actual maximum is reached. It was noteworthy that increasing the percentage of CMS 270ul above 10% did not increase the water uptake. This is significant because this modified starch is more expensive than the unmodified starch.

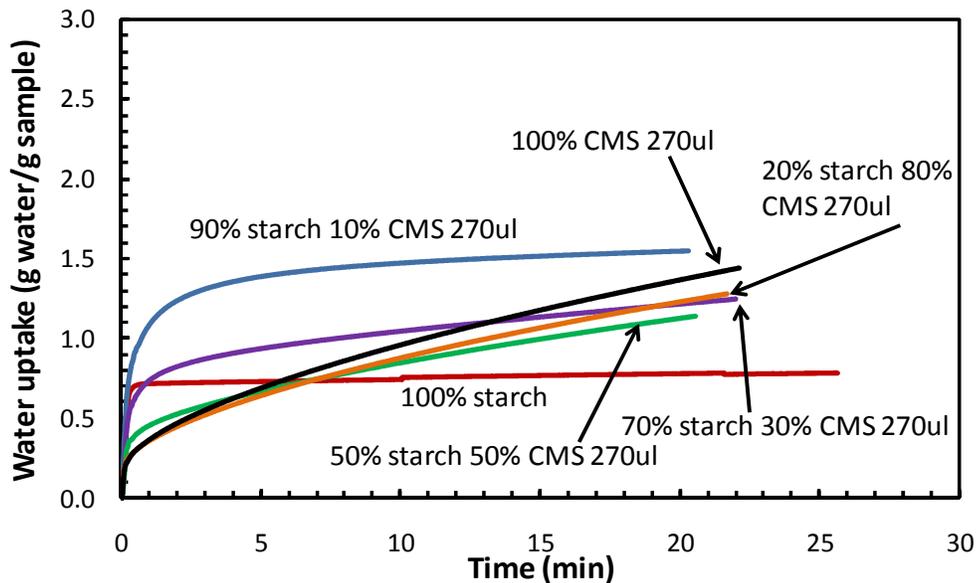


Figure 3-4: Water uptake (grams of water/gram sample) for blends of starch and CMS 270ul.

Table 3-8: Water uptake (grams of water/gram sample) at 1, 5 and 20 minutes for starch-CMS 270ul blends as a function of starch percentage.

	% starch					
	0	20	50	70	90	100
1 min	0.3702	0.3627	0.4578	0.7365	1.0880	0.7143
5 min	0.6941	0.6445	0.6705	0.9333	1.3864	0.7266
20 min	1.3718	1.23049	1.1266	1.2104	1.5448	0.7757

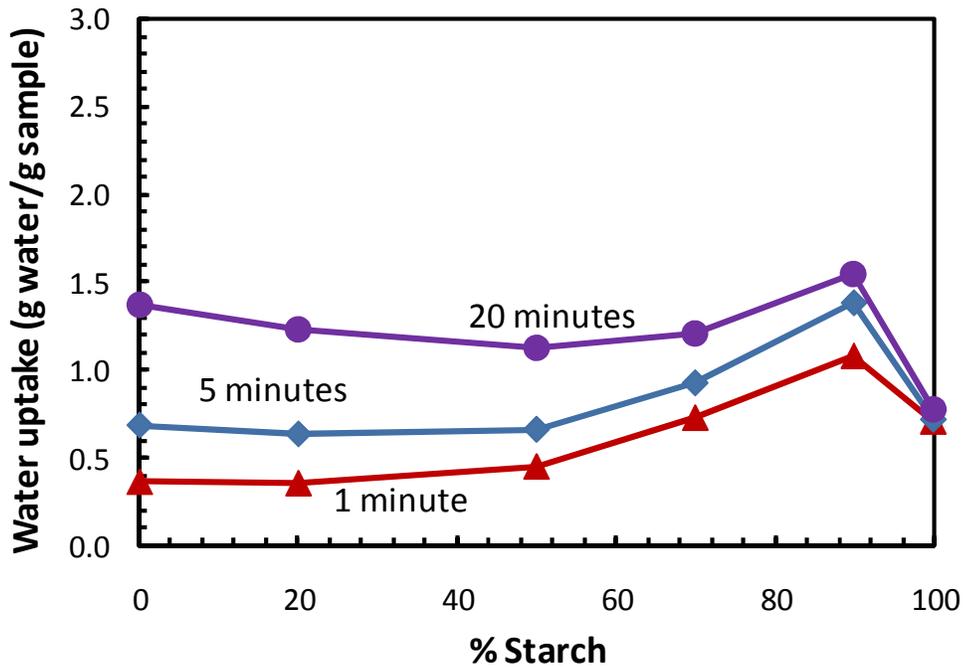


Figure 3-5: Water uptake (grams of water/gram sample) at 1, 5, and 20 minutes versus percent starch for blends of CMS 270ul and starch.

Starch and CMS 252ul Blends

The water uptake for starch and CMS 252ul blends at different ratios was plotted in Figure 3-6. The uptake at 1, 5, and 20 minutes is tabulated (Table 3-9) and plotted (Figure 3-7) as a function of percent starch. By comparing uptake as a function of percent composition it was possible to determine the trend for absorption and whether any synergistic effects by blending two materials exist.

Again, Figure 3-6 shows a sharp shoulder for starch alone. This abrupt nature decreased with increasing CMS 252ul content, in agreement with the starch and CMS 270ul data. For this carboxymethyl starch as well, there appears to be a maximum uptake level at 90% starch 10% CMS 252ul for all times (Figure 3-7).

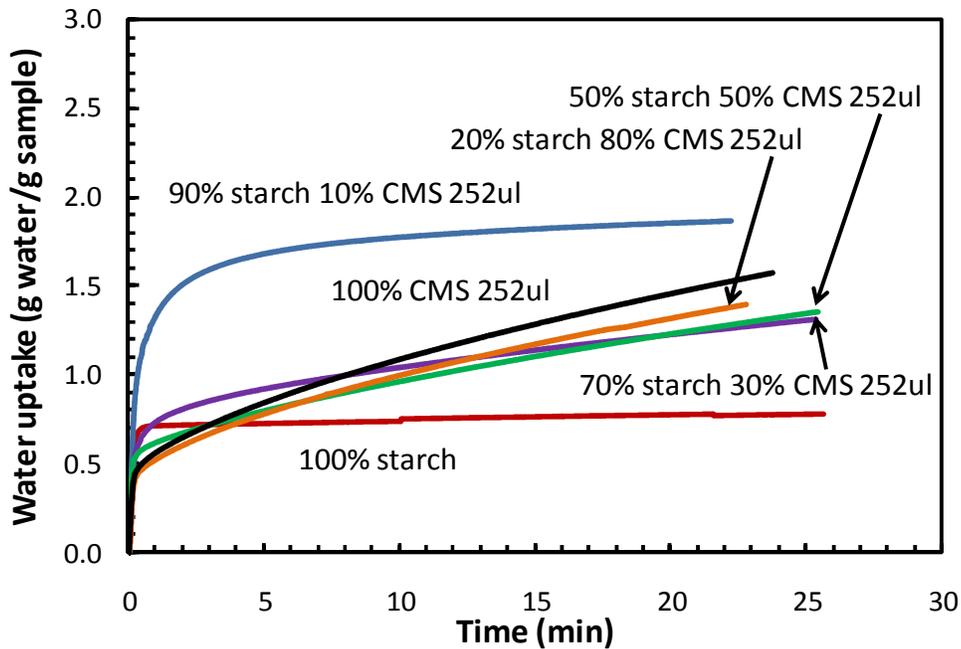


Figure 3-6: Water uptake (grams of water/gram sample) for blends of starch and CMS 252ul.

Table 3-9: Water uptake (grams of water/gram sample) at 1, 5 and 20 minutes for starch-CMS 252ul blends as a function of starch percentage.

	% starch					
	0	20	50	70	90	100
1 min	0.5630	0.5255	0.6222	0.7375	1.3349	0.7143
5 min	0.8429	0.7818	0.8004	0.9230	1.6830	0.7266
20 min	1.4528	1.3178	1.2333	1.2287	1.8553	0.7757

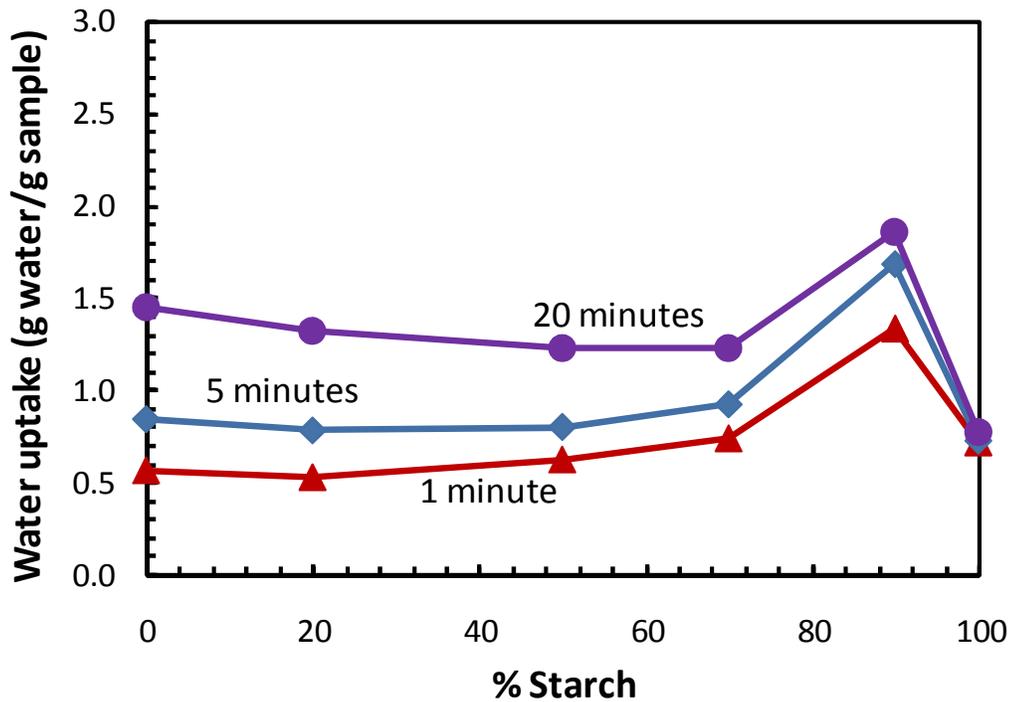


Figure 3-7: Water uptake (grams of water/gram sample) at 1, 5, and 20 minutes versus percent starch for blends of CMS 252ul and starch.

Starch and CMS 220ul Blends

The water uptake for starch and CMS 220ul blends at different ratios was plotted in Figure 3-8. The uptake at 1, 5, and 20 minutes is tabulated (Table 3-10) and plotted (Figure 3-9) as a

function of percent starch. By comparing uptake as a function of percent composition it was possible to determine the trend for absorption and whether any synergistic effects by blending two materials exist.

Unlike the high and medium DS materials, the lower DS CMS 220ul showed no maximum uptake at 90% starch 10% CMS 220ul (Figures 3-8 and 3-9). At 20 minutes, there was no significant dependence of water uptake with respect to % starch at % starch levels below 50%. There was no linear relationship between % starch and water uptake, however, there was a positive synergistic effect in blending the components.

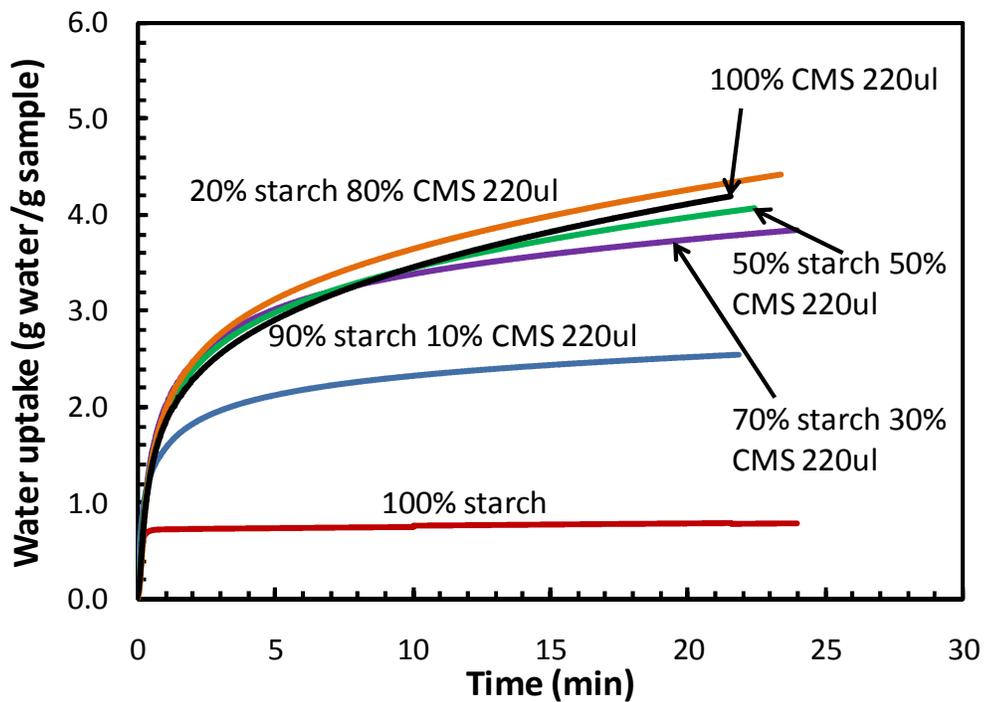


Figure 3-8: Water uptake (grams of water/gram sample) for blends of starch and CMS 220ul.

Table 3-10: Water uptake (grams of water/gram sample) at 1, 5 and 20 minutes for starch-CMS 220ul blends as a function of starch percentage.

	% starch					
	0	20	50	70	90	100
1 min	1.8033	1.9456	1.8825	1.9791	1.5562	0.7143
5 min	2.8940	3.1188	2.9695	3.0050	2.1225	0.7266
20 min	4.1008	4.2625	3.9607	3.7310	2.5201	0.775

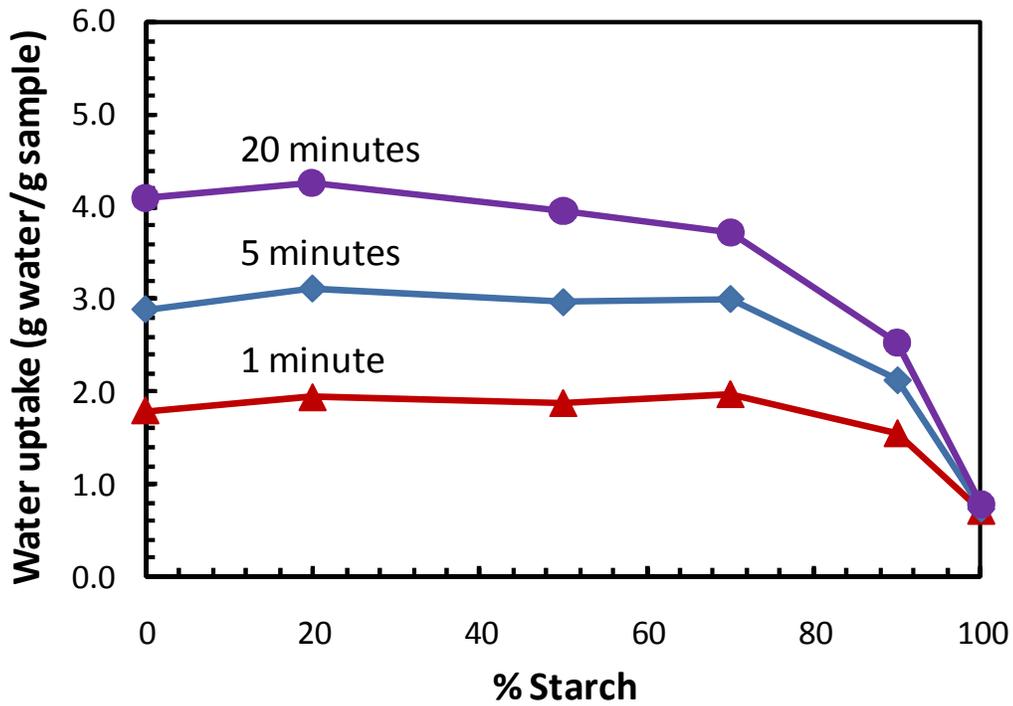


Figure 3-9: Water uptake (grams of water/gram sample) at 1, 5, and 20 minutes versus percent starch for blends of CMS 220ul and starch.

Starch and CMS 220x Blends

The water uptake for starch and CMS 220x blends at different ratios was plotted in Figure 3-

10. The uptake at 1, 5, and 20 minutes is tabulated (Table 3-11) and plotted (Figure 3-11) as a function of percent starch. By comparing uptake as a function of percent composition it was possible to determine the trend for absorption and whether any synergistic effects by blending two materials exist.

Similar to the uncrosslinked low DS material, the CMS 220x crosslinked samples showed no maximum uptake at 90% starch 10% CMS 220x (Figures 3-10 and 3-11). For all times, there was a steady dependence of water uptake with respect to % starch for all starch levels. There was no linear relationship between % starch and water uptake, however, there was a positive synergistic effect in blending the components.

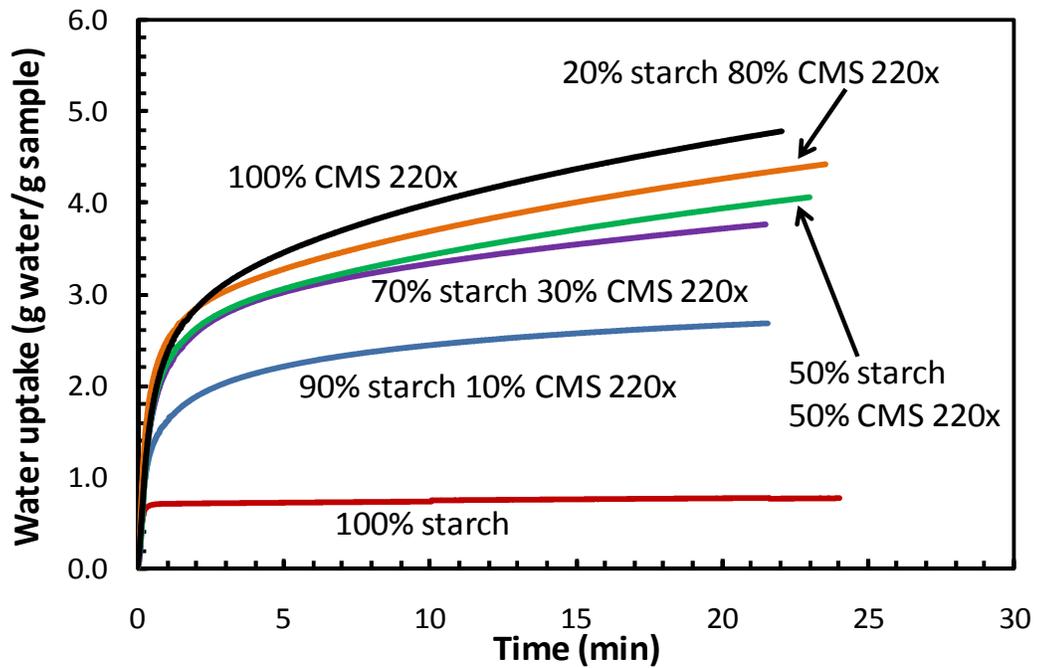


Figure 3-10: Water uptake (grams of water/gram sample) for blends of starch and CMS 220x.

Table 3-11: Water uptake (grams of water/gram sample) at 1, 5 and 20 minutes for starch-CMS 220x blends as a function of starch percentage.

	% starch					
	0	20	50	70	90	100
1 min	2.3279	2.4678	2.2222	2.1558	1.6050	0.7143
5 min	3.4493	3.2690	3.0573	3.0100	2.2137	0.7266
20 min	4.6703	4.2599	3.9427	3.7079	2.6684	0.7750

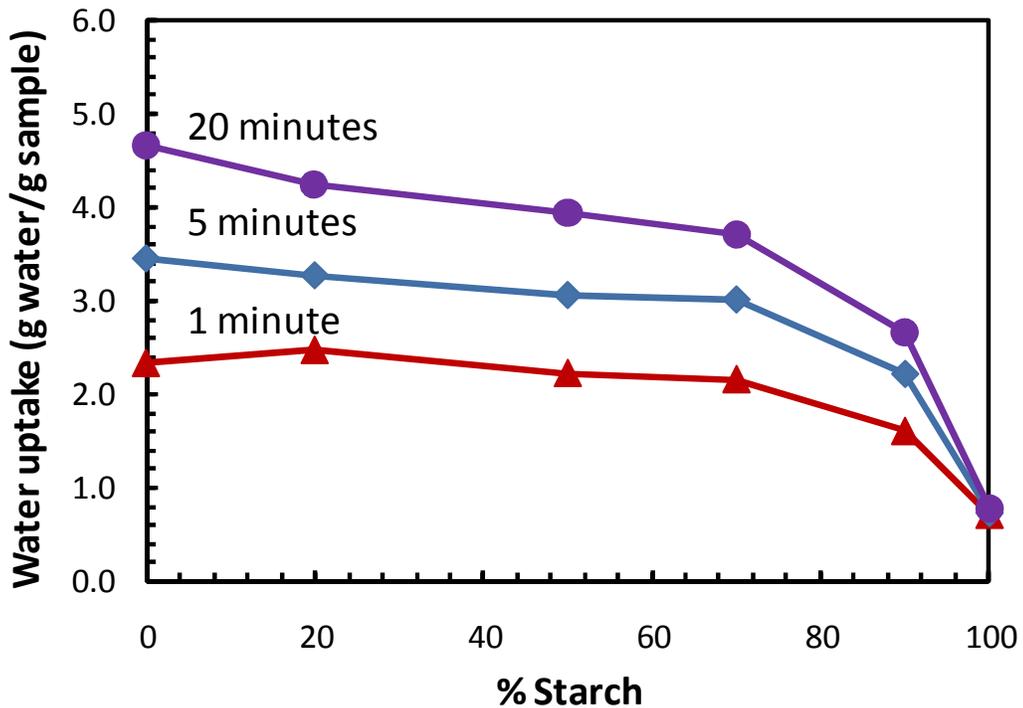


Figure 3-11: Water uptake (grams of water/gram sample) at 1, 5, and 20 minutes versus percent starch for blends of CMS 220x and starch.

Hemicellulose and CMS 270ul Blends

The water uptake for hemicellulose and CMS 270ul blends at different ratios was plotted in Figure 3-12. The uptake at 1, 5, and 20 minutes is tabulated (Table 3-12) and plotted (Figure

3-13) as a function of percent starch. By comparing uptake as a function of percent composition it was possible to determine the trend for absorption and whether any synergistic effects by blending two materials exist.

The hemicellulose CMS 270ul blends had the highest water uptake of all blends evaluated (Figure 3-12). Figure 3-12 shows a sharp shoulder for hemicellulose alone, similar to the shoulder seen for starch. This abrupt shoulder decreased with increasing CMS 270ul content, in accordance with gel blocking and slow swelling into the particle. Similar to the starch CMS 270ul blends, there appears to be a maximum in the water uptake level for the 90% hemicellulose 10% CMS 270ul blend for all times plotted (Figure 3-13). For all times, there was a steady dependence of water uptake with respect to % CMS 270ul for all CMS 270ul levels. There was no linear relationship between % CMS 270ul and water uptake, however, there was a positive synergistic effect in blending the components.

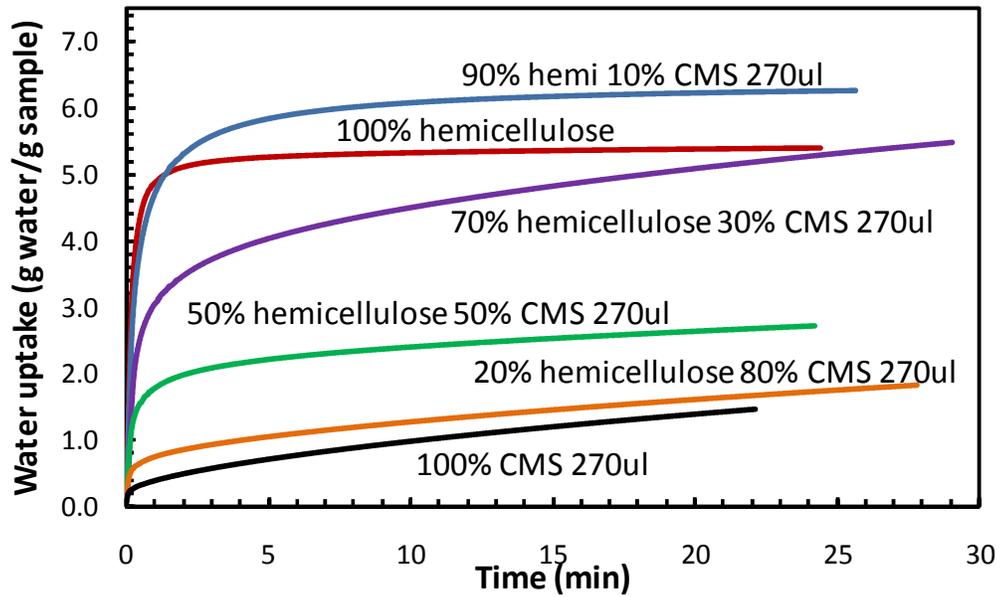


Figure 3-12: Water uptake (grams of water/gram sample) for blends of hemicellulose and CMS 270ul.

Table 3-12: Water uptake (grams of water/gram sample) at 1, 5 and 20 minutes for starch-CMS 270ul blends as a function of hemicellulose percentage.

	% CMS 270ul					
	0	10	30	50	80	100
1 min	4.8460	4.6709	3.0257	1.7616	0.7351	0.3702
5 min	5.2490	5.8305	4.0234	2.2048	1.0418	0.6941
20 min	5.3713	6.2204	5.0821	2.6289	1.6083	1.3718

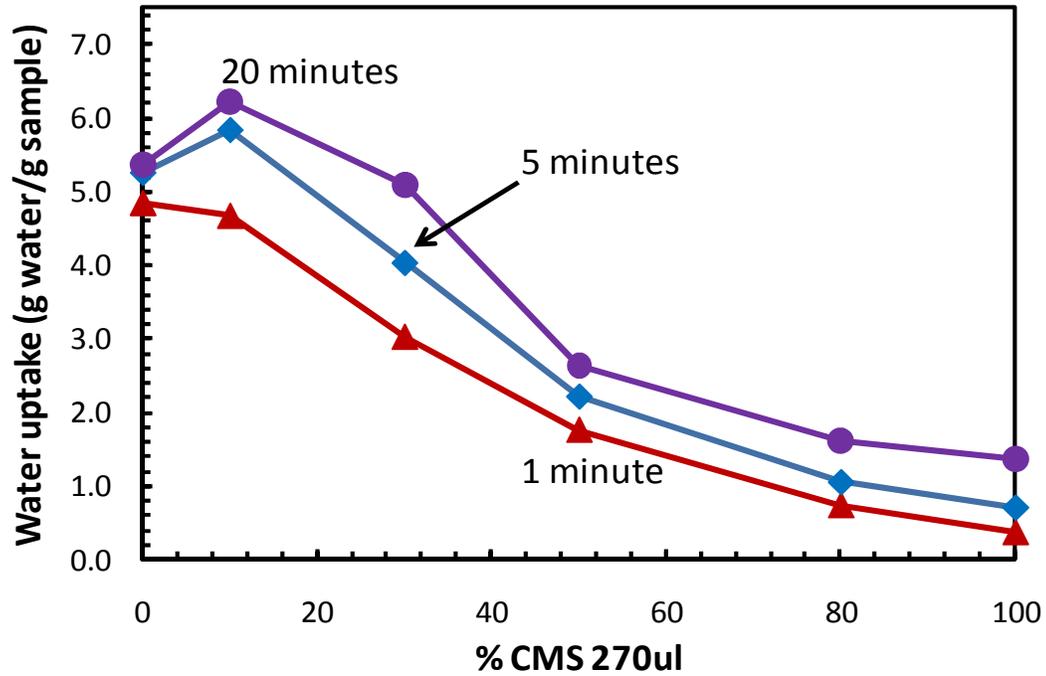


Figure 3-13: Water uptake (grams of water/gram sample) at 1, 5, and 20 minutes versus percent CMS 270ul for blends of hemicellulose and CMS 270ul.

Sand and CMS 270ul Blends

The water uptake for sand and CMS 270ul blends at different ratios was plotted in Figure 3-14. The uptake at 1, 5, and 20 minutes is tabulated (Table 3-13) and plotted (Figure 3-15) as a function of percent starch. By comparing uptake as a function of percent composition it was possible to determine the trend for absorption and whether any synergistic effects by blending two materials exist.

The overall presence of sand in the CMS 270ul sand blends decreases the water uptake. The addition of up to 50% sand to CMS 270ul, however, did not significantly decrease the water

uptake. This adds an element of cost-savings to these blends if up to half of the more expensive CMS 270ul can be replaced with sand. There was no linear relationship between % CMS 270ul and water uptake, however, there was a positive synergistic effect overall in blending the components.

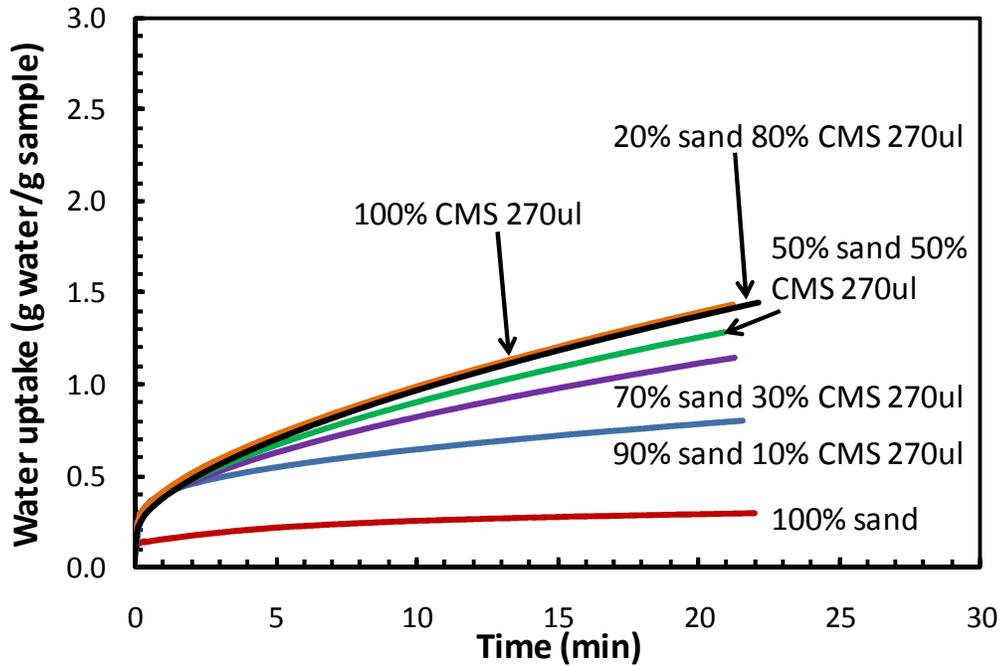


Figure 3-14: Water uptake (grams of water/gram sample) for blends of sand and CMS 270ul.

Table 3-13: Water uptake (grams of water/gram sample) at 1, 5 and 20 minutes for starch-CMS 270ul blends as a function of sand percentage.

	% CMS 270ul					
	0	10	30	50	80	100
1 min	0.1467	0.3959	0.3795	0.3822	0.4037	0.3702
5 min	0.2100	0.5432	0.6209	0.6635	0.7180	0.6941
20 min	0.2828	0.7819	1.1117	1.2576	1.3882	1.3718

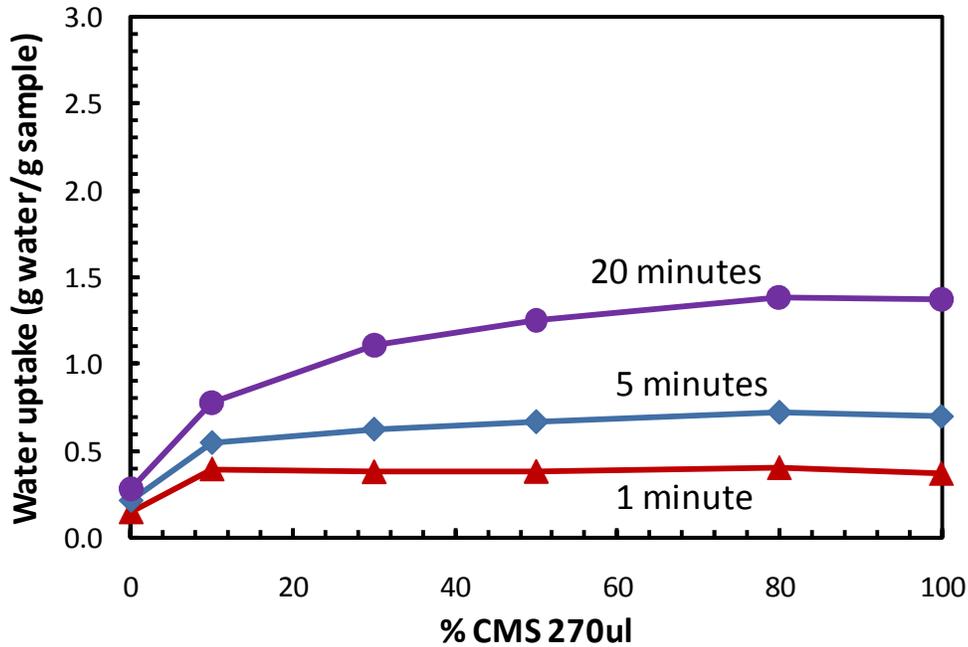


Figure 3-15: Water uptake (grams of water/gram sample) at 1, 5, and 20 minutes versus percent CMS 270ul for blends of sand and CMS 270ul.

Clay #1 and CMS 270ul Blends

The water uptake for clay #1 and CMS 270ul blends at different ratios was plotted in Figure 3-16. The uptake at 1, 5, and 20 minutes is tabulated (Table 3-14) and plotted (Figure 3-17) as a function of percent starch. By comparing uptake as a function of percent composition it was possible to determine the trend for absorption and whether any synergistic effects by blending two materials exist.

Figure 3-16 shows a sharp shoulder for clay alone. This abrupt shoulder decreased with increasing CMS 270ul content, in accordance with gel blocking and slow swelling into the particle, similar to the starch CMS 270ul blends. It appears that at 90% clay 10% CMS

270ul, there was a maximum uptake for all times plotted (Figure 3-17). It was noteworthy that increasing the percentage of CMS 270ul above 10% did not increase the water uptake any further, in fact the water uptake for 90% clay was higher than that for 100% CMS 270ul during the experimental time period. The clay absorbs water rapidly and levels off while the CMS 270ul takes up water slowly but will have a higher uptake overall.

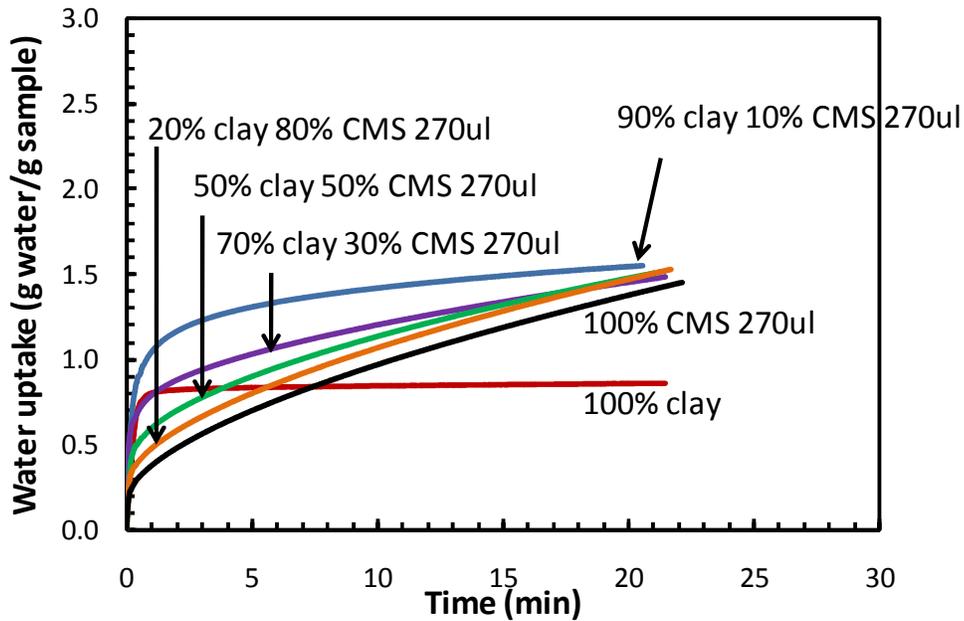


Figure 3-16: Water uptake (grams of water/gram sample) for blends of clay #1 and CMS 270ul.

Table 3-14: Water uptake (grams of water/gram sample) at 1, 5 and 20 minutes for starch-CMS 270ul blends as a function of clay #1 percentage.

	% CMS 270ul					
	0	10	30	50	80	100
1 min	0.8004	1.0356	0.7828	0.5886	0.4711	0.3702
5 min	0.8338	1.3005	1.0254	0.8921	0.7945	0.6941
20 min	0.8573	1.5375	1.4473	1.4683	1.4647	1.3718

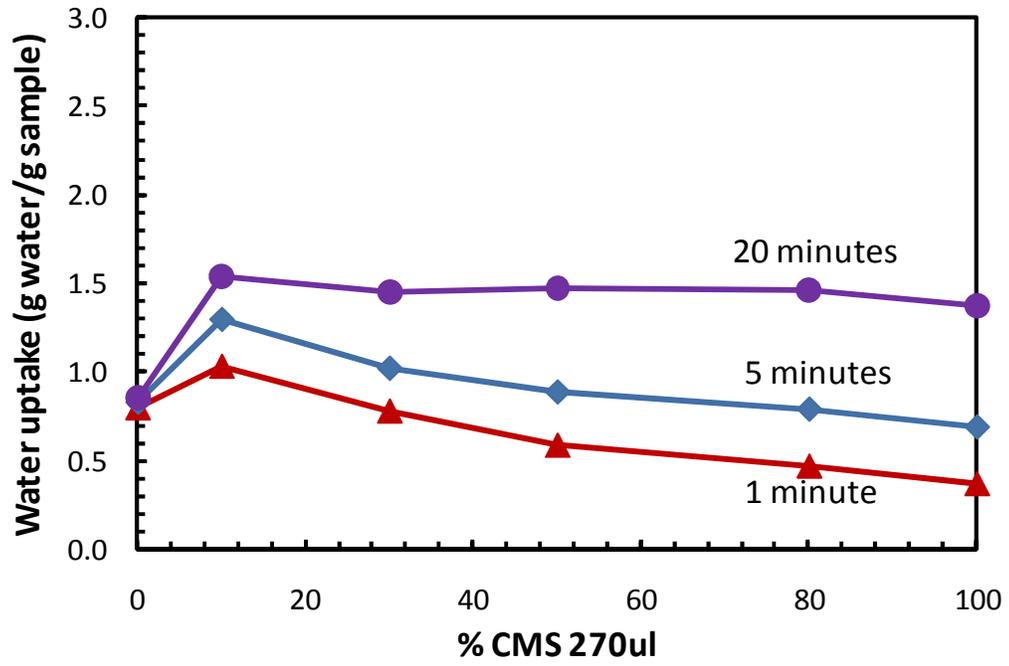


Figure 3-17: Water uptake (grams of water/gram sample) at 1, 5, and 20 minutes versus percent CMS 270ul for blends of clay #1 and CMS 270ul.

Conclusions

- Materials that are not expected to swell within the time limits of the experiment (unmodified starches and sand for instance) have a very fast initial water uptake rate that levels off to almost zero, indicative of capillary flow through a porous medium.
- Materials that are expected to swell within the time limits of the experiment (carboxymethyl starches) have a more gradual water uptake rate (absent a shoulder) that does not level off, indicative of gel blocking and the diffusion of water into the particles.
- Blending swelling and non-swelling materials can result in a synergistic effect. CMS and unmodified starch show a synergistic effect below 10% CMS 270ul and CMS 252ul in the blend. Blends of hemicellulose and CMS 270ul and of clay and CMS 270ul also have a similar synergistic effect when the level of CMS 270ul is below 10%.
- Some blends of materials that do not swell with materials that do swell produce maximum values of water uptake at low percent of the swellable material.
- For CMS materials, lower DS and the presence of crosslinking were associated with higher water uptake values, indicating that gel blocking is dominating the water uptake behavior of these materials.

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Chapter 4

Natural Polymer Films

Introduction

Absorbent hygienic materials are an important part of modern society, fulfilling serious health and safety needs. The demand for these materials is greater than 40,000 metric tons annually (Nexant, Inc. 2004). Typically these products are derived from non-renewable petroleum-based acrylic acid, making disposal and biodegradability in landfills a concern. As the price of oil rises, the price for these absorbent feedstocks also rises. Many recent research articles have focused on the preparation and utilization of bio-based absorbents.

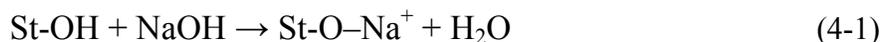
Grafted starch-acrylonitrile absorbents were developed in the 1970's by the USDA, but were never commercialized on a large scale (Gross 1990). Yamaguchi, Watamoto and Sakamoto (1987, 1988) prepared superabsorbents from these starch-polyacrylonitrile graft copolymers. Superabsorbents with swelling values of 70-390 gram/gram were prepared by Lanthong, Nuisin and Kiatkamjornwong (2006) using cassava starch.

The grafting of acrylic acid and acrylamide onto cellulose chains greatly increases the water-loving nature of cellulose. Non-potable water from three sources in India was passed through columns filled with the absorbent polymers and the unhealthy ionic content of the water was greatly reduced (Chauhan and Lal 2003).

Hemicellulose and carboxymethyl starch (CMS) are also effective biobased absorbents. Hemicelluloses are branched, amorphous, contain more than one type of saccharide, and have multiple functional groups. This allows the molecules to act in ways different than cellulose and starch. These hemicelluloses are soluble in aqueous alkali but insoluble in almost all organic solvents (Sun et al, 2004). The organic insolubility is probably due to the high density of hydrogen bonds within xylan (Jain, Sjostedt and Glasser 2001). Solubility can therefore be induced when some of the hydroxy groups are substituted by alkoxy or acetoxy functionalities (Jain, Sjostedt and Glasser 2001). Some of the structural and behavioral disadvantages can be overcome by chemical and structural modification. The chemical modification of hemicellulose was studied as early as the 1960's, focusing on modification of xylan. Applications for hemicelluloses and other lignin polymers include adhesives, coating and foam products, engineering plastics, food additives, thickeners, emulsifiers, gelling agents and adsorbents (Gabriellii and Gatenholm 1998). The reaction of xylan with propylene oxide in aqueous alkali produces a thermoplastic hydroxypropyl xylan with a low molecular weight, branched structure, and solubility in water (Sun, Sun and Tomkinson 2004).

Gabriellii and Gatenholm (1998, 2000) have used birchwood and aspen xylan as the base for hydrogels and combined them with chitosan. Beechwood xylan, barley husk xylan and carboxymethyl xylan are also viable biobased absorbent alternatives (Tanodekaew, Channasanon and Uppan 2006, Grondahl, Eriksson and Gatenholm 2004, Petzold, Schwikal and Heinze 2006).

Carboxymethyl starch (CMS) is obtained as a product of the reaction of starch (St-OH) with sodium hydroxide and sodium monochloroacetate (MCA) (Stojanovic, Jeremic, and Jovanovic 2000). This is a two-step reaction, the first step being the alkalization of starch followed by etherification:



These modified starches have increased water solubility as the degree of substitution (DS) is increased. For this reason organic solvents are used for the production of granular CMS like the ones used in this study (Stojanovic, Jeremic, and Jovanovic 2000).

For CMS, the degree of substitution is the average number of carboxymethyl groups on the starch repeat unit (Heinze, et al. 2004). Typically, CMS is used as an additive in the paper industry, as a thickener for textile printing pastes and as a tool for enhanced oil recovery (Stojanovic, Jeremic, and Jovanovic 2000).

Other plant and animal-derived polymers used as absorbents include red seaweed or carrageenan (Pourjavadi and Amini-Fazi 2007), pullulan, a polymer produced by fungus (Dulong, Mocanu and Le Cerf 2007) and chitosan (Yao et al. 1998, Mahdavinia et al. 2004, Crescenzi et al. 1997 and Yu and Hui-min 2006), just to list a few.

Chitosan, a material derived from the shells of crustaceans like shrimp and crabs, is the linear deacetylated highly-soluble form of chitin, $\beta(1-4)$ -2-amino-2-deoxy-D-glucose (Arguelles-Monal, et al. 2003, Sanford 1989). To produce chitosan, chitin is subjected to strong NaOH to hydrolyze the N-acetyl linkage and rinsed. The pH is adjusted and the material is dewatered. At this stage, the product can be made into flaked chitosan (Sandford 1989). Milling flaked chitosan results in a finer mesh powder which can be blended with an organic acid to obtain a self-dissolving chitosan acid.

Unlike chitin which is sparingly soluble, chitosan becomes water soluble after salts are formed with organic acids including formic, acetic, and ascorbic acids. Hydrochloric acid is the only mineral acid which makes chitosan water soluble. When chitosan is reacted with acids, a glucosamine residue with protonated amino groups is formed. This makes chitosan behave like a cationic polymer (Uragami and Tokura 2006). The pKa of chitosan is ~ 6.5 . Many biological materials like proteins and nucleic acids carry negative charges and therefore interact strongly with the chitosan to create electric neutrality (Sandford 1989). For medical uses it is a superior material due to its biocompatibility, non-toxicity, ability to clot blood, and ability to absorb liquids, while forming protective coatings.

The objective of this research was to investigate the static water uptake behavior of thin films made from bio-based polymers.

Materials and Methods

The materials in preparation of the natural polymer films include filter paper, starch, chitosan, CMS (220ul, 220x, and 270ul) and hemicellulose. The filter paper used was 55 mm Whatman #41 quantitative filter paper circles (Whatman # 1441-055). The average weight per circle was 0.1976 grams and the standard deviation was 0.0083 grams. The basis weight (g/m^2) was 83.1482 g/m^2 . The starch was Pearl B unmodified corn starch from Cargill. The chitosan used was medium molecular weight (190,000-310,000 g/mol) from Aldrich (448877). Three CMS powders from Aquasol (Charlotte, North Carolina) with different degrees of substitution (DS) were utilized in this study. The high and low levels of DS are 0.70 and 0.20, respectively and are represented by CMS 270ul and CMS 220ul. The low DS material, CMS 220ul is also tested in its crosslinked form (CMS 220x). The hemicellulose used was birchwood xylan (Aldrich- X0502).

Sample Preparation

Xylan and chitosan films

The films were made by dissolving the birchwood xylan and medium molecular weight chitosan in acidified water. Film preparation and characterization was based on the work of Gabriellii and Gatenholm (1998, 2000).

The initial set of films contained 1.5% solids, but the solids' content was increased to 3% to obtain a more durable film. The weights of the materials for each solution are listed in Table 4-1. The solid materials were dissolved in distilled water acidified with hydrochloric acid to pH 1.7. Hydrochloric acid is the only mineral acid, which makes chitosan water soluble and extremely low pHs are known to show favorable hydrogel swelling ratios (Uragami and Tokura 2006, Bajpai and Sharma 2006 Bajpai and Sharma 2006). The acidified water was prepared by slowly adding hydrochloric acid to a beaker of stirring distilled water. The pH was tested periodically after preparation to monitor any changes.

Table 4-1: Dry weight of starting materials for xylan and chitosan/starch films.

% Xylan	% Chitosan or Starch	Weight Xylan (g)	Weight Chitosan or Starch (g)
100	0	3.00	0.00
90	10	2.70	0.30
80	20	2.40	0.60
70	30	2.10	0.90
50	50	1.50	1.50
0	100	0.00	3.00

Four 600 ml beakers filled with 200 ml water were placed in a hot water bath set to 95°C.

Each film solution was prepared in an individual 250 ml beaker. Out of the total 100 ml solution, 3% was solids. The remaining 97% was the acidified water, so 97 ml of the water was added to each beaker. The xylan and chitosan were added and the contents were mixed thoroughly using a stirring rod. Each 250 ml beaker was placed inside a 600ml beaker in the water bath. The beakers were briefly removed from the water bath every five minutes for additional manual stirring. This process continued for twenty minutes at which time the

beakers were removed from the bath and allowed to cool for five to ten minutes. The slightly-cooled contents of the beakers were poured into a sectioned Teflon-coated shallow pan. The sheet was placed in an oven at 38°C and allowed to dry overnight, or approximately 18 hours. After drying the films were conditioned at 23°C and 50% RH for 24 hours.

Xylan and corn starch films

The films were made by dissolving the birchwood xylan and Pearl B starch in acidified water. Film preparation and characterization was based on the work of Gabriellii and Gatenholm (1998, 2000).

Originally, the films contained 1.5% solids, but eventually the solids content was increased to obtain a more durable film. Each film solution contained 3% solids, and the weights of the materials for each solution are listed in Table 4-1. The solid materials were dissolved in distilled water acidified with HCl to pH 1.7. The acidified water was prepared by slowly adding hydrochloric acid to a beaker of stirring distilled water. The pH was tested periodically after preparation to monitor any changes.

Four 600 ml beakers filled with 200 ml water were placed in a hot water bath which was set to 95°C. Each film solution was prepared in an individual 250 ml beaker. Out of the total 100 ml solution, 3% was solids. The remaining 97% was the acidified water, so 97 ml of the water was added to each beaker. The xylan and starch were added and the contents were

mixed thoroughly using a stirring rod. Each 250 ml beaker was placed inside a 600ml beaker in the water bath. The beakers were briefly removed from the water bath every five minutes for additional manual stirring. This process continued for twenty minutes at which time the beakers were removed from the bath and allowed to cool for five to ten minutes.

The slightly-cooled contents of the beakers were poured into a sectioned Teflon-coated shallow pan. The sheet was placed in an oven at 38°C and was allowed to dry overnight, or approximately 18 hours. After drying the films were conditioned at 23°C and 50% RH for 24 hours.

Carboxymethyl starch (CMS) films

The starting materials for the films were carboxymethyl starches (CMS) from Aquasol Corporation (Charlotte, North Carolina). The degrees of substitution (DS) were 0.2 and 0.7. One crosslinked material, DS = 0.2 was also tested. The films were made by dissolving the CMS in distilled water so the mixture was 3% solids. The nomenclature for these materials was CMS 220ul (DS 0.2, non-crosslinked), CMS 270UL (DS 0.7 non-crosslinked) and CMS 220x (DS 0.2, crosslinked). Film preparation and characterization was based on the work of Gabrielii and Gatenholm (1998, 2000).

Three 600 ml beakers filled with 200 ml water were placed in a hot water bath which was set to 95°C. Each film solution was prepared in an individual 250 ml beaker. Out of the total 100

ml solution, 3% was solids. The remaining 97% was the acidified water, so 97 ml of the water was added to each beaker. The CMS was added and mixed thoroughly using a stirring rod. Each 250 ml beaker was placed inside a 600ml beaker in the water bath. The beakers were briefly removed from the water bath every five minutes for additional manual stirring.

This process continued for twenty minutes at which time the beakers were removed from the bath and allowed to cool for five to ten minutes. The slightly-cooled contents of the beakers were poured into a sectioned Teflon-coated shallow pan. The sheet was placed in an oven at 38°C and was allowed to dry overnight, or approximately 18 hours. After drying the films were conditioned at 23°C and 50% RH for 24 hours.

Ethanol exchanged materials

Starch and xylan ethanol exchanged samples were prepared in a similar way to the films (Gabrielii and Gatenholm 1998, 2000), but processed in the attempt to produce foams. The foam structure should have significant pore volume (Bolivar et al. 2007), which could impart improved water uptake. The dry materials were weighed out (to 0.1 mg) and added to the pH 10 water to prepare solutions with 10% solids. The pH 10 water was prepared by slowly adding N/10 sodium hydroxide (4.0 grams NaOH/1 Liter water) to a beaker of stirring distilled water. The pH was tested periodically after preparation to monitor any changes.

Four 600 ml beakers filled with 200 ml water were placed in a hot water bath which was set to 95°C. Each solution was prepared in an individual 250 ml beaker. Out of the total 100 ml solution, 10% was solids. The remaining 90% was the basic water, so 90 ml of the water was added to each beaker. The xylan and starch were added and the contents were mixed thoroughly using a stirring rod. Each 250 ml beaker was placed inside a 600ml beaker in the water bath.

The beakers were briefly removed from the water bath every five minutes for additional manual stirring. This process continued for twenty minutes at which time the beakers were removed from the bath and allowed to cool for five to ten minutes. The slightly-cooled contents of the beakers were poured into plastic 6-inch square containers. The containers were placed in a cold room set to 4°C for at least 36 hours. This time period was sufficient to allow the solutions to gel.

After the gels warmed to room temperature, 300 ml of ethanol (3:1 ethanol:solids) was slowly added to each container. The ethanol was exchanged with the water in the gel for two hours, at which time the spent ethanol was decanted off. A total of three ethanol exchanges were performed on each sample. After the third and final exchange, the samples were conditioned at 23°C and 50% RH for 24 hours.

Sample Moisture Content

Each sample was conditioned for at least 24 hours at 23°C and 50% relative humidity before evaluation. A small portion of the sample was weighed (to 0.1 mg) and placed in a glass Petri dish. The dish and sample were placed in an oven at 105°C for two hours, and then transferred to a desiccator to cool. After cooling, the sample was weighed and the moisture content was calculated using the following formula:

$$MC \% = \left(\frac{\text{conditioned weight} - \text{oven dried weight}}{\text{conditioned weight}} \right) \times 100\% \quad (4-3)$$

This procedure was carried out for all film types and for the ethanol-exchanged materials.

Static Film Swelling

Determination of filter paper swelling

Before evaluating the water uptake of the films and foams by vacuum filtration, it was essential to determine the water uptake of the filter paper used during the tests. Several 5.5 cm Whatman #1 qualitative filter paper circles (Whatman # 1001-055) were placed in an oven for at least 2 hours at 105°C. One piece was removed from the oven and placed in a desiccator to cool. Once cooled it was weighed (to 0.1 mg) and placed in a Buchner funnel. The filtration flask and Buchner funnel were attached to house vacuum and 40 ml of distilled water was added to the funnel. After vacuum filtration was complete, the filter paper was

weighed and placed in a glass Petri dish in oven at 105°C for 2 hours. The mass loss and water uptake per gram of filter paper were calculated from this new oven-dried weight.

The same procedure was repeated using 5.5 cm Whatman #41 quantitative filter paper circles (Whatman # 1441-055). Mass loss and water uptake were determined to evaluate the difference between the two types of filter paper.

Vacuum filtration method

Approximately one gram of each sample was weighed and placed in a glass Petri dish. The sample was soaked in 25 ml distilled water for 30 minutes. A 5.5 cm oven-dry Whatman #41 quantitative filter paper circle was weighed and placed in a desiccator until needed. After 30 minutes, the filter paper was placed into a Buchner funnel attached to house vacuum. The contents of the dish were poured over the filter paper. The dish was rinsed with about 15 ml of additional water that was also poured into the funnel. Once the water was removed, the filter paper and its contents were weighed and placed in an oven at 105°C for two hours. After cooling in a desiccator, the sample was again weighed to determine mass loss and water uptake per gram of sample.

If the sample absorbed all of the water, an additional trial was run with an increased amount of water. Pure chitosan, for example, was tested by submersing it in 100 ml of water instead of the typical 25 ml.

Decantation method

The decantation method used to determine the water uptake of samples was adapted from the technique described by Gabriellii and Gatenholm (1998 and 2000). The equivalent of a 1.5 cm by 1.5 cm piece of each material was weighed (to 0.1 mg) and placed in a glass Petri dish of known weight. The sample was soaked in 25 ml of distilled water for 30 minutes. The water was carefully removed with a 25 ml pipette and the dish was dried with a paper towel. The dish and sample were weighed and placed in an oven at 105°C for two hours. After cooling in a desiccator, the dish and sample were again weighed to determine water uptake and mass loss.

Results and Discussion

Moisture Content versus Composition

The behavior of the films with regard to moisture content after conditioning is a function of the percentage of the chitosan or starch in the blend (Figure 4-1). Both the chitosan and starch film blends contain between 11% and 16% moisture on average. Neither the xylan/chitosan nor the xylan/starch blends show a significant moisture trend versus composition.

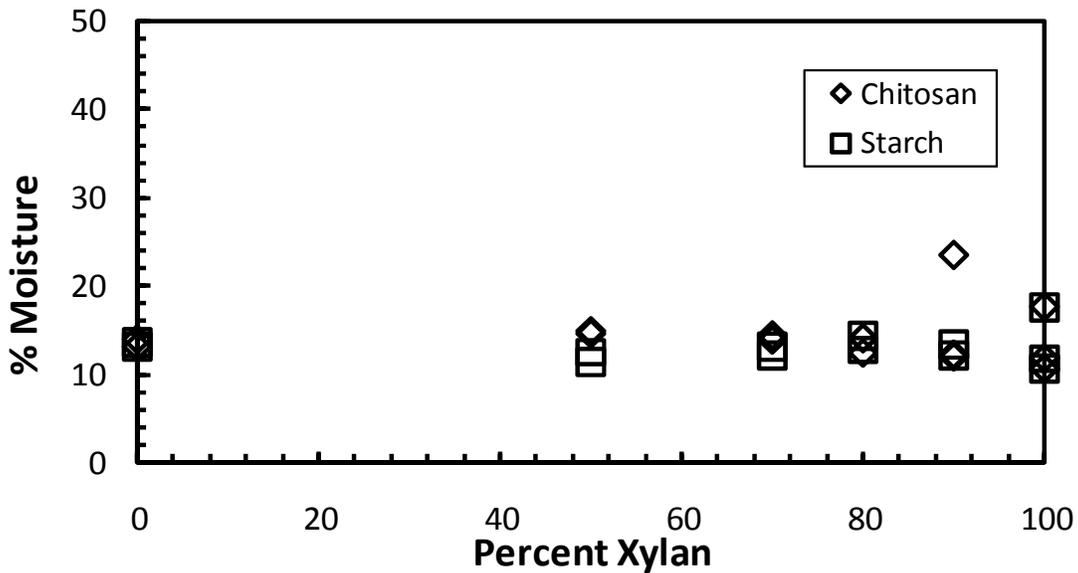


Figure 4-1: Moisture content after conditioning (23°C and 50% RH for 24 hours) for xylan/chitosan and xylan/starch blends.

The carboxymethyl starch films have moisture contents around 12% (Figure 4-2). There is no dependence between moisture content and DS or crosslinking. The modified starch materials have moisture contents that are very similar to the unmodified corn starch.

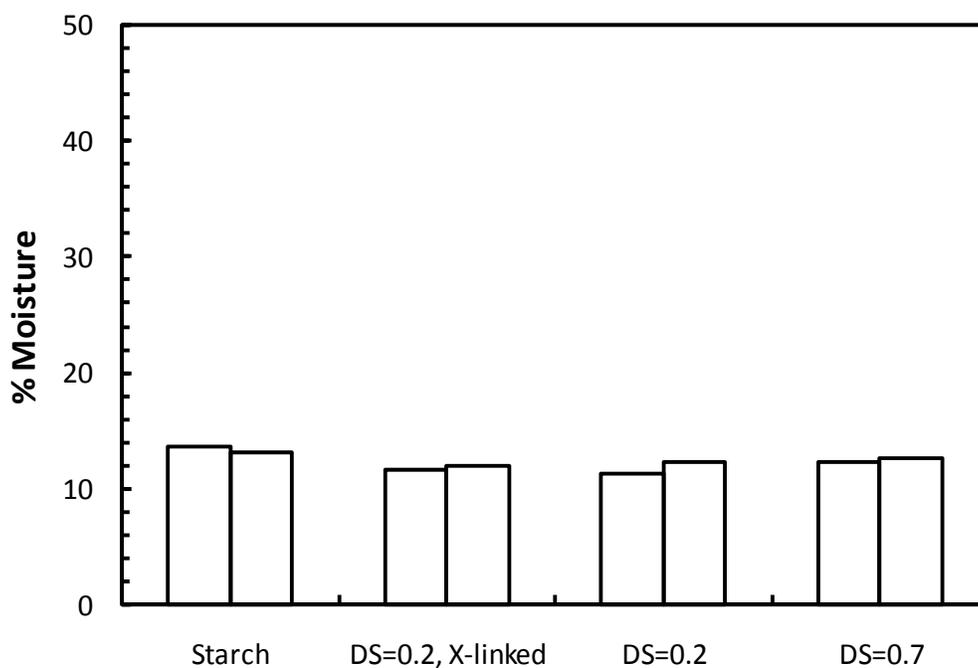


Figure 4-2: Moisture content after conditioning (23°C and 50% RH for 24 hours) for carboxymethyl starch (CMS) films. Duplicate runs are plotted.

A comparison can be made between the xylan/starch films and the xylan/starch foams. When solvent exchanged, the films became thick, opaque, less pliable, brittle, non-continuous films. The films, on average, have higher moisture content than the foams (Figure 4-3). This does not agree with results from similar studies showing that foams have slightly higher moisture content due to more extensive surface area (Bolivar et al. 2007).

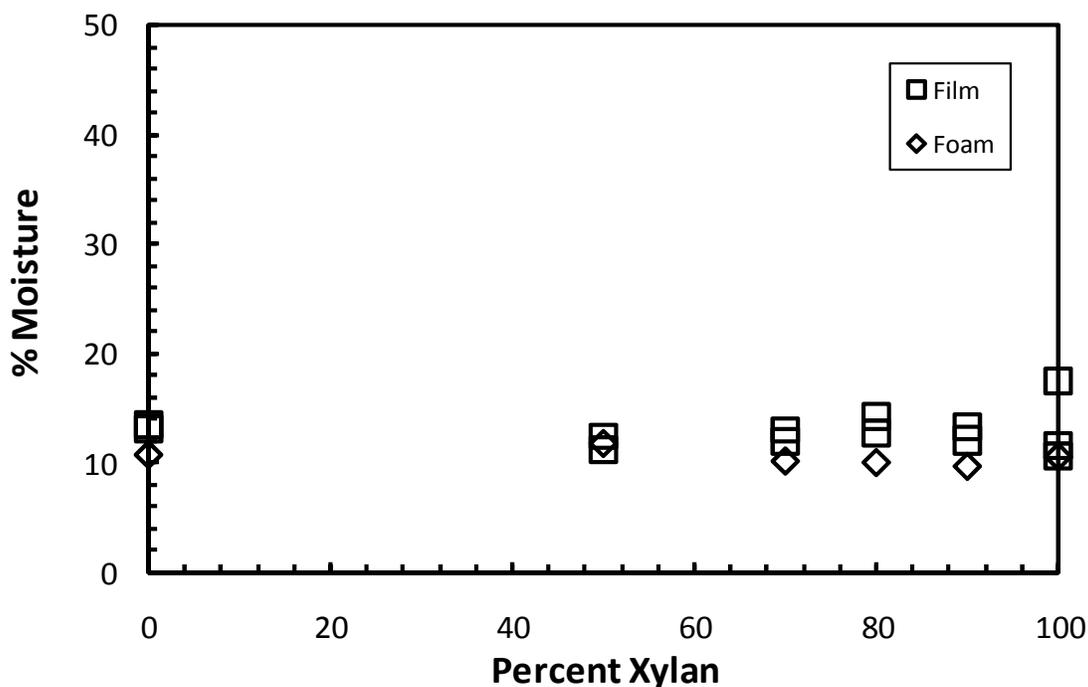


Figure 4-3: Moisture content after conditioning (23°C and 50% RH for 24 hours) for xylan/starch films and ethanol exchanged blend foams.

*Water Uptake and Mass Loss Percentage for Static Swelling
Filter Paper Swelling*

The qualitative paper takes in less water and loses less mass than the quantitative version (Table 4-2). The qualitative filter paper averages 0.7972 grams of water uptake per gram of paper while the quantitative filter paper averages 0.8556 grams. The mass loss percentage for the quantitative filter paper is also greater at 1.34% compared to 1.04% for the qualitative paper. The mass loss for both papers was small enough with regard to the sample size to be deemed insignificant. The quantitative filter paper, however, was used for subsequent measurements, because it is designed to retain the quantity of material filtered through it.

Table 4-2: Swelling and mass loss of quantitative and qualitative filter paper. Average quantitative filter paper weight is 0.1856 grams. Average qualitative filter paper weight is 0.2016 grams.

Sample	Quantitative		Qualitative	
	Water/gram	Mass loss %	Water/gram	Mass loss %
1	0.7771	1.91%	0.8682	0.79%
2	1.0905	1.12%	0.7537	1.03%
3	0.8609	1.58%	0.7799	0.86%
4	0.9050	0.96%	0.7784	1.16%
5	0.7493	1.43%	0.8061	1.38%
6	0.8531	1.22%		
7	0.7652	1.78%		
8	0.9341	0.93%		
9	0.8222	0.91%		
10	0.7982	1.54%		
Average	0.8556	1.34%	0.7973	1.04%
Std Dev	0.1021	0.36%	0.0438	0.24%

Water Swelling of Film Blends

Comparisons were made between the two types of blends using the two water uptake measurement methods. Both measurement techniques depict an increase in water uptake for xylan/chitosan blends as the percentage of xylan decreases, with a large increase for the 50% xylan blends (Tables 1 and 2 (Appendix D) and Figure 4-4). The increased water uptake is a result of the ionic interactions of chitosan and xylan. Photographs in the Appendix D (Figure 1) illustrate the water uptake and volume changes of the 50% xylan 50% chitosan film as a function of time. The average water uptake for the 90% xylan films is higher for the decantation method than the vacuum filtration method. This may be due to the vacuum method being a more aggressive water removal method than the decantation process.

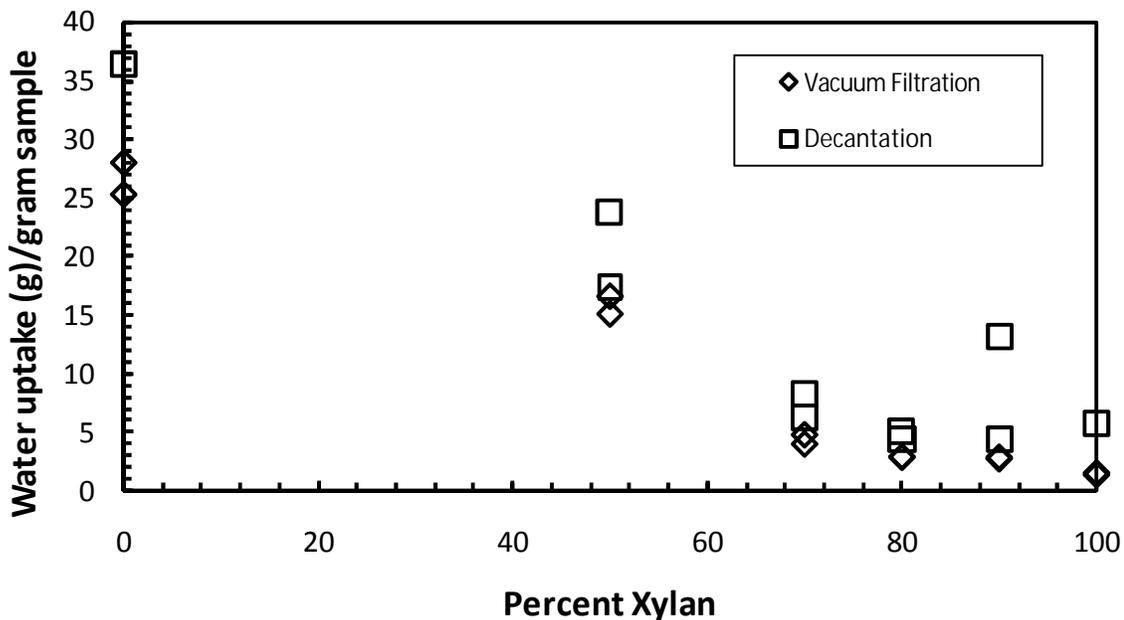


Figure 4-4: Swelling results for xylan/chitosan blends using both water uptake methods.

There is no significant trend observed between water uptake and percent xylan with starch, (Figure 4-5 and Tables 3 and 4 (Appendix D)), suggesting that xylan and starch have similar interactions with water, unlike chitosan. Also in Figures 4-4 and 4-5, the decantation method shows a higher uptake value relative to the vacuum filtration method. Again, it is possible that the vacuum filtration physically pulls water out of the film whereas the decantation method drains it from the exterior of the sample. Pure xylan did not form films like the blends nor did it have any significant water uptake. This data agrees with that of Gabriellii and Gatenholm (1998). Pure chitosan did not form films either because it readily dissolved in the water.

The major difference for the swelling is that the overall uptake for the chitosan blends is much greater than for the starch blends at the low xylan level. This is presumably due to the ability of chitosan's amino groups to complex with the glucuronic acid functionalities of xylan, forming a hydrogel (Gabriellii and Gatenholm 1998).

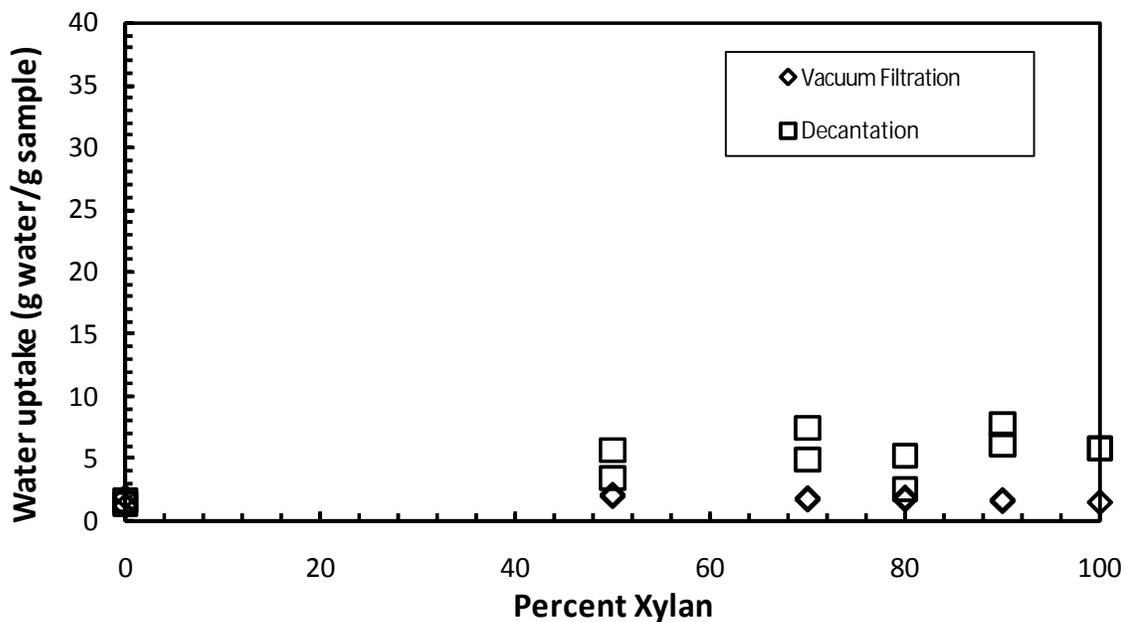


Figure 4-5: Swelling results for xylan/starch blends using both water uptake methods.

The CMS films have average water uptakes ranging from 12.2 to 24.0 g/g (Figure 4-6) with the vacuum filtration method. The values for water absorption are much higher than those for traditional starch (2.1 g/g). The highest DS corresponds to the highest water uptake due to the increased amount of functional groups. The crosslinked CMS 220x shows a slightly higher water uptake compared to CMS 220ul.

Although crosslinking strengthens a material and makes it more resistant to heat degradation, the chemical bonds reduce the material's elasticity and therefore its ability to swell. In this case, the crosslinking is probably reducing the gel blocking and therefore increasing the water uptake. It should be noted that the level of crosslinking for this material is unknown and therefore solid conclusions regarding water uptake versus crosslinking are not reliable.

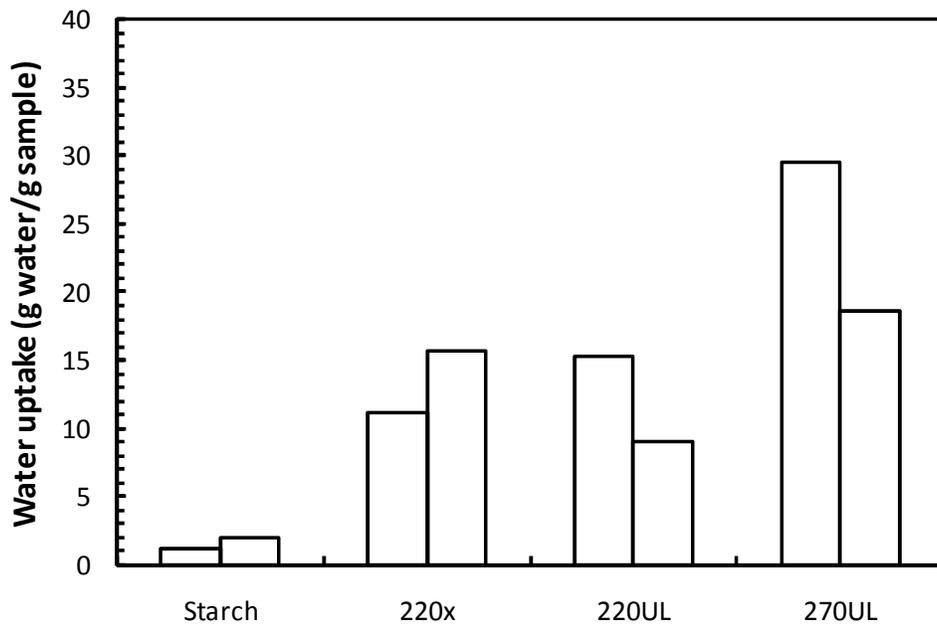


Figure 4-6: Swelling results using vacuum filtration method for carboxymethyl starch (CMS) films. Duplicate runs are shown.

Mass Loss

For the xylan/chitosan and xylan starch blends, the mass loss is higher for the decantation method (Figures 4-7 and 4-8). This is probably due to dissolved or broken film debris being decanted off inadvertently. Another theory is that the filter paper traps the film debris that would be decanted off, thus preventing some of the mass loss. The mass loss for the xylan/chitosan blends decreases with increasing chitosan percentage for both uptake techniques (Figure 4-7). The amino group of the chitosan has been reported to complex with acid groups that may be present in the hemicellulose, forming a more stable material with respect to water (Gabrielii and Gatenholm 1998). The chitosan may increase the degree of order within the xylan and the two materials may co-crystallize thus preventing mass loss. Gabrielii et al (2000) suspect that xylan forms crystallites and the chitosan, with its higher molecular mass, is able to tie the two materials together in co-crystallization. Mass loss for the xylan/starch blends (Figure 4-8) increases with a fairly linear relationship with increasing starch content, possibly due to solubilization of the starch in water. For comparison between the two blends, the mass loss percentage is greater for the starch than the chitosan blends (Figures 4-7 and 8), because starch is more soluble than chitosan.

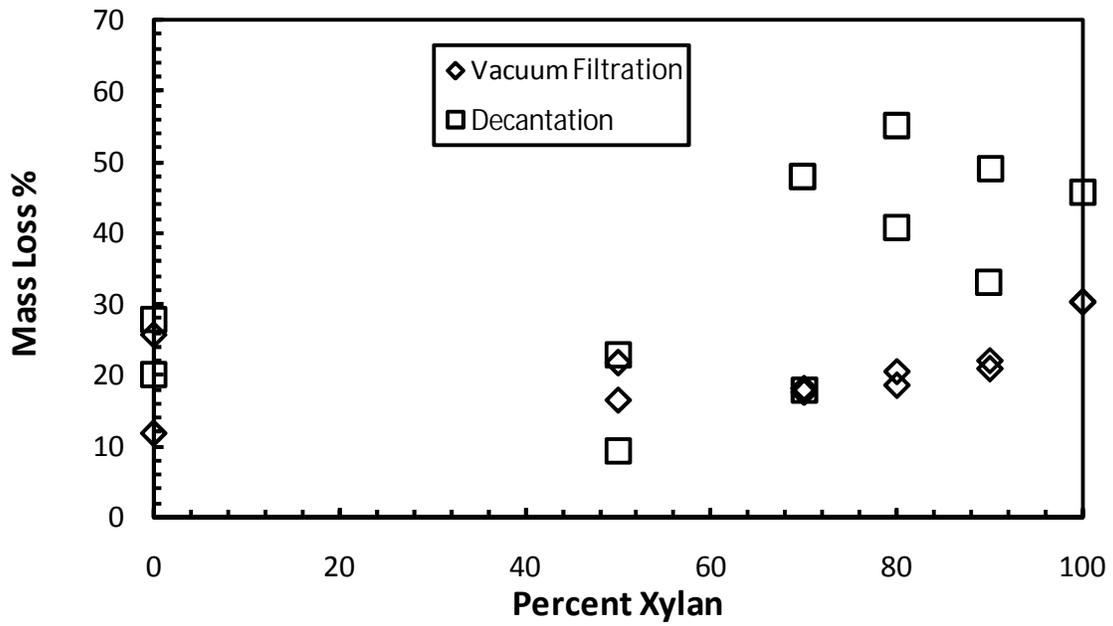


Figure 4-7: Mass loss % vs xylan in xylan/chitosan blends.

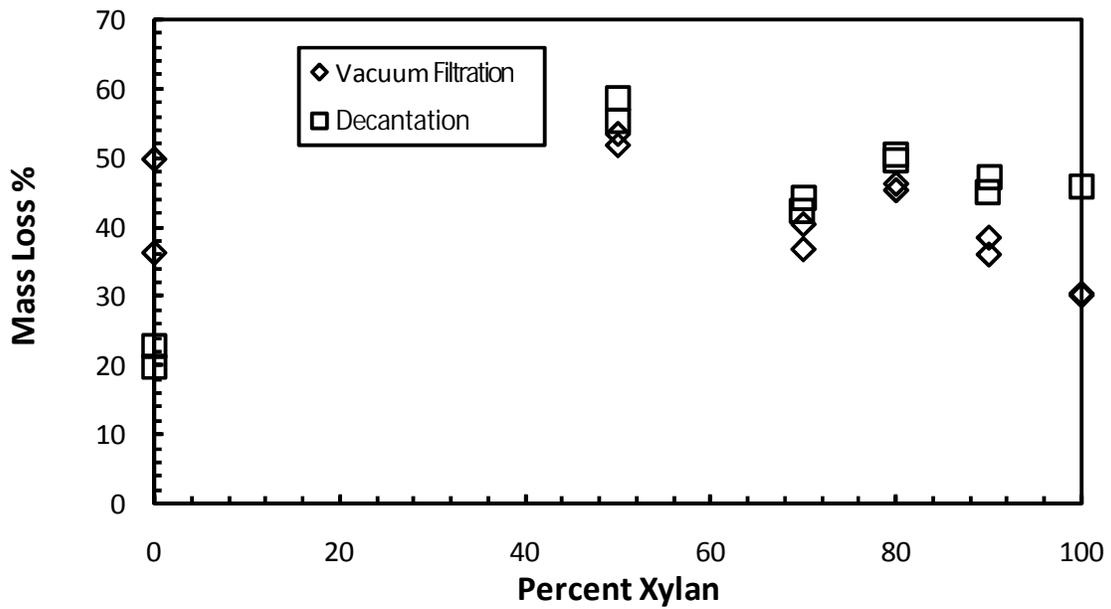


Figure 4-8: Mass loss % vs xylan in xylan/starch blends.

The average mass loss for starch and the modified starches varies with degree of substitution and the presence of crosslinking (Figure 4-9). The mass loss for starch is only 3% lower than the high DS CMS 270ul. The values for the low DS, both crosslinked and uncrosslinked, are lower than for CMS 270ul. It is possible that the added carboxymethyl groups are easily solubilized therefore increase the mass loss. Typically, crosslinking decreases mass loss, because the gel formation holds the polymer together. In this case, the presence of crosslinks actually increases the average mass loss by almost 5%.

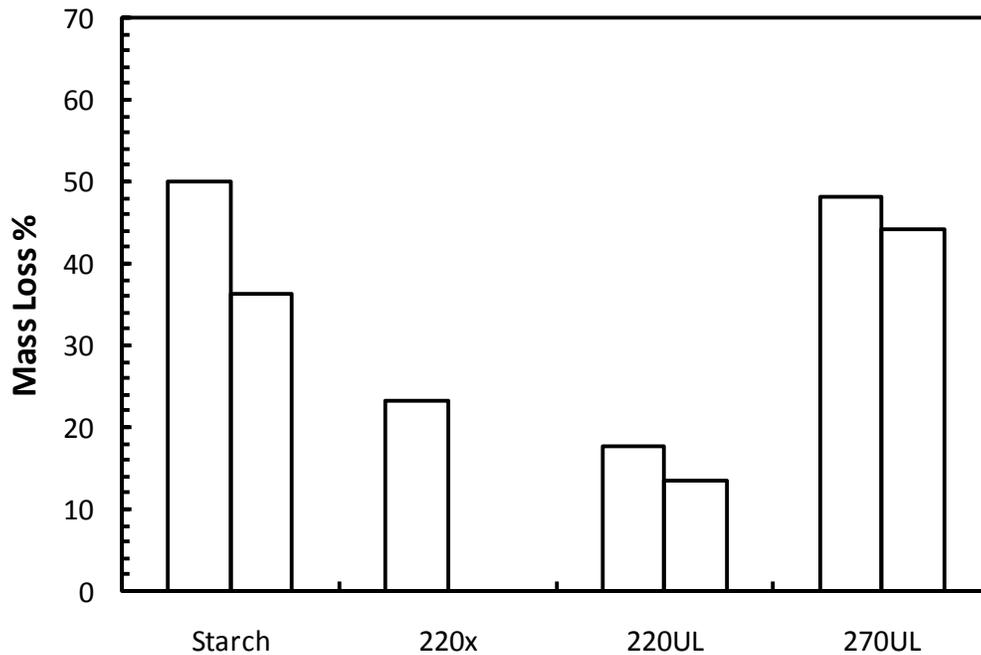


Figure 4-9: Mass loss % for carboxymethyl starch (CMS)-vacuum filtration method. Duplicate runs are shown.

Conclusions

- The presence of ionized groups at equilibrium increases water uptake along with the mass loss percentage for carbohydrate polymers.
- Crosslinking decreases the effect of gel blocking.
- Natural polymers like xylan, chitosan, starch and modified starches have potential as absorbents.

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Chapter 5

Conclusions

Chapter 2 DWA Description and Characterization

- The Dynamic Wetting Apparatus (DWA) is a convenient, repeatable, precise, cost-effective instrument that measures the dynamic water uptake of a variety of forms of materials.
- Several experimental factors are significant in the dynamic water uptake measured, including sample size, sample delivery method and sample coverage on the water delivery platform.
- The total water uptake measured in a DWA experiment can be divided into three categories: interface water, evaporated water, and water taken up by the sample.
- For samples that have fast uptake and equilibrate within the time frame of the experiment, the interface water amount can be identified, along with the known evaporation rate. Both are used to determine the true sample water uptake.
- For samples that are fully saturated, the equilibrium water uptake (grams of water absorbed per gram of sample) is independent of sample size. For samples that are not saturated within the experimental time frame, the sample size has significant impact on the recorded final (experimental) water uptake.

Chapter 3 Material Characterization and DWA Analysis

- Materials that are not expected to swell within the time limits of the experiment (unmodified starches and sand for instance) have a very fast initial water uptake rate that levels off to almost zero, indicative of capillary flow through a porous medium.
- Materials that are expected to swell within the time limits of the experiment (carboxymethyl starches) have a more gradual water uptake rate (absent a shoulder) that does not level off, indicative of gel blocking and the diffusion of water into the particles.
- Blending swelling and non-swelling materials can result in a synergistic effect. CMS and unmodified starch show a synergistic effect below 10% CMS 270ul and CMS 252ul in the blend. Blends of hemicellulose and CMS 270ul and of clay and CMS 270ul also have a similar synergistic effect when the level of CMS 270ul is below 10%.
- Some blends of materials that do not swell with materials that do swell produce maximum values of water uptake at low percent of the swellable material.
- For CMS materials, lower DS and the presence of crosslinking were associated with higher water uptake values, indicating that gel blocking is dominating the water uptake behavior of these materials.

Chapter 4 Natural Polymer Films

- The presence of ionized groups at equilibrium increases water uptake along with the mass loss percentage for carbohydrate polymers.
- Crosslinking decreases the effect of gel blocking.
- Natural polymers like xylan, chitosan, starch and modified starches have potential as absorbents.

Chapter 6

Suggested Future Work

- Evaluate ranges in crosslink density to determine effect of crosslinking on water uptake and gel blocking.
- Mix the absorbents with cellulose fluff to evaluate how a more realistic absorbent system would perform in personal hygiene products.
- Evaluate the behavior of the natural polymer films with the DWA.
- Investigate the absorbance of the CMS materials vs. different pH ranges and saline solutions using the DWA.
- Study the swelling of a larger set of materials as a function of time using a light microscope to determine whether or not gel blocking was present and whether or not DS had an effect on the water uptake (See Appendix E).

Appendices

Appendix A

Dynamic Wetting Apparatus (DWA) Operating Instructions

1. Fill water reservoir to black line. Place Petri dish cover over reservoir to reduce evaporation. Allow system to equilibrate.
2. Zero balance. Place 55 mm filter paper circle on green foam. Place 1.5" pvc pipe (sample holder) on top of filter paper with the smooth edge down. Start timer and allow filter paper to equilibrate for three minutes. Filter paper should take up approximately 0.9 grams of water.
3. After three minutes, zero balance. On 'Balance Read' program, click 'Start Collection' to begin gathering data. Be sure collection actually starts by checking the 'data' folder located on the computer desktop. Sprinkle sample evenly over filter paper. Place other Petri dish lid over sample holder to reduce evaporation.
4. Collect data for an additional 20-30 minutes.
5. On 'Balance Read' program click 'Stop Collection' to end experiment. Wait for program window to say 'done'. Remove lid, sample holder and filter paper from setup. Clean lid and sample holder.
6. Refill water reservoir, replace lid and allow system to equilibrate.
7. Repeat from step 2.

Balance Read Program Instructions

1. Open program using 'Shortcut to Balance Read' icon on Desktop.
 2. Check option to 'Save to Text File'. Data will be saved as Notepad file in C:\data.
 3. Type file name.
 4. Choose sampling interval. Smallest interval is 0.5 seconds.
- Helpful hints for Balance Read:
 - A negative weight indicates that the sample is taking up water.
 - S S with the weight value means the weight value is stable.
 - S D with the weight value means the weight value is non-stable (dynamic).

Appendix B

Water uptake behavior using GATS for 9 cm filter paper circles (Whatman #1441-090), Bounty-brand paper towels, Pearl B corn starch and CMS 220ul and 270ul.

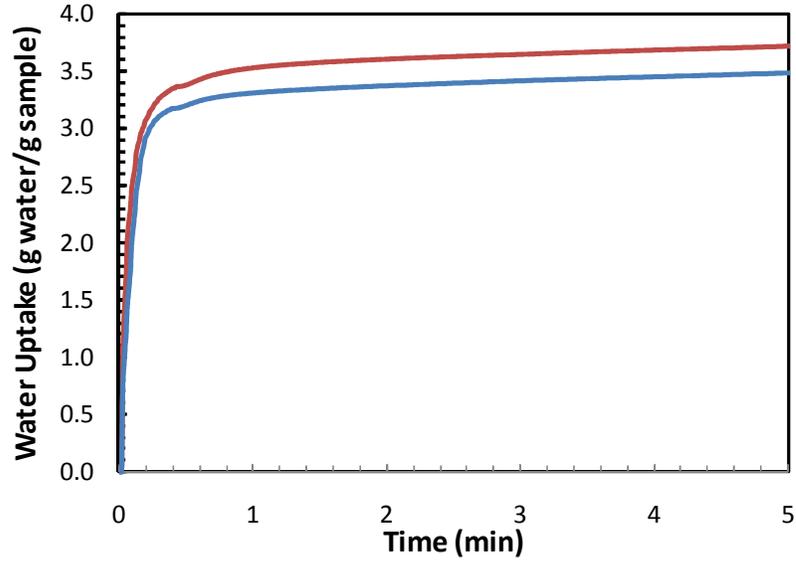


Figure 1: Water uptake (gram water/gram sample) for 9 cm Whatman filter paper circles (Whatman #1441-090) using GATS. Duplicate experiments are shown.

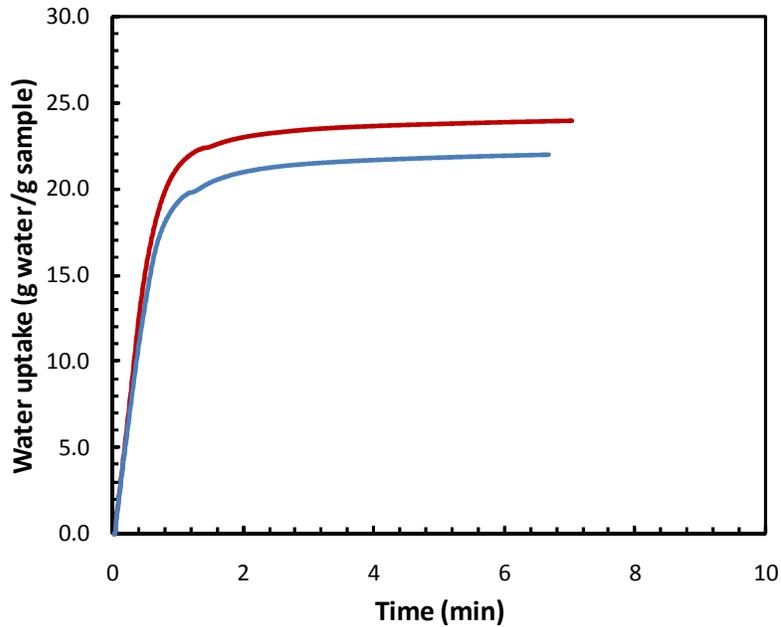


Figure 2: Water uptake (gram water/gram sample) for Bounty-brand paper towels using GATS. Duplicate experiments are shown.

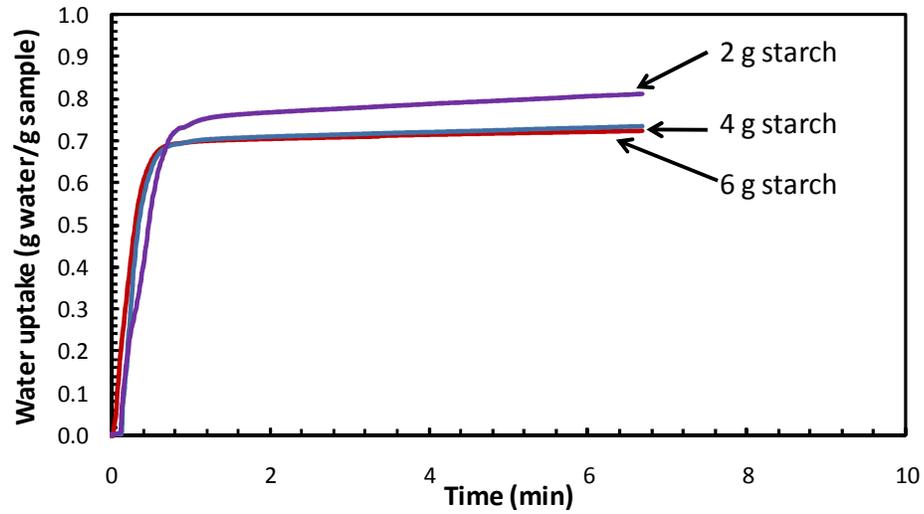


Figure 3: Water uptake (gram water/gram sample) for 2, 4, and 6 grams of Pearl B corn starch using GATS.

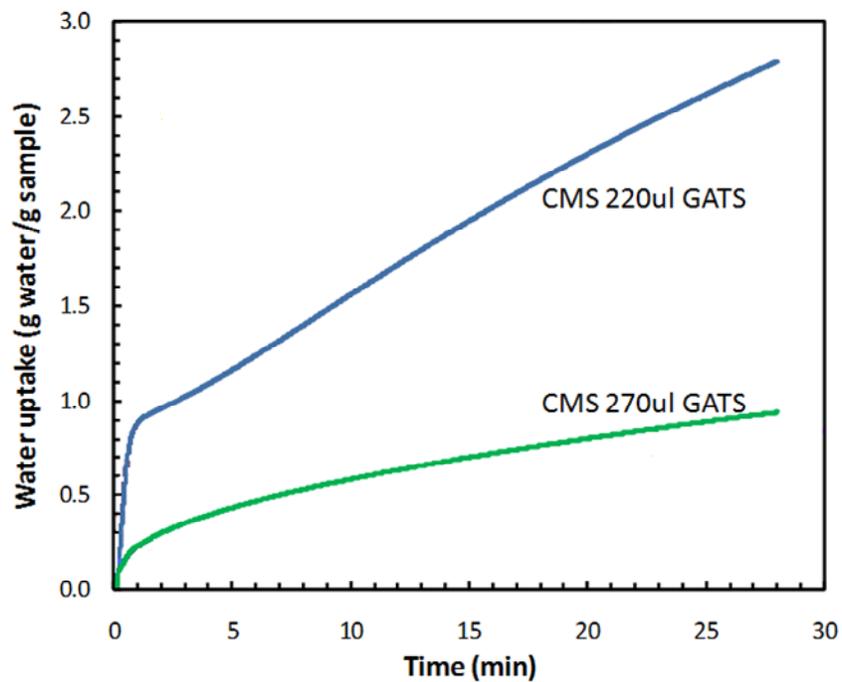


Figure 4: Water uptake (gram water/gram sample) for CMS 220ul and CMS 270ul using GATS.

Appendix C

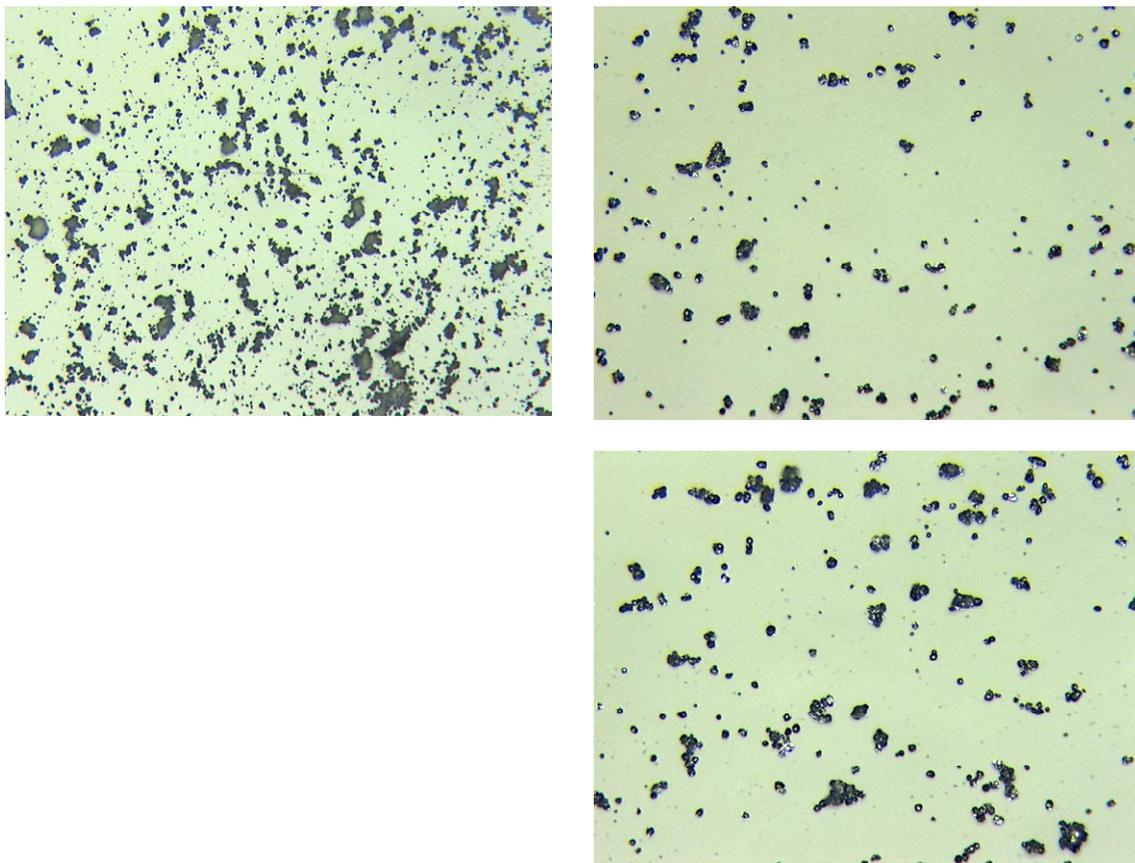


Figure 1: Light microscope images (10x magnification) of powdered materials. Clockwise from top left: hemicellulose, starch and CMS 220x.

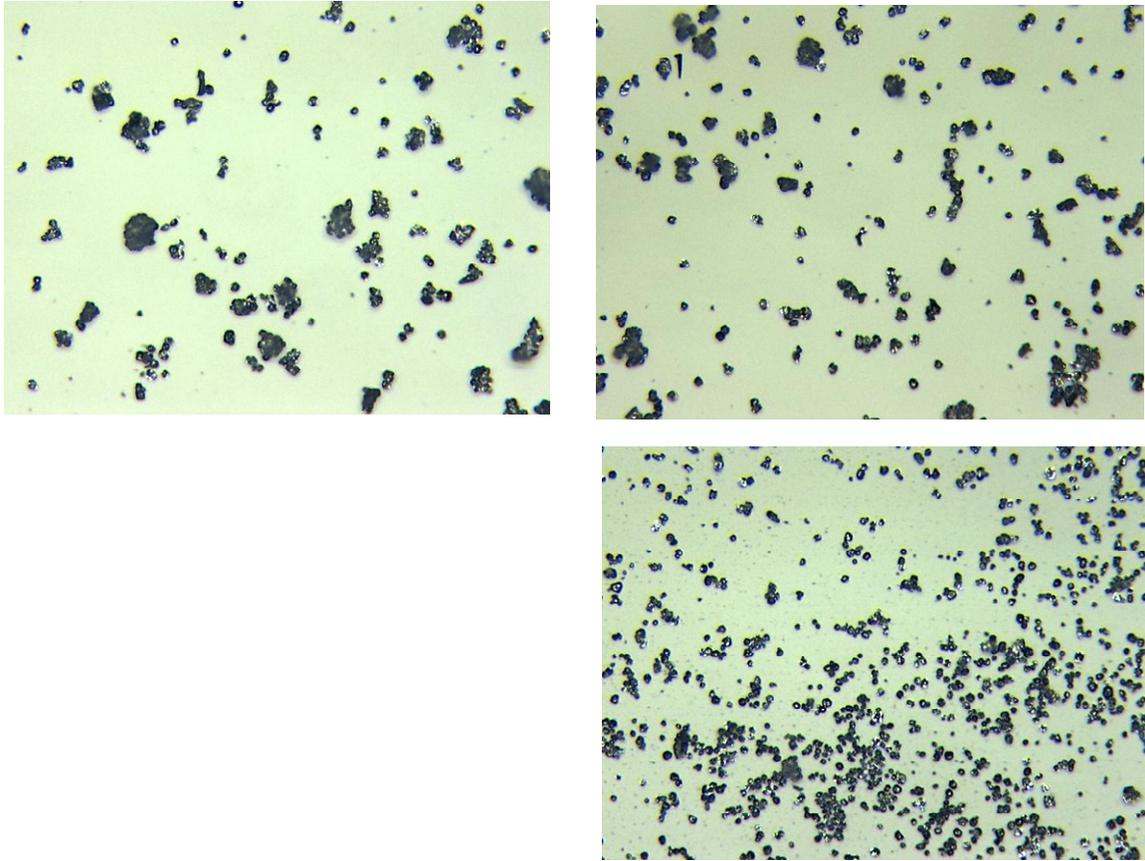


Figure 2: Light microscope images (10x magnification) of powdered materials. Clockwise from top left: CMS 220ul, 252ul and CMS 270ul.

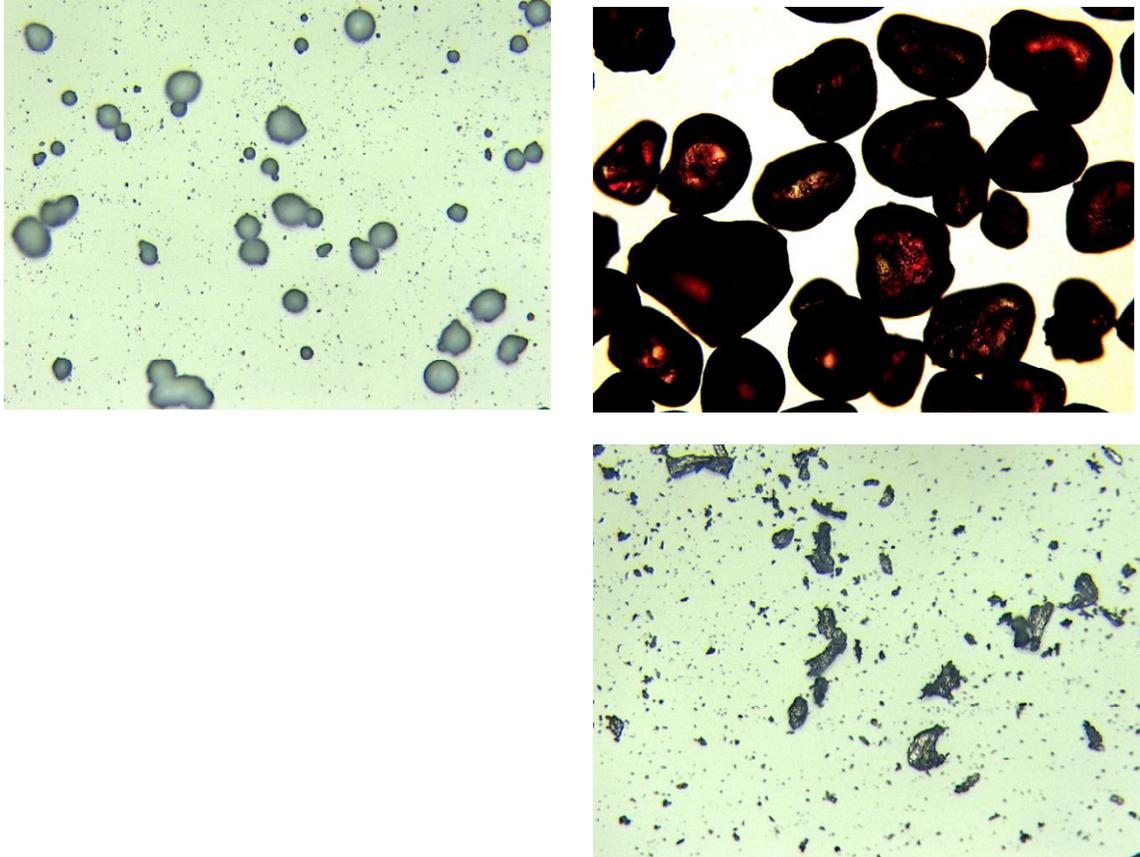


Figure 3: Light microscope images (10x magnification) of powdered materials. Clockwise from top left: clay, sand (5x magnification) and chitosan.

Appendix D

Table 1. Swelling results using vacuum filtration method for xylan/chitosan films.

Sample	Uptake (g)/gram sample	Mass Loss %
100X0C	2.1046	42.76%
90X10C	3.2339	35.61%
80X20C	3.6927	35.18%
70X30C	4.4728	35.63%
50X50C	15.9114	19.00%
0X100C	26.7082	18.72%

Table 2. Swelling results using decantation method for xylan/chitosan films.

Sample	Uptake (g)/gram sample	Mass Loss %
100X0C	5.7941	45.85%
90X10C	7.7579	37.02%
80X20C	5.0607	41.57%
70X30C	6.9446	30.32%
50X50C	20.5747	26.44%
0X100C	90.1356	41.68%

Table 3. Swelling results using vacuum filtration method for xylan/starch films.

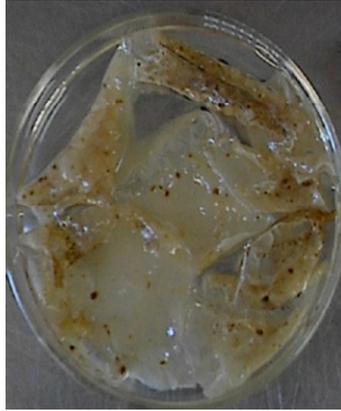
Sample	Uptake (g)/gram sample	Mass Loss %
100X0S	2.1046	42.76%
90X10S	1.6696	37.33%
80X20S	1.7854	49.33%
70X30S	1.8137	44.42%
50X50S	1.7052	55.36%
0X100S	1.5970	43.14%

Table 4. Swelling results using decantation method for xylan/starch films.

Sample	Uptake (g)/gram sample	Mass Loss %
100X0S	5.7941	45.85%
90X10S	6.9492	46.07%
80X20S	3.8807	50.21%
70X30S	5.8549	42.85%
50X50S	6.8168	58.66%
0X100S	1.5092	21.26%



50% xylan-50%
chitosan blend
after 24 hours
of conditioning



5 minutes
of soaking



15 minutes
of soaking



30 minutes
of soaking



Side view after 30 minutes
- Note swelling of film

Figure 1: Swelling over 30 minutes for 50% xylan 50% chitosan blend film.

Appendix E

Photographs of starch and CMS 270ul were taken using the light microscope at 10x magnification (Figures 1 and 2). Less than 1 ml distilled water was added to each material and a cover slip was placed on top. After 20 minutes, another set of photographs was taken (Figures 1 and 2). Seven particles present in the photographs for both times were evaluated for particle size. The percent change in particle size was calculated (Tables 1 and 2). A few particles moved out of view after water was added. The CMS 270ul particles swelled an average of 2.27% while the CMS swelled an average of 8.50%. The results are in agreement with the expectation that the ionized groups within CMS 270ul would increase osmotic pressure and therefore the amount of swelling.

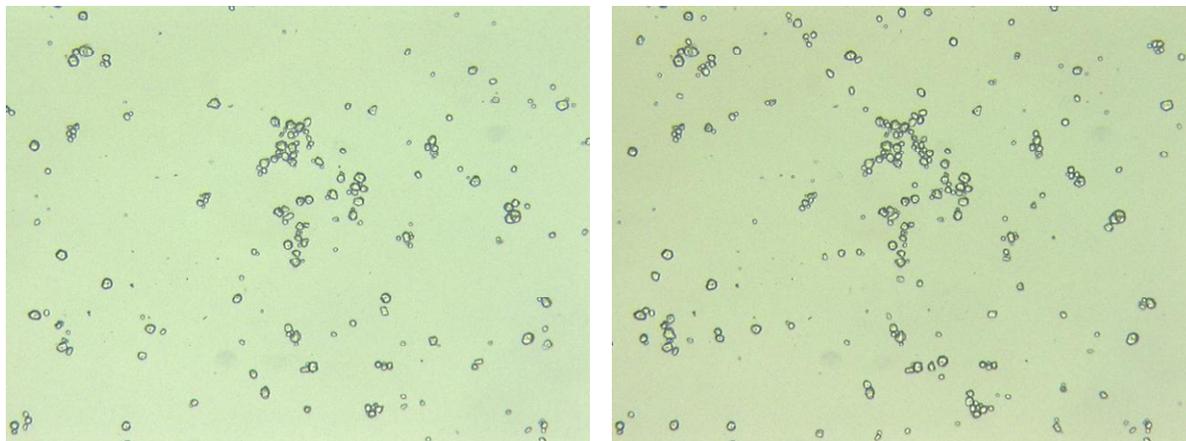


Figure 1: Particle swelling for starch in distilled water before (*left*) and after (*right*) 20 minutes.

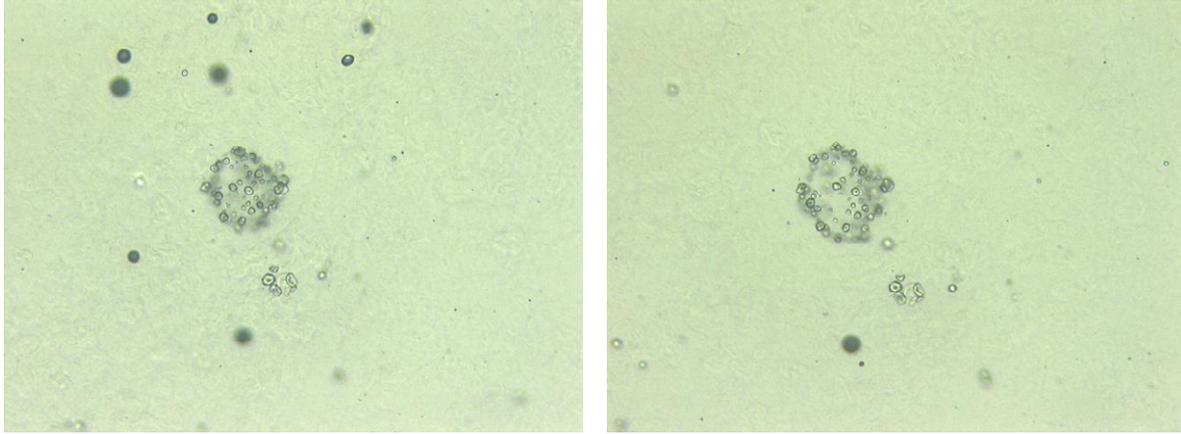


Figure 2: Particle swelling for CMS 270ul in distilled water before (*left*) and after (*right*) 20 minutes.

Table 1: Particle swelling for starch in distilled water after 20 minutes.

Sample	Size at start (μm)	Size after 20 minutes (μm)	% Change
1	0.02035	0.02080	2.21
2	0.01653	0.01653	0.00
3	0.01809	0.01974	9.12
4	0.02106	0.02106	0.00
5	0.02559	0.02569	0.39
6	0.02081	0.02207	6.05
7	0.01875	0.01839	-1.92
Average % Change:			2.27

Table 2: Particle swelling for CMS 270ul in distilled water after 20 minutes.

Sample	Size at start (μm)	Size after 20 minutes (μm)	% Change
1	0.00822	0.00890	8.27
2	0.01250	0.01410	12.80
3	0.02350	0.02650	12.77
4	0.02330	0.02470	6.01
5	0.02138	0.02138	0.00
6	0.01489	0.01653	11.01
7	0.01285	0.01396	8.64
		Average % Change:	8.50