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# DEVELOPMENT AND TESTING OF A MACHINE-COATABLE CHITOSAN COATING APPLIED TO A FLEXIBLE PACKAGING SEALANT

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DEVELOPMENT AND TESTING OF A  
MACHINE-COATABLE CHITOSAN COATING  
APPLIED TO A FLEXIBLE PACKAGING SEALANT

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A Thesis  
Presented to  
the Graduate School of  
Clemson University

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In Partial Fulfillment  
of the Requirements for the Degree  
Master of Science  
Packaging Science

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by  
Steffen Wolfgang Rau  
July 2009

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Accepted by:  
Dr. Duncan O. Darby, Committee Chair  
Dr. Kay Cooksey  
Dr. Ronald Thomas

## ABSTRACT

Chitosan is a naturally derived material that has anti-microbial properties. Studies have shown that chitosan is effective when it is in contact with the surface of the product upon which the antimicrobial effect is desired. This suggests that chitosan should be on the inside surface of the package. In this work, a machine coatable chitosan coating was developed for application to the sealable (LDPE) side of a PET/LDPE lamination. The viscosities and percent solids of the coating were evaluated over 12 days. The coating was tested using manual drawdowns (Mayer rods) and also on a gravure coating line. Adhesion properties and sealability were tested.

Chitosan was dissolved in an acetic acid / water mixture. Wettability against treated LDPE was not achieved with this blend, so ethanol was added. Good gravure coating qualities were noted with solutions that had 5 % chitosan dissolved in water with 8 % acetic acid and 30-35 % ethanol.

Viscosity of the chitosan coatings were initially high and decreased over time. Most of the change occurred over the first 4 days, then incremental changes were noted. Viscosity was also found to be dependent on the relative quantities of chitosan, acetic acid and ethanol.

Coating qualities were measured using a newly developed percent coverage test using iodine staining of the chitosan. To get sufficient wetting, the treatment level of the LDPE had to be a minimum of 52 dyne/cm. Percent coverages of the surfaces coated by hand using Mayer rods were found to be dependent on chitosan percentage in the formula (must be greater than 1.5 %), and on the relative quantities of chitosan, ethanol and acetic acid. The highest percent coverage of the surfaces found using

Mayer rod coating was 97 percent. It is believed that the time lost between coating and drying in the manual Mayer rod process explains the lower percent coverage.

Percent coverages of gravure coated materials ranged between 95 and 100 percent depending on line speed and drying conditions. The highest line speed for which a good percent coverage was achieved was 150 fpm.

Adhesion of the chitosan film to the treated LDPE passed the tape test (ASTM F2252). The chitosan coated film exhibited no sealability for any of the seal conditions.

## **DEDICATION**

Ordinary words cannot convey the immense debt of gratitude I owe to my loving parents, for their consistent encouragement and help rendered throughout this study. I would like to express my gratitude to my brother for his enormous help at home in Germany. I am deeply indebted to my Uncle Norbert and Aunt Christel for supporting my education in the United States of America.

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## CHAPTER ONE: INTRODUCTION

Several studies have been conducted on chitosan in the recent years, to test its potential in products, biomedical, chemical and food industry. Chitosan has been identified as a versatile biopolymer for a broad range of food applications (Shahidi et al. 1999). “The use of chitosan in food applications is particularly promising because of its “biocompatibility and nontoxicity” (Hirano et al., 1990).

Chitosan is an inherently antimicrobial polymer that is a derivative of chitin, the primary component of crustacean shells. Chitosan has been utilized in antimicrobial studies as solution, a coating, and a film. Various chitosan studies demonstrated a range of inhibition against various bacteria in form of solutions and as coatings (Campbell, 2003).

Antimicrobial films and coatings are innovations under the concept of active packaging and have been developed to reduce, inhibit or delay the growth of microorganisms on the surface of food in contact with the packaged product (Appendini and Hotchkiss, 2002).

Flexible packaging materials are a common way to contain food products. This was a \$25.6 billion industry in the United States 2008 (Flexible Packaging Association, 2008). Figure 1 shows the market breakdown.

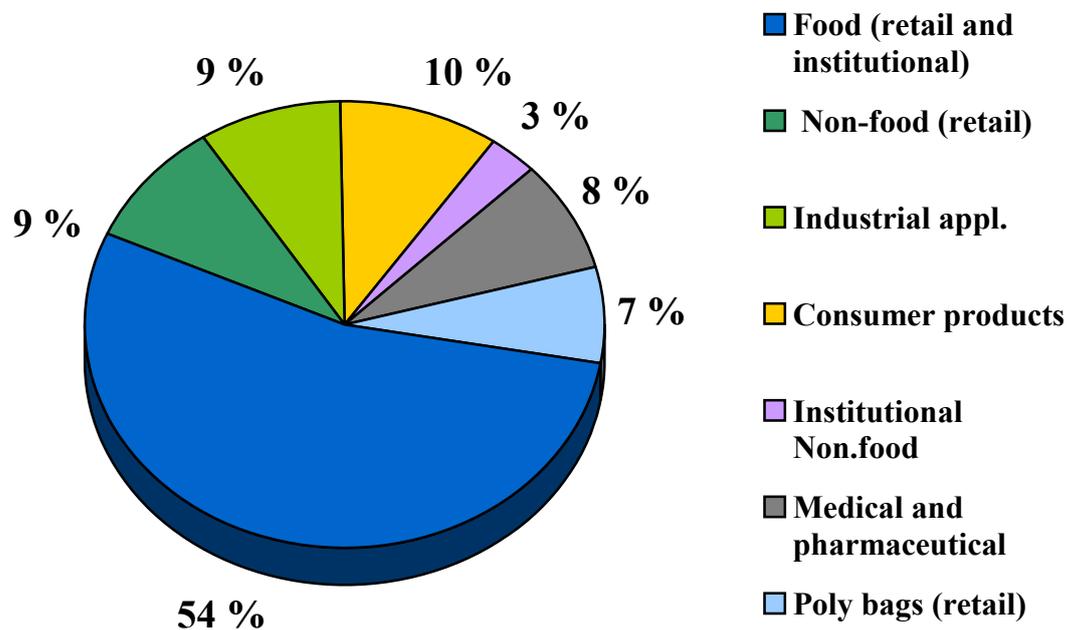


Figure 1: Flexible packaging materials market share 2008 (Adapted from Flexible Packaging Association, 2008)

Antimicrobial food packaging films can be conceptually divided into two categories. The first category includes films into which antimicrobial compounds are incorporated. The second category includes films with antimicrobial coatings (Joerger et al., 2008).

Based on the antimicrobial properties of chitosan, grafting of chitosan onto other polymer surfaces, especially for commodity polymers, is a good way to develop a functional polymer (Pasanphan and Chirachanchai, 2007). Testing of the antimicrobial function of a chitosan coating should include the testing of the inhibition properties, but should also include the technical implementation of coating the substrate and the processing required to do so. Since the coating needs to be on the

inside surface of the package to function properly, testing of the resultant sealability should also be considered.

The antimicrobial properties of chitosan coatings have been tested, and are continuing to be tested by researchers. However, limited research has been conducted on development and testing of chitosan coatings that can be used in commercial applications, or on the effects these coatings may have on the seal properties of flexible packaging.

The thrust of this research was:

1. To develop a chitosan coating that can be applied using commercially available coating processes
2. To characterize that coating's properties with respect to coating quality
3. To use a machine coater to apply the coating to a polyethylene sealant film.
4. To evaluate the coating quality
5. To test the effect of the coating on sealability of the polyethylene.

## **CHAPTER TWO: LITERATURE REVIEW**

### **2. What is packaging?**

For modern cultures, is it close to impossible to exist without packaging. Without a logistics system and a supply chain that includes packaging of goods, it would be impossible to manage cities with millions of people. Packaging enables products to be transported to areas of dense population and major consumption. The product and the package have become so interdependent that one cannot be considered without the other. Packaging, along with better transportation, has made it possible to centralize production facilities into areas where raw materials are concentrated and, therefore, take advantage of large-scale production (Hanlon et al., 1998). Packaging encompasses functions ranging from the purely technical to those that are marketing related in nature. The most commonly accepted technical functions of packaging are to contain, protect, preserve, measure, inform, dispense and store products (Soroka, 1999).

#### **Protective function of packaging**

The protective function of packaging essentially involves protecting the contents from the environment and vice versa. The function of “inward” protection is destined to ensure full retention of the utility value of the packaged goods. The packaging system protects the goods from loss, damage, or theft. The outward protection provided by the packaging must prevent any negative influence on the environment from the goods contained by the package, such as hazardous chemicals, for example. The target of primary importance, in this case, is the protection of human

beings and/or the environment. The packaging must prevent any contamination, damage or other negative impact upon other goods and the environment (GDV, 2008).

### **Food packaging**

Flexible packaging is the second largest packaging segment in the United States, garnering 18 percent of the packaging market. Approximately 54 % of the flexible packaging materials manufactured are used to package food (Flexible Packaging Association, 2008). Traditional food packaging is meant to provide support and protection from external influences. These external influences include, but are not limited to, oxygen, off-odors, light, moisture and microorganisms. Furthermore, packaging provides convenience in food handling. For instance, reclosable pouches can be used for preservation of food quality for an extended time period. The trends in the global market are influenced by different economic trends. For instance, an increase in single-person households in Europe has caused a trend toward smaller package sizes. Also, a change in the shopping behavior of consumers, from a big monthly shopping trip to nearly daily trips exerts impact on packaging decisions. These and other trends in the world have a direct influence on packaging development. In 2008, Dainelli, et al. stated that

“in addition, changes in retailing practices (such as market globalization resulting in longer distribution of food), or consumers way of life (resulting in less time spent shopping fresh food at the market and cooking), present major challenges to the food packaging industry and act as driving forces for the development of new and improved packaging concepts that extend shelf-life while maintaining and monitoring food safety and quality. New food

packaging technologies are developing as a response to consumer demands or industrial production trends towards mildly preserved, fresh, tasty and convenient food products with prolonged shelf-life and controlled quality” (Dainelli et al., 2008, p. 103).

Therefore, there are many different new needs in food packaging which could be addressed by the packaging system.

### **Preservation of food**

The preservation function refers to the extension of food shelf life beyond the natural life of the packaged product or the maintenance of sterility in food. As in all packaging functions, there is a need to define and quantify the preservation function. Walter Soroka (1999) offers a framework for determining the requirement for each condition, as shown in Table 1.

**Table 1: Conditions for preservation and the design requirements (Adapted from Soroka, 1999, p. 26)**

<b>Condition</b>	<b>Quantification or Design Requirement</b>
Oxygen	Determine required barrier level
Volatiles (moisture, CO <sub>2</sub> )	Determine nature and barrier level
Light	Design opaque package
Spoilage	Determine nature/chemistry
Incompatibility	Determine material incompatibilities
Loss of sterility	Determine mechanism
Biological determination	Determine nature
Deterioration over time	Determine required shelf life

There are more possibilities for food spoilage or deterioration which are not mentioned in the table above, such as material incompatibilities or pests.

### **Recent issues with microbial adulteration of food**

Based on data available at the web site of the United States Department of Agriculture Food Safety and Inspection Service (USDA/FSIS), the top five meat product recalls in the United States were:

- 18 million Kg of hot dogs/package meats potentially contaminated with *Listeria monocytogenes*, on December 22, 1998;
- 18 million Kg of various ready-to-eat poultry products potentially contaminated with *Listeria monocytogenes* on January 22, 1999;
- 14 million Kg of fresh and frozen ready-to-eat poultry products potentially contaminated with *Listeria monocytogenes* on October 12, 2002;
- 13 million Kg of ground beef potentially contaminated with *E. coli* O157:H7 on August 12, 1997;
- 9.5 million Kg of beef trimmings and ground beef potentially contaminated with *E. coli* O157:H7 on July 19, 2002 (Sofos, 2008).

### **Food spoilage by microorganism**

Mold, bacteria, and yeast are microorganisms (MO) naturally present in most foods. They may be harmless or beneficial. In some instances they may be deadly. Beyond a certain point, however, all biological activity will lead to spoilage and loss of product (Soroka, 1999). The danger from microorganisms is associated with the

proliferation of the microorganism population to the point of exceeding a limit which is considered to be hazardous. There are two commonly accepted boundaries, the tolerance level and the critical value. These are different by the species and are dependent on the type of food. Some foods have a high amount of microorganisms without the issues of freshness, such as fish and meat.

## **2.1. Shelf life**

Internal biological deterioration describes biological functions that continue even though the food has been harvested. For instance, fruits continue to ripen, and vegetables continue to respire. Fresh meat exhibits many of the processes associated with living tissue, especially after cutting meat into serving or packaging size. Biological deterioration is one of the main effects of microorganisms, so they have an important influence on the shelf life of foods. Many methods of extending shelf life are focused on preventing the growth of microorganisms on perishable products.

### **Extending shelf life**

The type of microorganism and the population of mold, bacteria, and yeast that are naturally present in the food product are important factors. When microorganisms grow beyond a certain population number, they become harmful to humans and the food is deemed spoiled. One way to increase the shelf life is to harm the microorganisms, so they can't grow. Walter Soroka (1999) classifies methods of increasing the shelf life of food into six basic groups.

- Reduced temperature
- Thermal processing
- Water reduction
- Modified atmospheres
- Irradiation
- Chemical preservation

These methods are used alone or in combination to extend the normal biological life of foodstuffs (Soroka, 1999). These methods can be achieved by concentrating ingredients that prevent the development of harmful organisms (fermentation). Another method is to assure that contact with the harmful organism is eliminated and renewed contact is prevented (pasteurization).

Some food additives, like preservatives, prevent the development of harmful organisms because they are lethal to them (curing with salt and nitrite salts). Removing oxygen, which is necessary for many microorganisms also helps prevent spoilage in foods.

Reduced temperature such as refrigeration slows down the growth of some pathogenic microorganisms. This requires management of the logistics and storage chain to prevent an undesirable temperature change (the specific temperature tolerances depend on the product and the microorganism).

Thermal processing refers to the preparation of the food using retorting, hot filling, pasteurization, and some other techniques which reduce the quantity of microorganisms, or completely eliminates them, by applying heat. The food and the packaging must be appropriately suited for these types of procedures.

Yet another technique to prevent microbial growth is to reduce water activity or dehydrate the food (drying). Water is an ingredient necessary to many of the microorganisms. Since most microorganisms need water to grow, the reduction of water activity decreases the possibility for microbial metabolism. The adsorption of water from the surface of food can also decrease the moisture content and reduce possibility of microbial growth on the surfaces of food.

With the techniques of modified atmosphere packaging, (MAP) it is possible to slow down the growth of aerobic and anaerobic organisms and the speed of oxidation reactions to improve the shelf life.

Microorganisms can be killed by irradiation. There are different kinds of irradiation used in sterilizing food products such as electron beam, X-rays and gamma rays. Because the irradiation is also absorbed by the food, there are a many regulations covering this practice. It is illegal in some countries, such as Germany.

Chemical preservatives work in various ways. Acids, such as lactic, acetic, propionic, sorbic, and benzoic acids produce environments which are not friendly to certain microorganisms. Alcohol also has a specific antibacterial effect (Soroka, 1999). The coating of fruit with wax is another chemical preservation technique.

However, chemical methods of food preservation rely on the inclusion of substances in the food, on the surface of the food, or within the package to act in opposition to potential spoilage reactions. The methods require that the substances have no harmful effects while achieving the preservation objective. Their action is directed toward a specific spoilage source, examples of which include molds and oxygen. Ethanol, for example, has inhibitory effects on microbes and is accordingly used on the surfaces of baked goods and fresh vegetables (Brown, 1992)

## **2.2. Active and intelligent packaging**

The key safety objective for traditional materials in contact with foods is to be as inert as possible, i.e., there should be a minimum of interaction between food and packaging (Dainelli, et al., 2008). Therefore, traditional packaging is limited in its ability to extend the shelf-life of food products. An alternative concept is active packaging. It is based on intentional interaction between the components of a package and the food system. These active systems can be placed inside, outside or in between different parts of the primary packaging. The interaction of the systems can be in indirect or direct contact with only the atmosphere surrounding the food, in contact with the food surface, or placed inside the food itself, to obtain a desired outcome. Active packaging concepts can be applied to every kind of packaging field in the industry, but in last few years, many new food packaging concepts have been developed as a response to consumer demands and to industrial production trends (Appendini and Hotchkiss, 2002).

### **Reason for modern view of food packaging**

More and more consumers are demanding and prefer food products that are fresh, tasty and convenient with an extended shelf-life, achieved without the use of synthetic food additives. These changes in consumer preference present major challenges to the food packaging industry and act as driving forces for the development of new and improved packaging concepts. Changes in retail and distribution practices, such as centralization of activities and internationalization of markets also affect the market. They result in increased distribution distances, longer storage times, and consolidation of sets of products with different requirements in the

same distribution system. This dictates a need for new packaging materials, such as active packaging materials, in the industry which can address these new realities (Vermeiren et al., 1999).

### **Types of active packaging**

In recent years, many new active packaging concepts have been developed. Active packaging concepts which interact with environmental components (including sensor interaction) are very important developments. These include substances that absorb gases (such as oxygen or ethylene), substances that control by absorption in MAP, (moisture traps, carbon dioxide absorbers), those which control-release carbon dioxide, ethanol vapor emitters, antioxidants and antimicrobial agents (Brown, 1992). Today sensors and indicator tags can monitor the freshness of the food revealing remaining shelf life or can provide warning when the cold chain has experienced disruptions in temperature control. Valves are commonly used in coffee packaging. This valve allows CO<sub>2</sub> released by the coffee beans or grounds to escape, stabilizing the pressure in a pouch. Also security and safety function have been developed. Color changing indicators in cups or lids have been developed to signal if the packaged has been opened.

### **2.3. Chitosan**

Chitosan is a linear polysaccharide of natural origin and a modified natural carbohydrate polymer derived from chitin. The application potential of chitosan is multidimensional, such as in food and nutrition, biotechnology, material science (like packaging science), drugs and pharmaceuticals (shows potential as a carrier in drug

and gene delivery), agriculture and environmental protection, and recently in gene therapy (Kean et al., 2005; Prashanth and Tharanathan, 2007).

### **Sources of chitosan**

Chitin is the second most abundant natural biopolymer after cellulose (Shahidi et al., 1999). At least 10 gigatons ( $1 \times 10^{13}$  kg) of chitin are synthesized and degraded each year in the biosphere (Jollès and Muzzarelli, 1999). Chitin can be extracted from different sources, such as from crustacean shells (crabs, cuttlefish, shrimp and crayfish) and can also be prepared from squid pens. Another source is from the exoskeleton of insects, either by chemical or microbiological processes. Chitin is also obtained from bacteria, and it can be produced by some fungi (*Aspergillus Niger*, *Mucor rouxii*, *Penicillium notatum*). Crab and shrimp shells, which are waste products from food-processing, are the current source of chitin and chitosan (Hirano, 1999; Devlieghere et al., 2004).

### **Chitin and chitosan characteristics**

The polymorphic forms of chitin differ in packing and polarities of adjacent chains in successive sheets; in the  $\beta$ -form all chains are aligned in parallel manner, whereas in  $\alpha$ -chitin they are antiparallel (Jollès and Muzzarelli, 1999).

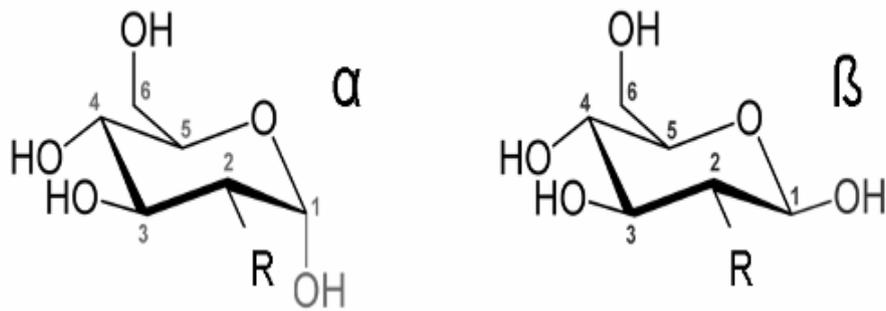


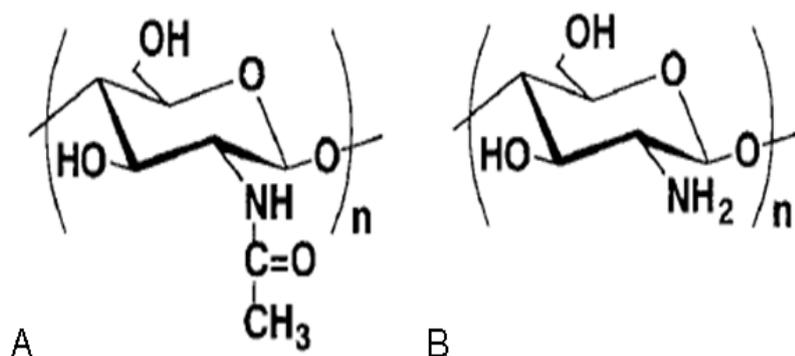
Figure 2: C1 different between  $\alpha$  &  $\beta$  Chitosan (Mills, 2007)

The solubility of chitin is remarkably lower than that of cellulose because of the high crystallinity of chitin, supported by hydrogen bonds mainly through the acetamide group (Jollès and Muzzarelli, 1999). The chemical structure of chitin is similar to that of cellulose with 2-acetamido-2-deoxy- $\beta$ -D-glucose (N-acetylglucosamine) monomers attached via  $\beta$ -(1, 4) linkages. Chitosan is the deacetylated form of chitin, which, unlike chitin, is soluble in acidic solutions (Shahidi et al., 1999).

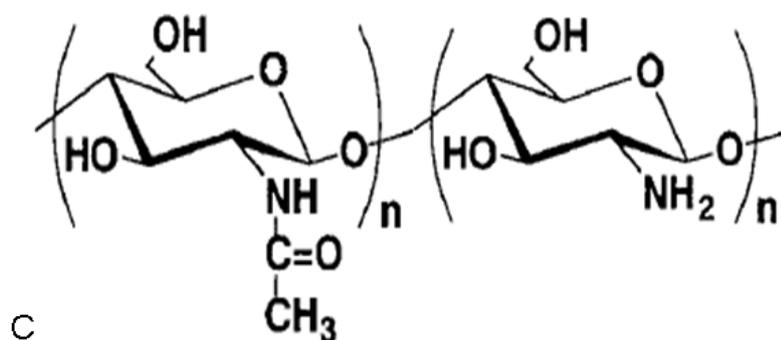
### Chitosan processing

The structural difference between chitosan and chitin are the acetamide groups, chitin has  $\text{NHCOCH}_3$ , whereas chitosan has amine groups,  $\text{NH}_2$ , so chitosan is composed primarily of 2-amino-2-deoxy-D-glucose (glucosamine) (Park, 2001). These groups are changed by treating the isolated chitin with concentrated  $\text{NaOH}$  (40-50 %) at elevated temperatures of  $100^\circ\text{C}$  or higher. The removal of the acetamide groups produces its deacetylated derivative, chitosan (Campbell, 2003). As a result, chitin is deacetylated to chitosan for the purpose of good solubility in some dilute organic acids (Kong et al., 2008). Chitin is a (1, 4)-linked N-acetyl- $\beta$ -D- glucosamine,

and chitosan is an N-deacetylated product of chitin show in Figure 2. Chitin has two hydroxyl groups while chitosan has one amino group and two hydroxyl groups in the repeating hexosaminide residue (Hirano, 1999).



**Figure 3: Chemical structures of chitin (A) and chitosan (B) (Hirano, 1999)**



**Figure 4: Chitosan copolymer by average degree of acetylation characterized (C) (Hirano, 1999)**

### Characteristic of chitosan

Chitosan varies in composition depending on the manufacture. Chitosan could be defined as chitin sufficiently deacetylated to form soluble amine salts. The degree of deacetylation (DA) in commercial chitosan is around 90 %. When the degree of

deacetylation of chitin reaches about 50 %, depending on the origin of the polymer, it becomes soluble in aqueous acidic media and is called chitosan (Rinaudo, 2006). The deacetylation necessary to obtain a soluble product must be 80 % or higher; i.e. the acetyl content of the chitosan product must be < 4 - 4.5 % (as cited in National Toxicology Program,)1999). Chitosan has a mean molecular mass of up to 1 MDa and is charged with cation at lower pH values ( $\text{pH} < 6$ ) due to the protonation of its amino groups (Choi, et. al., 2001).

### **Antimicrobial mechanisms**

The antimicrobial activity of chitosan depends on different factors such as the deacetylation degree, molecular weight, the pH of the medium, the temperature, the presence of several food components, and others (Devlieghere et al., 2004). The exact mechanism of the antimicrobial action of chitin, chitosan and their derivatives is still unknown, but different mechanisms have been reported (Shahidi et al., 1999). Most of research on the antibacterial activities of chitosan and its derivatives against microorganisms was focused on the antimicrobial results and not on the mechanism by which chitosan affects microorganism. Because of the positive charge on the C-2 of the glucosamine monomer below pH 6 level, interaction can occur between the electropositive charged chitosan and the electronegative charges on the cell membranes. This interaction leads to the leakage of intracellular electrolytes and proteinaceous constituents (Devlieghere et al., 2004). However, it also may be possible to dissociate the chitosan molecule in solution, with lower molecular weight (< 5000 kDa), that could bind with DNA and inhibit synthesis of mRNA (Kong et al., 2008).

### **Antimicrobial properties of chitosan**

Commercial availability, relatively low cost and activity against Gram-negative and Gram-positive bacteria (and even yeasts and molds) make chitosan an attractive antimicrobial agent. The variability in molecular weight and degree of deacetylation are important factors that influence antimicrobial activity and are a source of difficulties in comparing different studies (Joerger, 2007).

### **Antimicrobial agent**

Kong (2008) reported that chitosan was known for its antibacterial properties, higher killing rate, and lower toxicity toward mammalian cells, and that it not only possessed a wide inhibition spectrum against Gram-positive and Gram-negative bacteria, but also sterilized some yeasts and moulds.

The antimicrobial contribution of chitosan has been verified many times. In one case, a film composed of chitosan exhibited approximately the same antimicrobial activity against low numbers of *L. monocytogenes* inoculated onto TA medium as did the same film containing stearic or citric acid. Chitosan-based films mostly reduced microbial counts by 3 or less log<sub>10</sub> units. One study with paperboard coated with chitosan reported high log<sub>10</sub> reductions in food and non-food systems (Joerger, 2007).

In another study, the growth of *Escherichia coli* was inhibited in the presence of more than 0.025 % chitosan. Chitosan also inhibited the growth of *Fusarium*, *Alternaria* and *Helminthosporium*. Cationic amino groups of chitosan probably bind to anionic groups of these microorganisms, resulting in growth inhibition (Hirano, 1999).

## **FDA approval**

Even though chitosan is generally nontoxic, the use of this natural material in foods has been limited by regulatory considerations in the United States (CAS# 9012-76-4). Chitin, chitosan and their derivatives are not currently approved for food additives or food packaging materials in the United States. Chitosan is not a food additive in Europe, but it is approved for cosmetics and food processing activities in Europe (Park, 2001).

## **2.4. Flexible packaging**

Food is the largest market for flexible packaging, accounting for more than 57 percent of shipments. Flexible packaging is widespread in nearly all food categories (Butcher, 2007). Flexible packaging is the second largest packaging segment in the United States, garnering 18 percent of the U.S. \$135 billion packaging market (Flexible Packaging Association, 2008).

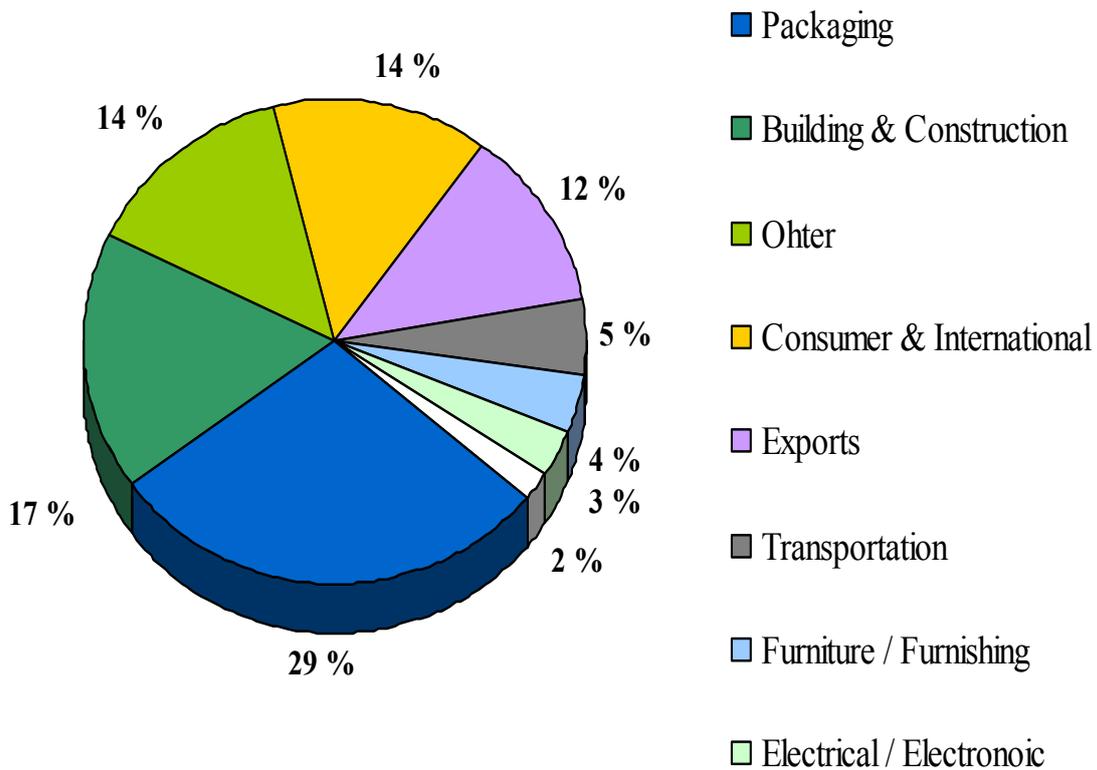


Figure 5: Major North America markets of plastics market share, 2003 in % (Selke et al., 2004)

### Multilayer Laminations

Today's package is designed for the needs of products and manufacturing engineering. In many cases, single layer materials cannot address all these needs. The functional properties of webs used in packaging food can be affected by coating or by laminating. Lamination transforms two or more films or sheets into products with properties that are useful for the needs of the packaged product and line. Needs of the production line include the ability of webs to run smoothly through complex, high speed packaging machines (such as erectors, fillers, closers and sealers) and providing performance for the subsequent processes (such as retort heat in processing foods).

The properties of individual plastic films are optimized by combining them in layers of lamination. Lamination layers are often classified and named according to their functional performance in the structure.

Paper or PET, for example, may be included as a strength layer, to boost stiffness and, resistance to tearing, pinholing and folding. Aluminum foil may act as a barrier layer for exclusion of light, transmission of gases and moisture vapor. A heat-sealable layer (sealant) may be included to provide a seal between two substrates. A printable layer may be included for acceptance of printing or labeling. Protecting the printing surface or providing abrasion resistance to the package surface can be achieved with a protective layer or coating. Combinations of films often provide benefits which reduce total costs lower than those that would occur if mono layered webs were used for same purpose. It has become increasingly common to find multilayered films as food packages and there appears to be no limit to their applications (Brown, 1992).

### **Converting of flexible film packages**

The majority of flexible packages are closed by a sealing method. A seal allows a film to contain a product and protect the product from influences from the environment. The seal closes the package from the environment, allowing the material to perform its barrier function. An example of a package including seals is a pouch. One or more flexible layers are combined using energy and pressure for a fixed time. The polymer is softened and flows across the seal interface.

Eighty-seven billion pouch units are expected to be sold in 2008, which was expected to represent 5 percent of all US packaging demand that year. Value-added

features such as resealability, spouts, and retort and aseptic properties are driving growth (AllBusiness, 2004).

## **2.5. Sealing of flexible films**

The heat sealing of a packaging film is one of the most important properties. The final package integrity is ultimately dependent on the results of the sealing process. Many factors are involved to determining the quality of a heat seal. They can be classified as machine factors and film factors. The machine factors which influence the seal are: energy (often temperature), pressure, dwell time, and the jaw design (Selke et al., 2004). Differing levels of energy are required for differing materials, thicknesses, package types and processing steps, Dwell time should be able to be controlled to fractions of a second and be easily adjustable. Likewise, the pressure between the jaws should also be easily adjustable. These factors will need to be changed when different materials are heat sealed.

Film properties affecting the seal are: gauge, chemistry (such as crystallinity and number of layers being sealed and treatment of the material (e.g. for printing). The density, crystallinity, molecular weight and additives in the resin change the film properties and affect sealing conditions too.

All of these factors tend to interact in a complex way. For example, the amount of heat available may be limited by the capacity of the heating elements, by the rate of heat transfer of the sealing bar and its coating, or the type of product being packaged. Increasing the dwell time (i.e. the time during which heat is applied) will increase the heat available, but this may prove to be economically unfeasible since fewer units will be able to be handled per minute (Robertson, 1998).

## **Seal methods**

The principal differences between the common types of seal devices are in how they supply the energy and/or pressure to the sealant in the seal area. For production lines, the output (pouch per minute) is an important factor. Also, the filling technique and the consistency of product exert influence on the sealing process by contaminating the seal area and blocking the contact between the surfaces to be sealed. This problem can be solved in different ways, such as with ultrasonic sealing systems.

Conductance sealers (also named conductive sealer or heated-tooling-sealing) are the most common type of heat sealers in commercial use. These systems typically consist of two metal jaws, one or both of which are electrically heated.

There are other means of supplying heat to the seal. In impulse-sealing, heat is supplied by a wire or ribbon. In this case, the energy to the seal area is provided by sending an electrical impulse into a resistant wire or ribbon.

In dielectric sealing, energy is supplied by an alternating electric field which heats up polar sealants. Induction sealing (RF) also uses an alternating field, but by induction, so this method requires a metal in the sealing area to heat. Laser sealing transfers the heat when the sealing area absorbs heat from the laser light frequency. Ultrasonic sealing supplies heat by friction of the sealant due to ultrasonic vibrations. Cold sealing is the alternative for heat sensitive products. The seal is achieved without heat by adding mechanical pressure to make the seal between two layers of cold seal coatings.

### **Different seal bars**

The most common heat seal bar is flat type, but there are different types available. Patterned, serrated or embossed seal bars give the seals extra strength. Serrated jaws can be used to ensure that the two webs are stretched into intimate contact with pressure, and they can also improve appearance. Many seal bars are covered by a non-stick coating or layer of mostly Teflon® (poly (tetrafluoroethylene)) impregnated cloth or tape. These are used to prevent sticking of the packaging materials to the jaws and to prevent buildup and damage to the jaws.

### **Sealing as a pouch making process**

A pouch is generally a folded sheet/web sealed at three or more sides. There are a lot of different types of pouches in use. The seals are important features of all pouches. Therefore, the influence of a film coating which may affect the sealability is also important to pouch manufacturers. Pouches can be made in a variety of styles. The majority can be classified into four groups e.g. pillow pouches, three-side seal pouches, four-side seal pouches and stand-up pouches. Some pouches are required to resist the change of pressure variations such as those that occur in a retort process or in transport by aircraft.

### **Testing method for seals (ASTM F 88-05)**

The strength of the heat seal is often determined by measuring the force required to pull apart the pieces of film which have been sealed together in a dynamic load test. The ASTM standard F88-05 for the testing of heat seals describes the procedures to be followed, thus enabling useful comparisons to be made between the

seal strength of different materials and/or different sealing methods (Robertson, 1998).

## 2.6. Materials in flexible packaging

Thermoplastics make up the greatest share of plastics usage in food packaging because they can be rapidly formed economically into any shape needed to fulfill the package function, and are especially amenable to recycling and waste-to-energy conversion. Thermosets are also used in closures and trays rather than flexible packaging structures. The principal families of thermoplastics in food packaging are the polyolefins, styrenics, polyesters, and vinyls (Brown, 1992).

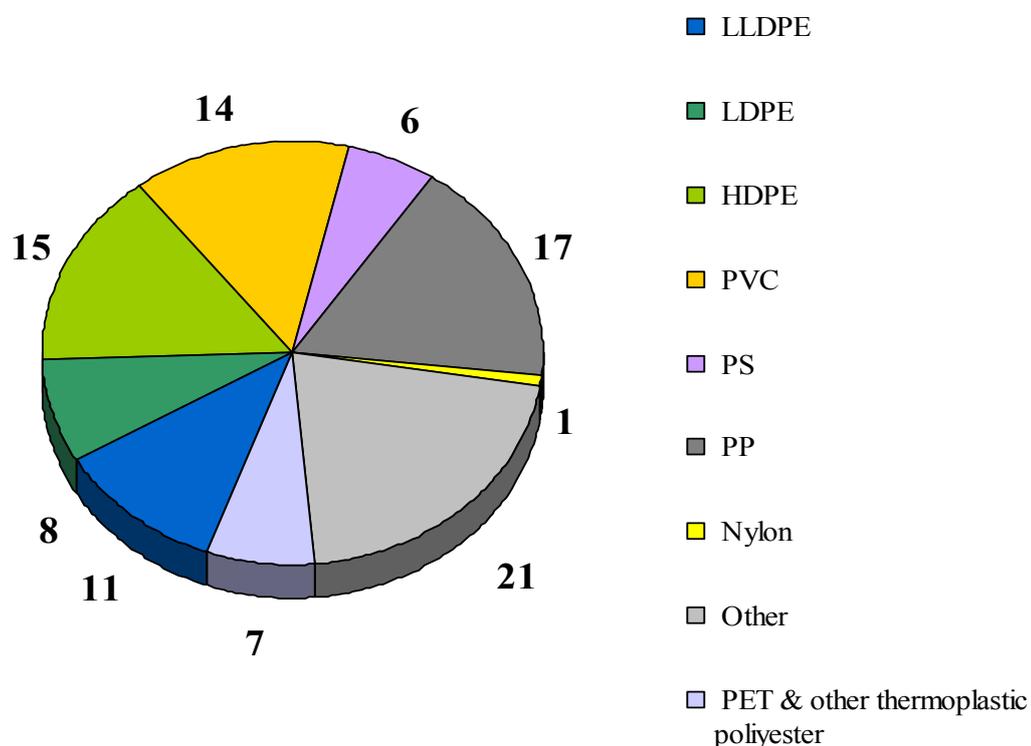


Figure 6: Types of plastics use in North America 2003, in Million tons (Selke et al., 2004)

## **Polyolefins**

Polyethylene, polypropylene, and olefinic copolymers are among the most widely used food packaging plastics, finding use as films, moldings, coatings, adhesives and closures. A great variety of types and grades is available, growing steadily as manufacturers find new compositions to satisfy specific needs (Brown, 1992). Typical polyolefins are polyethylene (PE) and polypropylene (PP).

## **Polyesters**

Polyesters represent a large class of versatile plastics widely used in food and beverage packaging, and are especially known for their prominence in the carbonated beverage container market. Members of the class found in food uses include several forms of polyethylene terephthalate (PET) and polycarbonates (Brown, 1992).

## **Substrate (web)**

Substrate is a term used in material science to describe the base material on which processing is conducted to produce a new film or layers of material such as deposited coatings. Coating processes involve the application of a thin film of functional material to a substrate, such as paper, polymers, metal, fabric or other textile.

## **Heat seal layer**

Low Density Polyethylene (LDPE) is the most common and economical general-purpose heat-sealing medium. The flexibility, softness, moisture protection, toughness, chemical resistance, light weight, and low cost of LDPE are its most

outstanding attributes. LDPE films are in wide use for a great range of products. LDPE is useful for wrappers and bags for products ranging from fresh produce, baked goods, and frozen foods to chemicals, hardware, and garments. LDPE is readily heat sealable by hot-wire cut-off and bar sealers, (Hanlon, et al., 1998). The heat seal temperature for LDPE is around 230°F (Selke et al., 2004). The sealers are often protected in some manner with Teflon® because LDPE tends to stick in the melting process to the jaws.

However, there are some disadvantages to LDPE. It is not practical for many rigid containers, and in flexible packages it can be difficult to open because of the way the film stretches without tearing (Hanlon et al., 1998). When opening a seal of a lamination of LDPE/PET, it can be seen that the PET layer breaks first, because the elongation of LDPE is higher. Furthermore, PE's are not recommended for oily products, which may migrate through the PE. This can cause delamination and/or make the outside sticky to the touch. PE is also a poor barrier to gases, and has a strong tendency to develop a static charge that attracts dust, which can be unsightly on a retail shelf (Hanlon et al., 1998).

There are now dozens of different grades of LDPE. These may be formulated with other additives or copolymers to improve selected adhesive qualities (Soroka, 1999). Metallocene catalysts (abbreviated mPE) are said to create even better strength and toughness, sealability, barrier properties, and clarity. But metallocene polyethylene (mPE) also is more expensive at this time and still can be difficult to process (Hanlon et al., 1998).

## **FDA Approval**

All PE's are acceptable for packaging food and drug products, provided that no unacceptable additives or mold-release agents are used in the manufacturing processes (Hanlon et al., 1998).

## **mPE**

An improvement in polyolefin film properties has resulted from a family of catalysts called "metallocenes", which are said to be a mixture of such metal as zirconium and titanium with oligomeric alumoxane co catalysts. Like their predecessors, the metallocenes have many reactive sites (Hanlon et al., 1998).

A study about effect of polyethylene blends on heat sealing properties between mPE, LDPE and mPE/LDPE by Shih et al. (1998) found that films made with mPE blend had better sealing properties at lower sealing temperatures among the three films tested. The heat sealing properties are strongly influenced by morphology. An mPE/LDPE film with smaller crystal sizes can be melted quickly. Smaller crystal sizes with lower melting points induce a rapid and partial melting at bonding temperatures. Film made of mPE/LDPE blends had also the highest hot tack and seal strength as well as lower haze and higher light transmission. The seal strength depends on bond formation and strength, which explains why mPE/LDPE film had high tack and heat seal strength compare to mPE or LDPE (Shih et al., 1998).

## **Strength layer**

Polyethylene terephthalate (PET) is a high-performance film. About 7 million tons were used in U.S. packaging in 2003 (Selke et al., 2004). PET has remarkable

tensile strength (over  $7.0-10.5 \times 10^3$  psi or 48.2-72.3 mPa) and a 30-3000 percent elongation over a wide temperature range, giving it good impact strength. It can be used for boil-in-bag and bake-in foods because of its high melt point and high crystallinity. It has good dimensional stability, toughness, clarity, stiffness, and some barrier properties. Although chemically resistant to weak acids, bases, and most solvents, PET has only moderate barrier for gases like oxygen. Usually PET contains no plasticizers.

Oriented 48 gauge (12.3  $\mu\text{m}$ ) PET films are common and maintain an excellent tensile strength. Impact resistance is good, but tear and puncture resistance are not as good as that of the softer films. Uncoated PET film is not heat-sealable at reasonable temperatures. Hot-wire seals are possible, but tend to be weak and not leakproof. Orientation enhances all of PET's properties. Biaxial oriented PET creates a very stable film and lamination or coating can be used to add to the barrier and sealability properties (Selke et al., 2004).

### **Lamination**

The major processes used to enhance certain properties of pre-made films are orientation, coating, and lamination. These processes may be incorporated into the main manufacturing processes of casting, extruding, and calendaring or they may be stand-alone. Laminations have been defined as combinations of two or more polymer films (Harper and Petrie, 2003). Most of the layers are polymer, but a metal foil or paper web may be used as substrates too (Abdel-Bary, 2003). An individual polymer cannot meet all requirements for every application, (like production speed, sealing, printing, storage and handling together) so multilayer materials may be necessary.

These can be prepared by extrusion of further layers on to existing films or adhering existing films together. This process is called lamination.

### **The purpose of a lamination**

The borders between conventional methods of laminating are blurred. Five basic methods are divided between two broad categories, adhesive and extrusion lamination. There are a number of different methods for doing the combining, as well. Adhesive lamination depends on the use of adhesives to hold the substrates together into a single structure. The adhesives themselves can be solvent or water-based.

In the “wet-bonding” process, a water-based adhesive is applied to one of the primary substrates and the secondary substrate is joined. The bonding process is complete when the water evaporates from the adhesive. For evaporation, at least one substrate must be permeable to allow the water to escape.

In “dry-bonding“, a water-based or solvent-based adhesive is applied to a primary substrate, the coated web is dried to remove the solvent and then combined with a second substrate in the laminator by pressure and thermal energy.

Hot-melt lamination process uses a purely solid hot-melt adhesive. This adhesive is heated until it becomes fluid, and applied to the substrates, joining them as it cools down.

Thermoplastic extrusion laminating is like hot-melt laminating, but in extrusion laminating, a polymer such as polyethylene is melted in an extruder, whereas in hot-melt lamination the plastic melts at relatively low temperatures and is melted in a heated tank.

In thermal laminating, heat activates a heat-seal coating on one web, which then joins with the second web. Sometimes combinations of these methods are used, too (Miller, 1994, Selke, 1997).

A basic requirement for a lamination is a good bond between the materials, by reaction between the materials and the adhesive. It is important to create surface tension by setting up electrostatic forces, which generate surface energy. The complete “wetting” of the surface to create flawless adhesive laminations is particularly important in the union of such non-polar materials as the polyolefins (Hanlon et al., 1998).

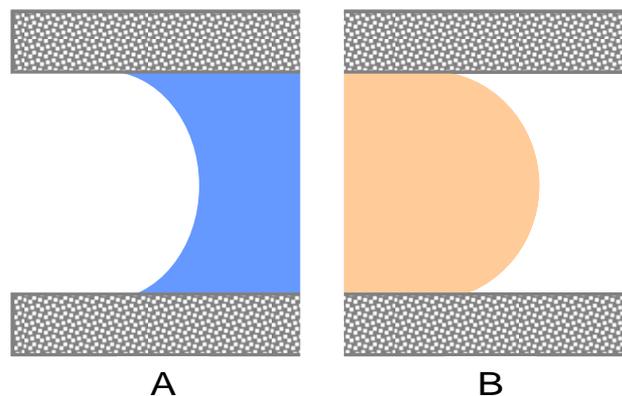
## **2.7. Wettability**

There are various theories of bonding systems, and there are multiple mechanisms of bonding (Pizzi and Mittal, 2003). In laminating, adhesives may utilize these different types of bonding. A mechanical bond (mechanical interlocking) can exist between such materials as paper into which the adhesive can penetrate into pores. Bonding to materials that cannot mechanically bond may require the use of chemical bonding. A chemical bond can occur by reaction between the materials and the adhesive, creating a surface tension by setting up electrostatic forces, which generate surface energy. The ability of adhesives, inks, and coatings to adhere to the surface of a substrate is not guaranteed. It depends on compatibility issues such as polarity and also on surface energy of the substrate and the surface tension of the liquid (adhesive, ink, or coating). A surface is said to wet when the liquid distributes upon it, instead of forming beads.

## Adhesion and cohesion

Surface tension is an attraction property of the surface of a liquid. It is what causes the surface portion of liquid to be attracted to another surface, such as that of another portion of liquid. Liquids generally have the tendency to minimize their surface. The forces of intermolecular attraction acting within a material are termed cohesive forces and attempt to decrease the surface area of a liquid.

However, there is also interaction with the environment in which the liquid exists. Attractions to surfaces are called the adhesive force. In a lamination process, adhesives are used to join two substrates. The adhesion forces develop at the interface between the substrates (adherend) and the adhesive. The cohesive forces in an adhesive depend upon its molecular and physical structure, and are not influenced by the interfacial force. For good wetting and bonding, the adhesive force must be greater than the cohesive force. In this case, the adhesive builds a concave meniscus as opposed to a convex meniscus if the cohesive forces are higher than the adhesive forces (Figure 7).



**Figure 7: Concave meniscus (A) and convex meniscus (B)**

The strength of the bonded structure depends on the surface tension of both substrate and adhesive (Selke et al., 2004). To obtain maximum adhesion, the adhesive bond strength between the adhesive and adherend should be greater than the cohesive bond strength of the adhesive.

### **Surface tension– solid (substrate)**

Some substrates have relatively low surface energies (e.g. nonpolar polyolefins are around 32 dynes/cm). For adequate bonding, the surface energy of the substrates, reflected in its surface tension, must be greater than the surface energy of the coating, ink, or adhesive. The dyne level of the substrates must be usually about 10 dyne/cm higher than the surface tension of the wetting liquid (Soroka, 1999). Substrates with a low surface tension require a surface modification before successful coating, printing or laminating is possible. If the surface is not conducive to laminating, the adhesive releases from this layer. Surface modifications to increase the probability of a satisfactory bond to other substances may be accomplished by corona discharge, gas plasma treatment, etching with chemicals, or by gas flame treatment (Brown, 1992).

### **Surface energy - liquid**

To ensure spreading and wetting, the fluid coating should have a surface tension higher than the critical surface tension of the substrate. If a liquid is placed on a surface, the liquid's cohesive forces work to reduce the surface area, while the adhesive forces to the surface work to spread the liquid. At some droplet size, the two forces are in balance. For a liquid, the surface tension and the surface energy density

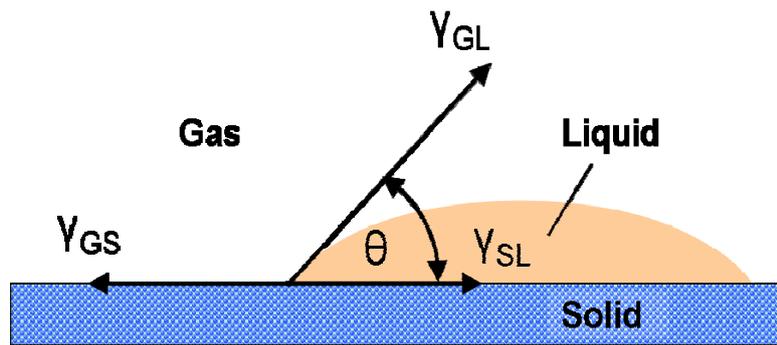
are identical. The surface tension unit of liquids is dyne/cm and the reference is measured against air.

### **Viscosity influence**

The viscosity of the adhesive (or other coating) is another factor for the wettability of the surface. The viscosity must be low enough to allow the easy and homogeneous application of it onto the adherend surface. The adhesive viscosity must be also low enough to be able to fill completely any pores and surface irregularities of the substrate adherend at the moment of application, for the purpose of producing a homogeneous coating of the adhesive (Selke et al., 2004).

### **Measurement of surface tension or surface energy**

Surface tensions can be defined by measuring the angle between a drop of liquid with a known surface energy and the test surface (solid) with an unknown surface tension. Three vectors  $[\gamma]$  represented interfacial energies, the solid-liquid interface represent by  $\gamma_{SL}$  vector, the gas-liquid interface represent by  $\gamma_{GL}$ , and vector named  $\gamma_{GS}$  represents the gas solid interface. The angle  $\theta$  between  $\gamma_{SL}$  and  $\gamma_{GL}$  vectors is named contact angle, show in Figure 8 (Brown, 1992).



**Figure 8: Wetting/Contact angle and interface vector**

A contact angle goniometer is used to measure the angle occurring between a liquid drop and the solid surface. The units for the surface tensions are dynes per centimeter. Another common method is to use a series of solutions of known dyne levels and observe whether they “wet out” or “bead up” on the surface.

### **Measuring with dyne pens**

ASTM D 2578, Standard Test Method for Wetting Tension of Polyethylene and Polypropylene Films, is a common test method for testing the surface tensions using preparation of known dyne solutions. This solution is made of mixtures of formamide, ethyl Cellosolve and a dye (to make the mixture visible on film surfaces). The balance of formamide and ethyl Cellosolve gives the solution a range between 30 dyne/cm to 60 dyne/cm. These solutions are applied to the test surface of the substrate. Whether the solution wets the surface or not is determined by the presence of beading or wetting out. Varying solutions are applied to the test surface in increasing dyne increments until the solution that forms an even film (does not bead up for at least two seconds) is found. The solution defines the “dyne level” (surface tension in dyne/cm) of that material (Soroka, 1999).

### **Surface treatment (film)**

There are several reasons to treat the surface of a material. The term surface treatment includes all types of alterations to the surface characteristic of a material, including cleaning. Surface treatment is often used to increase the surface tension of polymer substrate. Several polymer substrates require surface preparation to enable successful coating, printing or laminating.

Polyolefins such as polyethylene and polypropylene are basically nonpolar. They have relatively low surface energies and must be treated to increase the probability of them adhering to other substances, such as adhesives. The surface tension of the substrate polymer must be greater than the surface energy of coatings to get an acceptable bond to those coatings (Brown, 1992; Soroka, 1999; Hanlon et al., 1998).

Corona discharge, gas flame treatment, gas plasma treatment and priming are common types of surface treatments to increase the surface energy of the film. Most of them use some highly reactive atmosphere to impart some degree of oxidation to the surface of the polymer. Corona discharge treatment uses electrically ionized air as the reactive atmosphere above the film surface. In the ionized air, some of the oxygen oxidizes the surface of the film. The polar groups left by these processes provide stronger secondary bonding characteristics, improving the adhesion of inks, coatings and adhesives (Selke et al., 2004).

### **Negative influence of the treatment**

While treatments successfully increase the surface tension of the polymer facilitating the bond, it may also inhibit the sealability and change the coefficient of

friction (COF) as well. High levels of treatment can often lead to blocking of the film in the roll. Blocking means that the layers stick together, interfering with the unwinding process. Films with high treatment levels are also more likely to lose treatment level over time than films with moderate or low treatment.

### **Loss of treatment**

Treated surfaces revert slowly back to their original surface tension over time. The rate at which reversal takes place is variable and depends on many factors. The effectiveness of corona discharge treatment dissipates somewhat over time, faster than with flame treatment. The treatment starts to decrease with the first contact between the treated and untreated side by the film winding. Every wind or contact with rollers can produce losses of treatment level. Therefore, it is common to have both the initial corona treatment, and an additional treatment on the conversion line immediately before the coating or laminating (Selke et al., 2004).

### **2.8. Coating**

In the lamination process the adhesive is coated on the primary web. However, a coating can be generalized to mean any covering that is applied to a material to protect it, change its appearance or change its properties. In flexible packaging, coating is the process of applying one or more layers of a fluid or melt to the surface of a substrate with the goal of improving the performance of webs such as paper and plastic films. The surface of bottles and jars are also coated, changing the structure of the surface to lower the crack property (Brown, 1992).

## **Performance properties of web coating**

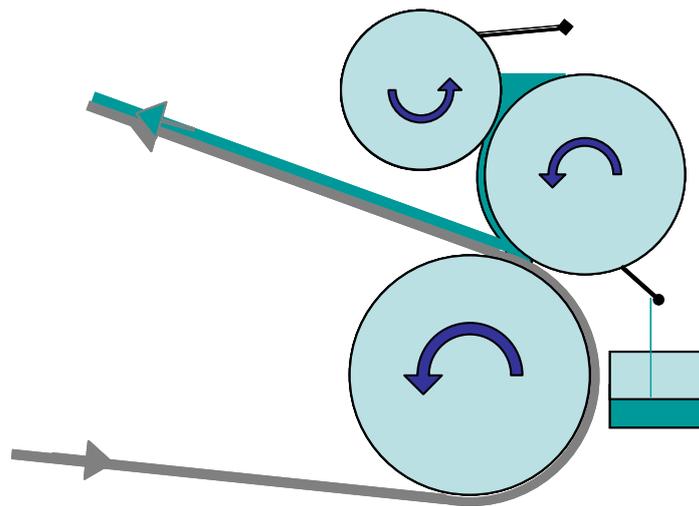
Some examples of the possible uses of coatings are to protect the web surface or the printing on the web, surface properties modification with a primer for higher adhesion or to get a better ink reception on the substrate. Some coatings reduce the electrostatic properties of the surface by a conductive anti-static agent. Sealants may also be applied as a coating (e.g. cold seal coatings) to change the sealing ability of the web. It is also possible to change the permeability of the structure using a barrier coating. A coating can also include agents to increase the UV absorption. Antimicrobials coatings, like chitosan, can be used for reducing and/or inhibiting the growth of microorganisms.

## **Coating methods**

Coatings used for the manufacture of flexible food packaging materials are usually applied to a moving web of material (Brown, 1992). There are many different systems in use, including roller coating, spray, immersion (dip) coating, metallizing, knife-over-roll, air-knife, extrusion coating and others. Figure 9 show a type of a roller coater, specifically a reverse roll coater.

One method by which a coating system can be classified is by the application and metering systems used. Application systems transfer the coating to the substrate. Metering systems control the amount of coating. Coating weights are measured in mass per area, such as pounds per ream (lb/ream) or grams per square meter (gsm). Coatings can be applied and metered in two steps (such as in Mayer rod coating), or in one step, (such as the direct gravure roll coating). The method of applying a coating is determined somewhat by the coating viscosity. For example, air knife, blade, and rod

coaters will not handle very viscous materials, but perform well with emulsions, clays, and other pigments (Hanlon et al., 1998). The coating must be of correct viscosity to have appropriate flow characteristics for process.



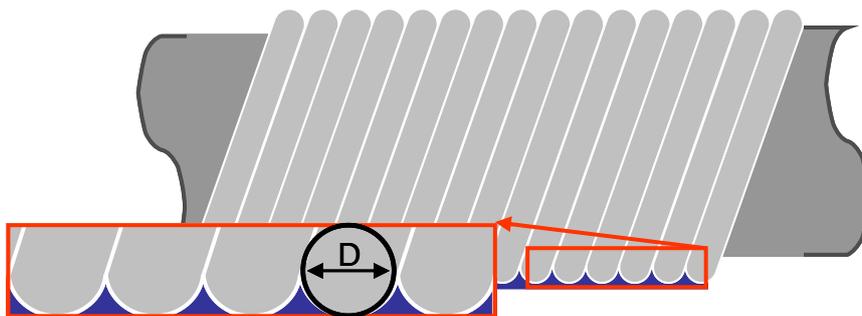
**Figure 9: Principle of a reverse roll coater**

A commonly used system for applying adhesive or a coating with intermediate viscosities is the roll coating system. Roll coating systems typically meter the coating before or during the application to the web. The roll coater is used in various forms to control the coating amount, such as multiple roll coating and gravure roll with doctor blade. Some systems apply the coating directly or with a separate application roll. In roll coating, the coating material is applied by contact between the moving web and rotating application roll (applicator). The applicator roll picks up the coating material from a source, either another roll or a bath, and transfers it to the substrate web (Brown, 1992). Rollers can be run in the same direction (nip coater or forward roll coater) as the web or in reverse (reverse roll coater) to change coating thicknesses and characteristics.

## Mayer or wire wound rod

One of the oldest ways to coat non-stretchy webs is to use a rod wrapped in wire to distribute the coating evenly over the web (Brown, 1992). Mayer rod coating is one of the most popular manual coating methods, and is also used in automated machine coaters. The Mayer rod is a stainless steel rod. The common Mayer rod is wound tightly with a stainless steel wire of a given diameter, shown in Figure 10. Different wire sizes provide a range of coating volume, and there are also different rod versions such as gapped and smooth type available. Mayer rods are typically labeled with a numeral punch. These numbers are related to the diameter of the winding wire.

The rod is used to meter off the excess coating solution and control the coating volume. The wet thickness after metering is controlled by the diameter of the wire used to wind the roll and is around 0.1 times the wire diameter (Brown-1992).



**Figure 10: Metering is controlled by the diameter (D) of the wire**

The normal force of the Mayer rod in the direction of the web surface (pressure against the web) and the coating speed both have influence on the coating weight. To manually apply coatings with the Mayer rods, the sheet to be coated is

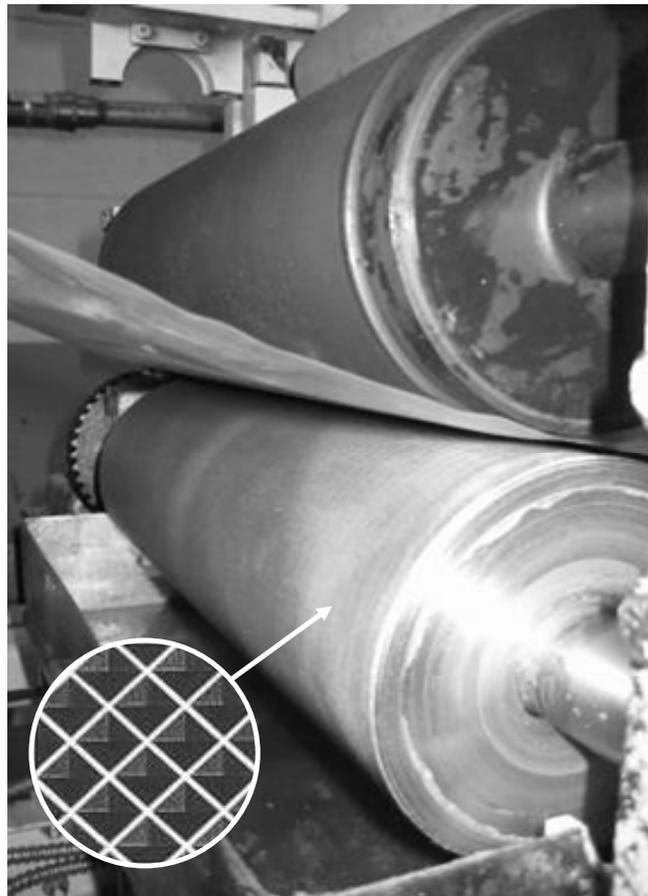
placed on a smooth surface, like a glass sheet. The Mayer rod is placed on the top of the sheet and coating solution added in front of the rod in the coating direction. The coating solution is “drawn down” the sheet with the rod to give the desired coating thickness. Typical operating conditions for Mayer rods are viscosities between 10-1000 centipoises (cP), possible thicknesses range from 4-80 microns (0.25-9 mil) and the coating accuracy is approximately 10 % (Cohen, 2005).

### **Gravure coating**

Gravure coating is the one of most uniform and reproducible methods for applying a coating to a moving web material. This system uses the adhesion between the liquid and the web to transfer the coating. The gravure roll is a metal roll covered with engraved cells. Gravure roll coating applies a predetermined amount of coating solution from these engraved cells. The volume of the cells is part of the metering system of gravure coating. The coating process relies on an engraved roller running in a coating pan. Here the coating solution fills the engraved dots or lines of the roller surface. The excess coating on the roller is wiped off by a metal blade (doctor blade). The coating is then deposited onto the substrate as it passes the nip between the gravure roll (engraved cylinder) and the impression roll. In the nip, the coating is pulled out of the cell and deposited on the substrate.

Many types of coating may be applied by gravure roll systems. The method is not specific to any substrates and works well with plastic films, foils and papers. The gravure roll coating process is thought to be independent of web tension, thickness variation and the line speed of the web. A given gravure roll can bring only one fixed amount of coating to the substrate. An engraved roll typically has a uniform pattern

over its entire face or lines. Coating can be applied in different patterns and coatings of different properties can be adjusted to perform as desired. The thicknesses of the coatings are typically 3 to 25  $\mu\text{m}$ . An example of the face of a design of gravure rolls is depicted in Figure 11. A great variety of designs is possible to accommodate the different thicknesses required and the different viscosities of coatings. The coating interfacial tension to the substrate and gravure roll determines how the coating divides from the roll to the substrate and coating formulation and impression roll hardness (Brown, 1992). The applied weight is determined by the number of patterns (dots) or lines and the amount of solids in the coating. The unit for a gravure roll is the number of or lines per inch (Quad [Q]).



**Figure 11: Sample for the surface (dpi) of a gravure roll**

## **2.9. Viscosity**

Viscosity can be defined as resistance to flow. Higher viscosity means more resistance to flow of fluids such as gases and liquids. Viscosity is related to shear stress and the rate of shear in the fluid. Two kinds of viscosity are measured in this study, the dynamic and kinematic viscosity, depending on the range and nature of the equipment used. The dynamic viscosity measures a fluid's resistance to flow, without considering the influence of gravity. The kinematic viscosity includes the influence of gravity to measure viscosity.

### **Influence of the viscosity of a coating**

The viscosity is one of the important factors for a coating. If the viscosity is too low, the coating can move on the substrate (into drops, etc.) before it dries. Otherwise, if the viscosity is too high, the flow may be too low and the coating may not transfer to the substrate in an effective manner. Liquids with a high viscosity bead up (build drops) more slowly than those with a low viscosity.

### **Viscosity mechanism of chitosan solutions**

Shear stress and viscosity of chitosan solutions increases with increasing chitosan concentration. Shear-thinning behavior has been observed for large chitosan concentrations. In general, the motion of individual chains gets restricted with an increasing number of entanglements as the polymer concentration increases. The chains, which are disentangled by hydrodynamic forces, cannot form new entanglements because of the lack of mobility in a highly concentrated solution.

Disentanglement becomes dominant at high shear rates and the non-Newtonian behavior becomes more pronounced (Cho et al., 2005).

However, the viscosity of chitosan solutions has different viscosity change rates with different acids and solvents. Viscosity of chitosan solutions also depends on solvent evaporation. over time, as reported by Uragami and Tokura (2006).

### **Zahn cup viscosity measurement**

Zahn cups measure the kinematic viscosity of the liquids, because these instruments use the gravity to flow. The Zahn cup is a common viscosity measurement system in the coating, laminating and printing industries. The accuracy is good enough for the production, and the cups are calibrated to within a 3 % tolerance.

The time between when the filled cup is removed from the coating pool and the first break of the liquid stream is the measured (efflux time [ $t_{\text{flux}}$ ] in seconds). This efflux time can be converted to kinematic viscosities in centistokes (cSt). The range to measure the viscosity with the Zahn cup is fixed for each cup and is somewhat limited. To convert the efflux time to the viscosity unit (centistokes), different equations are used for different Zahn cups. Equations for no. 1 and 2 Zahn cups are shown in the Material and Methods chapter

### **Brookfield viscometer viscosity measurement**

Higher viscosities than around 240 cSt are out of the range of the Zahn cup 2. For high viscosity levels, a Brookfield rotation viscometer can be used. The Brookfield viscometer determines the required torque for rotating a spindle in a fluid

at a known speed. The force exerted on the cylinder (torque) is measured, which can be converted to a shear stress. The speed of rotation determines the shear rate. These two factors can be combined to determine the viscosity of the fluid.

## **2.10. The drying process**

Coatings which contain a solvent require a drying process. The drying process evaporates the solvent from a coating in a controlled way. The most common procedure for drying webs is to apply heated air to the web surface. The solvent evaporates from the coated surface into the air and solvent from inside the coating moves to the surface of the coating to evaporate. Normally a dryer unit includes a hot-air blower with nozzles and an evacuation blower, to remove the solvent-laden air. The adjustable parameters for a dryer include the air temperature and the air pressure. The drying process is related to the line speed, which determines the residence time of the web in the dryer (drying time). A web speed increase decreases the drying time for the coating.

Drying depends on two principles, heat transfer and mass transfer. Heat transfer is the transfer of energy from the warm air to the wet coating layer and the mass transfer is the process to release solvent or water (diluent) from the coating by evaporation into the surrounding air. Dryers for commercial coating lines commonly have more than one dryer in series. The temperature difference between these dryer “zones” are important, the first dryer temperature is often lower than the second one to prevent “skinning” of the coating. Skinning occurs when the coating is dry on the surface, but still wet below the surface.

## The process of a machine run

Many commercial machine lines do both coating and laminating. The main difference is that a coating system doesn't use a secondary web. The process of a lamination includes the operations of winding (unwinding and rewinding), coating (applicator), drying (oven) and laminating (nip), as shown in Figure 12.

The winding systems, tension transducers and the nips measure and control the tension of the web. The web is unwound (Primary unwind) and transported into the adhesive application station (Coater). Here, the coating is applied to the web by a gravure roll. An oven dries the wet coating on the web. A secondary web (secondary unwind) meets the adhesive coated web in the lamination nip of two rolls. The nip roll pushes the adhesive side to the other web surface. The nip can be heated and the pressure is adjustable. In the nip the adhesive between both webs bond them to one. This finished lamination is then wound into a finished roll (Rewind).

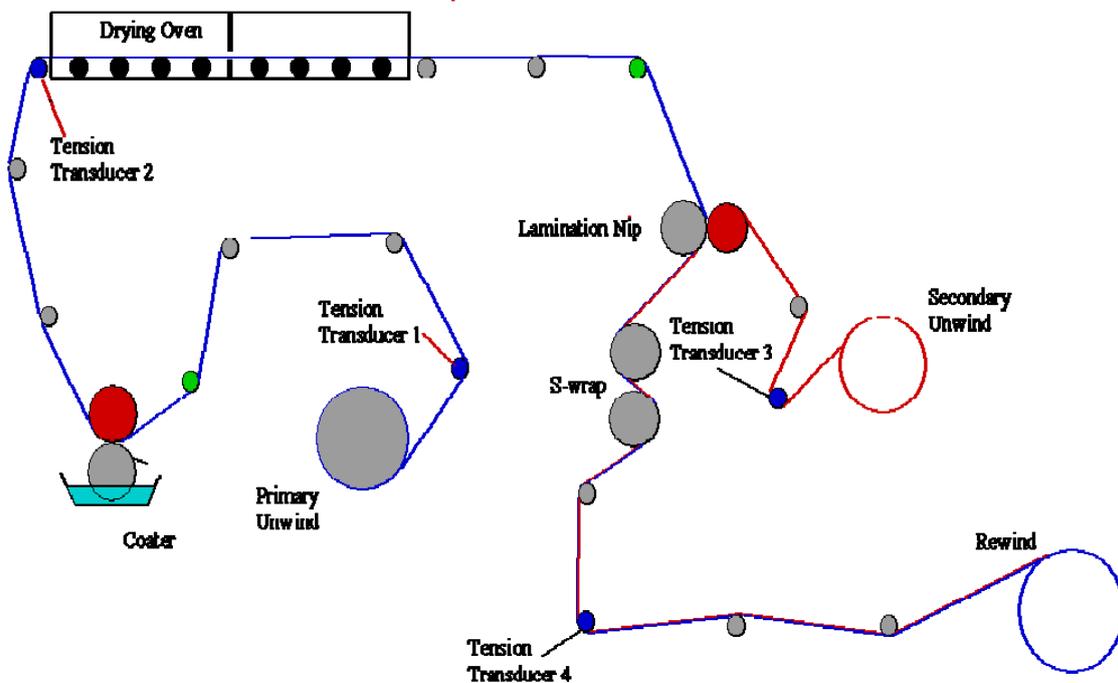


Figure 12: Lamination and coating machine process (Source: Darby, 2008)

## MATERIALS AND METHODS

### 3. Material

#### Chitosan

The chitosan used for this work was provided by the manufacturer Shanghai Freeman. The country of origin was China and it was delivered by Parchem © Trading Ltd. New York (LOT # 20070920). Chitosan was provided as an off-white, odorless powder. The charge analysis of the chitosan gave a deacetylation degree (DA) of 90.29 %. The particle size was 100 mesh. The chitosan exhibited a moisture level of 8.77 %. The source of this commercial chitosan grade and the parameters under which it was processed are unknown. The molar mass of chitosan is 161 g/mol.

#### Acetic acid

Acetic acid has the structure  $\text{CH}_3\text{COOH}$ . It was purchased from J.T. Baker (CAS NO: 64-19-7) with a degree of purity 99.9 %. Acetic acid is a colorless clear liquid. The analysis states that the molar mass was 60.05 g/mol and the density 1.049 g/cm<sup>3</sup>. The function of the acetic acid was as part of the solvent system for the chitosan. Acetic acid has a density of 1.05 g/cm<sup>3</sup> and a mol mass of 61 g/mol. The surface tension of acetic acid is about 27.6 dyne/cm at 20°C.

#### Ethanol

Ethanol has the structure formula  $\text{C}_2\text{H}_6\text{O}$  and was purchased from Pharmco-AAPER (CAS-NO: 64-17-5) with a degree of purity 99.7 %. It is a colorless clear liquid. Ethanol has a molar mass of 46.07 g/mol. The specification tests showed the density to be 0.789 g/cm<sup>3</sup>. The use of ethanol for this work was as a wetting agent to

lower the surface energy of the coating solution. The molar mass of ethanol is 46.07 g/mol and the density is 0.789 g/cm<sup>3</sup>, according to manufacturer data. The surface tension of ethanol is ~ 22.34 dyne/cm at 20°C.

### **Iodine solution**

A brown stain was used in this work to identify the percent coverage of the chitosan coating. The stain solution was made with an iodine mix purchased from Humco (2 % Iodine, 2.4 % Sodium Iodide and 47 % alcohol) with 25/75 (v/v) ethanol.

### **Water**

The coating solutions formulated for this research were made using only de-ionized distilled water.

### **Sealant layer**

The sealant used was a commercially available Low Density Polyethylene (LDPE). The film was a coextruded (mPE + LDPE / C6 LLDPE+LDPE / mPE + LDPE), produced by ISO Poly Films. The LDPE film was delivered on a 3 inch core. The film was 14.5 inches (368 mm) wide. The film thickness was denoted by the manufacturer as 200 gauges (50 µm). The treated side was on the outside of the roll and was measured at 54 dyn/cm<sup>2</sup> with dyne pens.

### **Strength layer**

The strength layer used was polyethylene terephthalate (PET) polyester from the producer Mitsubishi. The PET film was clear transparent, colorless and biaxial orientated. The thickness of the PET film was 48 gauge (12 $\mu$ m) and the width of the web was 14 inches (356 mm). The one side treatment of the surface was 46 dyne/cm, ascertained with dyne pens.

### **Adhesive**

Tycel® 393 adhesive, made by Henkel, was used for the lamination. It is a single-component solvent based adhesive, based on polyurethane (synthetic resin), for flexible packaging laminating. The adhesive is optically clear (slightly yellow), odor free and elastic, is used for standard laminations. Solids content 74-76 %. All components of this adhesive system compositionally comply with the FDA 21 Code of Federal Regulation 175.105. This adhesive was mixed 50/50 (w/w) with the solvent Ethyl Acetate (CAS No.:141-78-6). This adhesive is a commonly used adhesive in the industry, and is used for film to film laminates in food, pharmaceutical and cosmetic packaging applications.

### **Laminated film**

The treated sides of the PET and LDPE films were laminated to each other. The lamination width between the two films was 13.5 inches (343 mm) wide. The lamination had common properties of this type of lamination, strength, stiffness, ductility and a higher melting point at the outside (PET) than on the inside (LDPE).

The surface treatments were 48-50 dyne/cm at the laminated surfaces and 30-32dyn/cm on the inside of the roll.

#### **4. Methods**

##### **4.1. Lamination**

Prior to coating chitosan solutions, the flexible packaging structure was assembled on a solvent based laminator at Clemson. The first step was to slit the film to the correct width (13.5 inches) for the coating & lamination machine. The corona treated side of the polyester film was laminated to the corona treated side of the LDPE film. This was done using Tycel 393 adhesive, mixed with ethyl acetate in a 1:1 ratio. The adhesive was applied at using an 110Q cylinder. Dry applied adhesive weight was 2.08 lb/ream (3.39 g/m<sup>2</sup>). The drying temperatures (two-zone dryer) were 165°F and 185°F. The laminating nip was set at 150°F. The line speed used was 75 fpm. The room temperature was 75°F and humidity was 31 % RH.

##### **Corona treatment**

After the lamination, the treatment level of the LDPE side of the structure was measured using a treatment pen set to be under 36 dyne/cm. Since coating adhesion would be unlikely at this level, it was decided to treat the film to a level over 50 dyne/cm. At the SONOCO pilot lab in Hartsville, S.C., the laminated film was treated on the LDPE side with a ceramic corona treater to a level of 54 dyne. This was verified with treatment calibration liquid in a pen form. The treater used was an Enercon with a Compak II dual output power supply. Run 1 at 52 fpm and power

output at 1.7 kW, with a resultant treatment level of 46 dyne/cm. Run 2 at 33.6 fpm with a resultant treatment level of 54.

#### **4.2. Solution preparation**

The first batches of solutions were made with water, chitosan and acetic acid to test the influence of different ratios between the chitosan and acetic acid. These coatings did not wet the film surface evenly. In the second round of coatings, a wetting agent was added to the solution. Increasing the concentration of acetic acid was not used because of the limited corrosion resistance of the equipment and machines limits acid content to around 12 %. Ethanol was utilized as a wetting agent and it showed good results. Ethanol concentrations up to a value of 40 % were determined to be possible. Since a coating with this level of solvent is flammable, appropriate safety precautions were taken during coating.

#### **Solution preparation (Mayer rod)**

Early experiments failed because clumping of the chitosan occurred and could not be resolved by stirring. Stirring for over two days stirring time did not eliminate all clumps. The order of the procedure was then changed and the solution became “ready” to use in less than 24 hours (see Viscosity change). The preparation of the solution was found to be the most important step. A weighed sample of chitosan was placed in a beaker, to which was added the appropriate quantity of deionized distilled water. This mixture was stirred (Fisher Veramix 145, stir bar size depended on the beaker size, highest possible speed) to a dispersion. Next, the acetic acid was added to the continuously stirred mixture. The acid was added reasonably quickly to prevent

the solution from gelatinizing before all of the acetic acid was added. It was determined that the best way to add the acetic acid was to add it in one step. The best results were accomplished when the stirring process was continuous. The complete chitosan solution turned in to a golden honey-colored transparent liquid mostly after 4 hours. Later Mayer rod coatings included ethanol as a wetting agent. Batch sizes of at least 350 ml were made in order to allow measurement of viscosity with the Zahn cup or Brookfield viscometer.

### **Solution preparation (Gravure roll)**

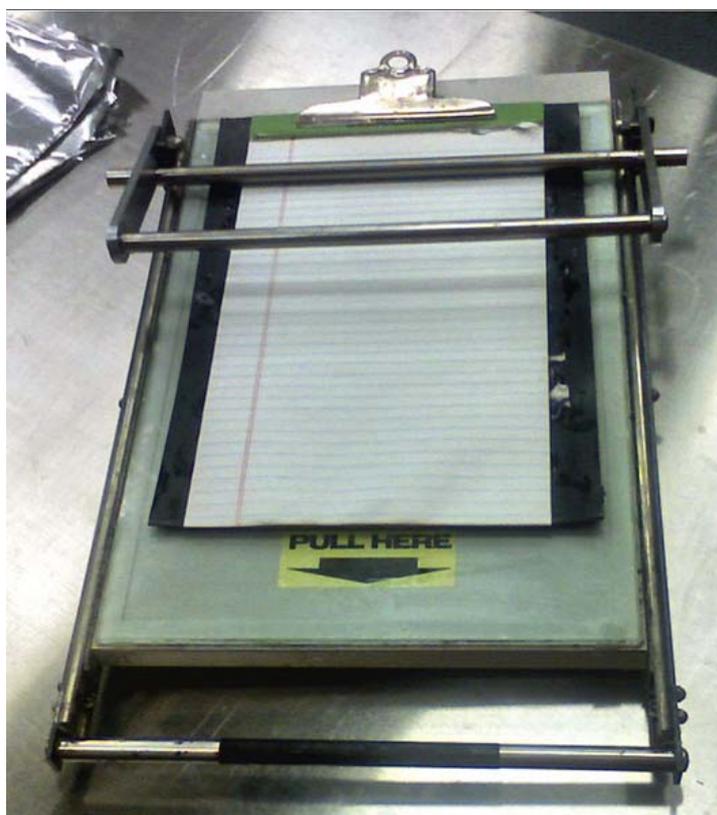
For gravure coating, the smallest batch made was 500 ml, to allow for measurement of the viscosity and for application of the coating. Again, the first step was to add a weighed sample of chitosan into a beaker. Then, ethanol and deionized distilled water were added. As stated above, stirring was important when the acetic acid was added. The acid was added in a single step. Depending on the mixture, the solution tended to harden or thicken, so stirring time (at the highest possible speed) varied from 10 minutes to 72 hours, dependent on the mixing proportions. It was also noted that the viscosity of the chitosan solution decreased in time, and that the complete solution turned into a golden honey-colored transparent liquid. The time that it took for the viscosity change was dependent on the formula. When the chitosan solutions were complete, filtration was the next step. A stainless steel filter with a mesh of 0.00015 inches (3.8 micron) was utilized. The filtration was conducted under a vacuum of 7.25 psi (0.5 bar) at room temperature (72°F). If the vacuum or temperature were higher, condensation occurred at the rim of vessel, and the solutions

started to build foam. While under vacuum, the solution was stirred slowly to remove bubbles. The vacuum pump used was acid resistant.

### **4.3. Coating techniques**

#### **Mayer rod**

The laminated material was cut into sheets with a length of 10 inches. A Mayer rod table was used (ACCU-LAB Drawdown Machine DP-1240 from GARDCO). In this system, a rod was selected and placed into the weight arm assembly. Then, the substrate sample was mounted on the even surface and the weight arm assembly was lowered into place. Next, the coating was spread near the rod using a spatula. Then, the handle was pulled with a smooth, even stroke.



**Figure 13: Drawdown Machine**

This system removes the human variable with respect to the rod pressure and the angle. The speed is still a variable, but care was taken to pull at about 0.3 m/sec. Mayer rods are numbered based on the diameter of the wire wound onto the rod. Mayer rods no. 12, 20, 30, and 40 were used.

## **Gravure roll**

Three different gravure rollers were used. Gravure rollers are characterized by the number and shape of the gravure cells on the roller. Larger cells mean less cells per inch, but more coating weight. As more coating gets applied, the line speed may need to be adjusted to assure drying. For this work, the following cylinders were used:

- 85Q (85 cells per inch.)
- 150Q (150 cells per inch.)
- 200Q (200 cells per inch.)

## **5. Testing**

### **5.1. Viscosity measurements**

Two different methods were used for measuring viscosity. The Zahn cup is a fast, well-established method in the printing and coating industry used to measure the viscosity. However, a rotational viscometer is more accurate than a Zahn cup for the large viscosity range of the solutions used in this work. For this reason, the Brookfield viscometer was used if the viscosity was outside of the range of the Zahn cup.

### Zahn cup (ASTM D 4212)

In order to measure viscosity with the Zahn-Cup (GARDCO EZ™ Zahn cup), there must be enough liquid to completely immerse the cup (depends on the beaker). The measurement range for each cup is fixed. The cups are calibrated to within 3 % tolerance. The liquid volume is calibrated to 45ml. Gravity is the force to flow. The solution must be free from bubbles or foam.

To measure viscosity using this method, the cup was completely submerged in the solution. Then the cup was lifted completely out of the solution in an uninterrupted motion. The time between when the cup completely broke the surface of the solution and the first interruption of the dripping stream was measured by a stop watch. The atmospheric conditions in the laboratory when viscosity was measured were  $78 \pm 4^\circ\text{F}$  ( $26 \pm 2^\circ\text{C}$ ), and  $47 \pm 4\%$  RH. The viscosity of each sample was measured three times. The equation to calculate the viscosity from the measured time [ $T_z$ ] in centistokes [cSt] and the range for the Zahn Cup's are shown in Table 2.

Table 2: Viscosity -GARDNER P.1330 Zahn cups no.1 and 2

Specification Cup Number	Seconds Range	Centistokes Range	Equation from sec to cSt
Zahn Cup No. 1	31-60 sec	15 to 78 cSt	$1.59 \times T_z - 1070 / T_z$
Zahn Cup No. 2	19-60 sec	39 to 238 cSt	$4.18 \times T_z - 760 / T_z$

### Rotation viscometer

Viscosities of the chitosan solutions were measured at time intervals, using a viscometer (Brookfield LV1). For the measuring, the rotator (Brookfield LV1 and LV2) and the rotation speed of 6 to 30 rpm were selected. The viscosity of the chitosan solutions were measured and recorded. The atmospheric conditions in the

laboratory were  $78 \pm 4^\circ\text{F}$  ( $26 \pm 2^\circ\text{C}$ ), and  $47 \pm 4\%$  RH. Quantities above 300ml of the chitosan solution were measured in a 350 ml beaker, after stirring for five minutes and measuring of the solution temperature. The selected spindle was dropped in the solution to the spindle shank mark. After the spindle had turned five times at the selected speed the result was read from the scale. This measurement was repeated three times. The size of the spindle and the speed of rotation depended on the viscosity level and were chosen so that the result was in the last third of the scale range. The result was multiplied by the factor specific to spindle size and speed (provided by Brookfield in tabular form) to get the measurement in centipoises [cP].

**Table 3: Brookfield table for the calculations factor**

<b>Spindle speed factor</b>	<b>6 rpm</b>	<b>12 rpm</b>	<b>30 rpm</b>	<b>60 rpm</b>
LV 1	10	5	2	1
LV 2	50	25	10	5

### **pH test**

The pH levels of the solution were tested using EMD Chemicals Inc. pH indicator strips colorpHast®, (pH Range: 0-6 / sensitivity: 0.5). The solutions pH ranged between 3.5 and 4.5.

### **Percentage solids basis weight**

The percentage of solids of the solutions was measured by the change in the weight of the liquid after drying. An aluminum pan was lined with PET (48 gauges) film to avoid any reaction between the acetic acid and the aluminum pan which might have an influence on the results. The weight of each pan with film liner, the weight of the pan/liner with the solution, and the weight after drying were recorded.

Approximately the same amount of solution was placed in each prepared pan. The pan with the solution was placed in an oven to dry. The temperature of the oven was  $150 \pm 20^\circ\text{F}$  ( $54.4\text{-}76.7^\circ\text{C}$ ). The drying time varied according to the solution. The weight of the dried solution was found by subtracting the weight of the pan and liner. The dried weight was divided by the wet weight of solution and multiplied by 100 to get the percent of the solids in the solution.

## **5.2. Substrate test**

### **Thickness (ASTM F 2251)**

The thickness of the substrate was measured using an electronic micrometer (Nikon MFC-101 with a Nikon Digimicro Stand MS-11C). Three measurements were taken on five specimens at random locations on each film. The ambient air temperature and relative humidity were  $78 \pm 4^\circ\text{F}$  ( $23 \pm 2^\circ\text{C}$ ),  $47 \pm 4\%$  RH. The mean thickness of the five specimens were calculated and recorded for use in tensile strength and elongation tests.

### **Tensile strength (ASTM 882)**

Each film was cut into one inch by four inches strips. The test was conducted in ambient condition  $78 \pm 4^\circ\text{F}$  ( $23 \pm 2^\circ\text{C}$ ),  $47 \pm 4\%$  RH. The measurement followed the description of the ASTM 882 using the SATEC Model No T10000 with the load cell Honeywell 060-0571-07 range 500 lb. The initial separation between the grips was 2 inches. The speed of the separation was 8 inches per minute. The software used was from Instron (Bluehill version 2.5).

### **5.3. Coating**

#### **Application weight (ASTM F 2217)**

The procedure used to determine the weight of the coating on the films was ASTM F2217. According to this procedure a predetermined area of coated film was cut. The weight of the coated specimen was measured and recorded. The coated specimen was then washed with a 7 % acetic acid solution. After washing, the specimen was placed in an oven (Laboratory Oven LR 2700 The Grieve Corporation) to dry at 80°F for 2.5 to 5 minutes. The weight of the dried specimen was taken. The weight of the coating was found by subtracting the weight of the dried specimen from the initial weight. Because the coating was difficult to see, iodine staining was used to assure that all of the chitosan coating was removed during the washing operation.

#### **Adhesion tape test (ASTM F 2252)**

The adhesion of the coating to the films was tested per ASTM F 2252. Strips of Scotch™ 610 tapes were pressed by hand to the coated side of the substrate without entrapped air and wrinkling. The strips were then peeled off the by hand. As outlined in the previous section, iodine staining was used to verify the removal. The area of coating removed from the film was recorded.

#### **Adhesion strength test**

An additional adhesion test was conducted in an attempt to quantify the adhesion of the chitosan to the film. The first step was to apply Scotch™ 610 tape to the coated side of the film. The force necessary to peel the tape off after 48 hours, at a

90° angle, being pulled at 12 in/min (5 mm/s) was tested using the SATEC Model No T10000.

### **Coating continuity and iodine solution test**

It was deemed important to quantify the amount of the surface that was covered with the chitosan solution. A graphical technique using iodine stain, a computer, scanner and software was developed. Coated specimens were stained using an Iodine solution. The brown stain solution was made by mixing 2 % Iodine, 2.4 % Sodium Iodide in a 47 % Alcohol solution, diluted with 25/75 (v/v) Ethanol. The Iodine solution had a brown color. When applied to the films, this treatment could be removed with water. Samples 8.5 inches in length were cut from the roll of coated material. The coated samples were stained with the Iodine solution using a Mayer rod no. 5 and the drawdown table. It was important to remove any excess stain from the samples by immediate washing to avoid any interference with the results. The stained samples were washed in a water bath. The stained and washed samples were rinsed by hand without mechanical influence, and without touching the stained surface. The water was allowed to drip off and the wet substrate was placed face down on a cloth. The backside was blotted with cloth and allowed to dry. Lastly, the washed sheet was suspended in the air for 30 minutes to air dry.

The stained, washed and dried specimens were scanned using a flat bed scanner (HP C3108) and the program Paint Shop Pro from Jasc Software. The software allows the identification and labeling of the number of pixels in a certain area by choosing the color spectrum. The substrates were scanned with Paint Shop Pro9 into a JPG file. All scans were done using the same parameters; specifically area

to output dimension (100 %) and gamma adjust of 2. All other parameters such as highlight; shadows and midtones and color adjustment were set to level zero. The sharpen level for the image scan was set at medium level. Each scan had around 72 dpi (2550 x 3466 pixels). Modification by graphic software of gamma, contrast, brightness, color balance was done by using the “Histogram Adjustment”.

To establish a baseline for the color of the uncoated films, the color intensity of each uncoated substrate was measured with the Histogram function. The averages of five samples of clear film were 239 for red, 238 for green and 236 for blue. These color intensity readings are based on a maximum of 255. If all three were present at 255, the color would be white.

After scanning coated, stained and dried samples, the “Threshold” tool was used to transfer the image from 32 bit true color into a 2 color, 1 bit image. In order to distinguish between a coated area and the substrate, a level of 240 was set for the Threshold function. This caused the conversion software to set anything at 240 or higher as white and anything below that as black.

The Crop tool was used to choose a representational area of the coating image. The area varied from drawdown to drawdown from 15 to 25 in<sup>2</sup>. With the Histogram function, it was possible to count the black and white pixels in the scan. The Histogram function gave the percent of black pixels in the coating area. The same procedure was used for all samples in order to make the results comparable.

### **Retained solvents**

It is a common practice in the coating of flexible packaging to test for the presence of retained solvents in coated materials. It is important to assure that the

solvents are evacuated in order to assure that the coating can function properly, as well as to assure that the product is not adulterated by the solvents.

To conduct this type of testing, the coating was injected into the GCMS system (QP 2010 S SHIMADZU Gas Chromatograph Mass Spectrometer with a GS-2010 SHIMADZU Gas Chromatograph). The response was used as the standard against which the test sample is compared.

When the sample testing was conducted, the coating was washed off of a known area of coated material with acetic acid. This was then injected at the same conditions. The intensity of the response of the standard and the test vial were compared and related the quantity of retained ethanol in the sample to that of the standard.

#### **5.4. Sealing**

##### **Sealing (ASTM F 2029)**

ASTM F 2029 was used to determine whether the samples could be heat sealed. The comparison was based on a heat seal curve of apparent seal strength versus sealing temperature. The heat seals were made using a Sentinel Heat Sealer 12-12AS with a one inch seal bar. Both bars were heated at the same temperature. The jaw pressure was constant at 30 lb/in<sup>2</sup>. Dwell times used were 1 and 2 seconds. Temperature range used was from 180°F to 240°F and ambient conditions were 76 ±2°F and 49 ± 4 % RH.

### **Seal strength between the coated substrates (ASTM F 88)**

The measurements followed ASTM F 88 using the SATEC Model No T1000o with the Honeywell load cell (Nr. 060-0571-07 range 500 lb). The software used was Instron Bluehill. The test was conducted in ambient condition  $78 \pm 4^{\circ}\text{F}$  ( $23 \pm 2^{\circ}\text{C}$ ),  $47 \pm 4\%$  RH.

### **Statistics**

There were several opportunities in this research to study the effects of input variable on output variables. In most cases, there were multiple levels of input (such as percent chitosan) and multiple replications were run on each output test. The same sample size was used for testing each population. The population mean in this type of testing was not known. Tukey's W Procedure a commonly used statistical method for this type of scenario (Ott and Longnecker, 2001), was chosen for this work. This method is based on the student t- test, but is adapted to test for more than two populations. The test provides for testing each mean against each other mean for whether the difference between them is statistically different ( $p < 0.05$ ) or not (Ott and Longnecker, 2001).

## RESULTS AND DISCUSSION

### 6. Substrate preparation

#### Lamination bonds

As outlined in the materials and methods section, polyester film and LDPE film were laminated together. To verify that the lamination was successful, bond strengths were measured between the two films. These are shown in Table 4.

Table 4: Lamination bonds

Sample No.	Average Load [gf]	First Peak [gf/25 mm]	Maximum Load/width [gf/25 mm]
1	72.01	890.52	890.52
2	41.56	1117.13	1117.13
3	68.27	1287.58	1287.58
4	52.76	1598.59	1598.59
5	53.35	1248.87	1248.87
Mean	57.59	1228.538	1228.538
Std. Dev.	11.1379	231.3032	231.3032

All bonds were found to be destruct bonds, meaning that the bond of the adhesive is higher than the strength of the PET layer. For all samples the PET substrate tore.

#### Corona treatment

Surface tension is an important factor in the bond between the substrate and the coating. Generally, the dyne level of the web should be around 10 dynes lower than the surface energy of the coating solution. The coating solution did not wet the surface in tests with substrates that had a surface tensile lower than 48 dynes. The

coating beaded up and created droplets. The bond was too low and the dry coating scaled off easily. The coating started to bond when the surface tension of the substrate was about 50 dynes but the solution still beaded up too quickly.

The corona treatment step was conducted at the Sonoco Products facility in Hartsfield, SC. The substrates were subjected to corona treatment in two passes, which provided an even treatment. All treatment levels were found to be about 54 dyne/cm. The treatment level was also checked before coating with chitosan. There was no evidence of treatment deterioration. Spot checks of treatment tests showed no difference between the samples.

## 6.1. Viscosity

### Effect of chitosan concentration on viscosity

The viscosity was measured for solutions in which the acetic acid concentration was held constant and different quantities of chitosan were added. The formulas are shown in Table 5.

**Table 5: Solution ratio for chitosan/water/acetic acid coatings**

<b>Solution Index</b>	<b>Chitosan [g]</b>	<b>Water [ml]</b>	<b>Acetic acid [ml]</b>
A 1 %	2.50 g	247.50 ml	2.50 ml
B 2 %	5.01 g	247.50 ml	2.50 ml
C 3 %	7.50 g	247.50 ml	2.50 ml
D 3 %	8.75 g	247.50 ml	2.50 ml
E 4 %	10.00 g	247.50 ml	2.50 ml
F 4.25 %	10.62 g	247.50 ml	2.50 ml
G 4.5 %	11.25 g	247.50 ml	2.50 ml
H 5 %	12.50 g	247.50 ml	2.50 ml

The viscosity was measured using a no.2 Zahn cup multiple times over a period of days. It was observed that the viscosity changed with time. The Zahn cup method uses cup efflux time as a measure of viscosity. These results were translated into centistokes and are presented in Table 6. Figure 14 shows a graphical representation of the data. The convention used for time throughout this work is that day 1 is equal to 24 hours after combining the mixture.

**Table 6: Measurement of viscosity vs. time converted from Zahn cup data**

<b>Solution</b>	<b>Day 1</b>	<b>Day 2</b>	<b>Day 4</b>	<b>Day 8</b>	<b>Day 12</b>
A 1 %	32.79 cSt SD 0.92 cSt	29.27 cSt SD 0.12 cSt	27.64 cSt SD 0.66 cSt	20.00 cSt SD 0.13 cSt	19.07 cSt SD 0.08 cSt
B 2 %	35.37 cSt SD 0.18 cSt	33.10 cSt SD 0.62 cSt	29.70 cSt SD 3.02 cSt	23.41 cSt SD 0.97 cSt	21.94 cSt SD 0.41 cSt
C 3 %	42.80 cSt SD 1.09 cSt	37.94 cSt SD 0.44 cSt	34.98 cSt SD 0.23 cSt	30.52 cSt SD 0.24 cSt	27.86 cSt SD 0.13 cSt
D 3.5 %	58.79 cSt SD 0.15 cSt	50.39 cSt SD 0.11 cSt	36.31 cSt SD 0.16 cSt	32.81 cSt SD 0.15 cSt	30.34 cSt SD 0.05 cSt
E 4 %	86.31 cSt SD 2.24 cSt	67.94 cSt SD 0.58 cSt	40.83 cSt SD 0.24 cSt	36.97 cSt SD 0.30 cSt	33.92 cSt SD 0.02 cSt
F 4.25 %	139.49 cSt SD 0.37 cSt	109.60 cSt SD 0.14 cSt	45.36 cSt SD 0.14 cSt	38.08 cSt SD 0.96 cSt	36.13 cSt SD 0.07 cSt
G 4.5 %	200.45 cSt SD 1.32 cSt	140.49 cSt SD 2.64 cSt	54.27 cSt SD 0.87 cSt	38.68 cSt SD 0.31 cSt	36.93 cSt SD 0.10 cSt
H 5 %	410.40 cSt SD 31.5 cSt	169.91 cSt SD 0.28 cSt	62.83 cSt SD 0.49 cSt	41.40 cSt SD 0.06 cSt	39.52 cSt SD 0.11 cSt

As can be seen in the Table 6 and Figures 14 and 15, the 5 % chitosan solution showed a change in viscosity from 410 cSt to 41.4 cSt in 8 days. The 1 % chitosan solution showed a change of less than 25 cSt after 8 days. The highest shift of the viscosity occurred in all cases between day one and day four. After 8 days, the

viscosity changes for all mixtures level out to around the same values, with a mean value of 30.71cSt and a standard deviation of on 6.85cSt.

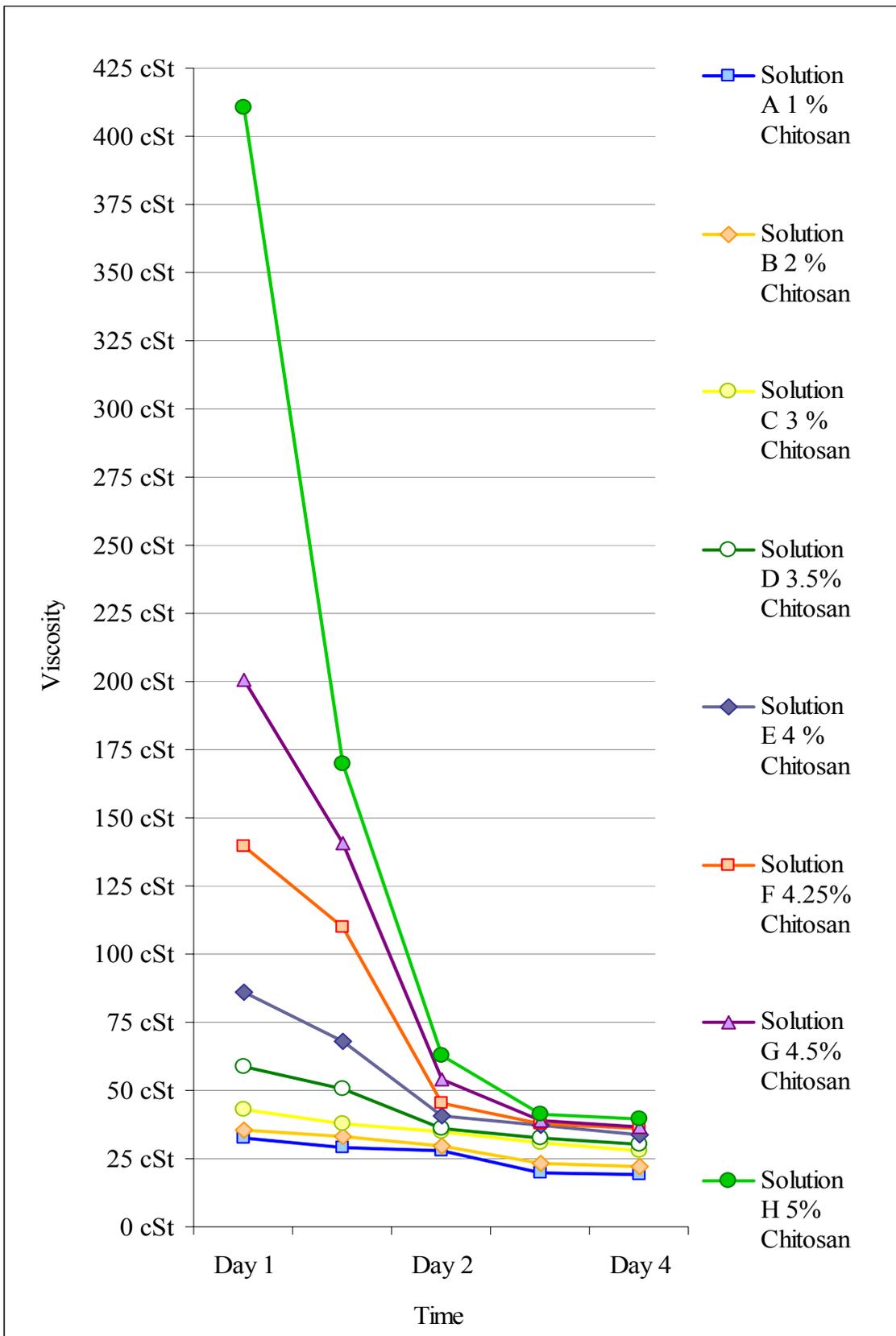


Figure 14: Change of viscosity of different ratio of chitosan

It appears that the viscosity is largely dependent on the time and that all the solutions seem to converge to the same level of viscosity. This is shown in Figure 15. The graph shows the viscosity of each formulation (0-5 % chitosan), with each bar color representing the day of measurement. This graph demonstrates that there was a large difference in viscosity based on chitosan percentage on day 1 and a much lower difference on day 12.

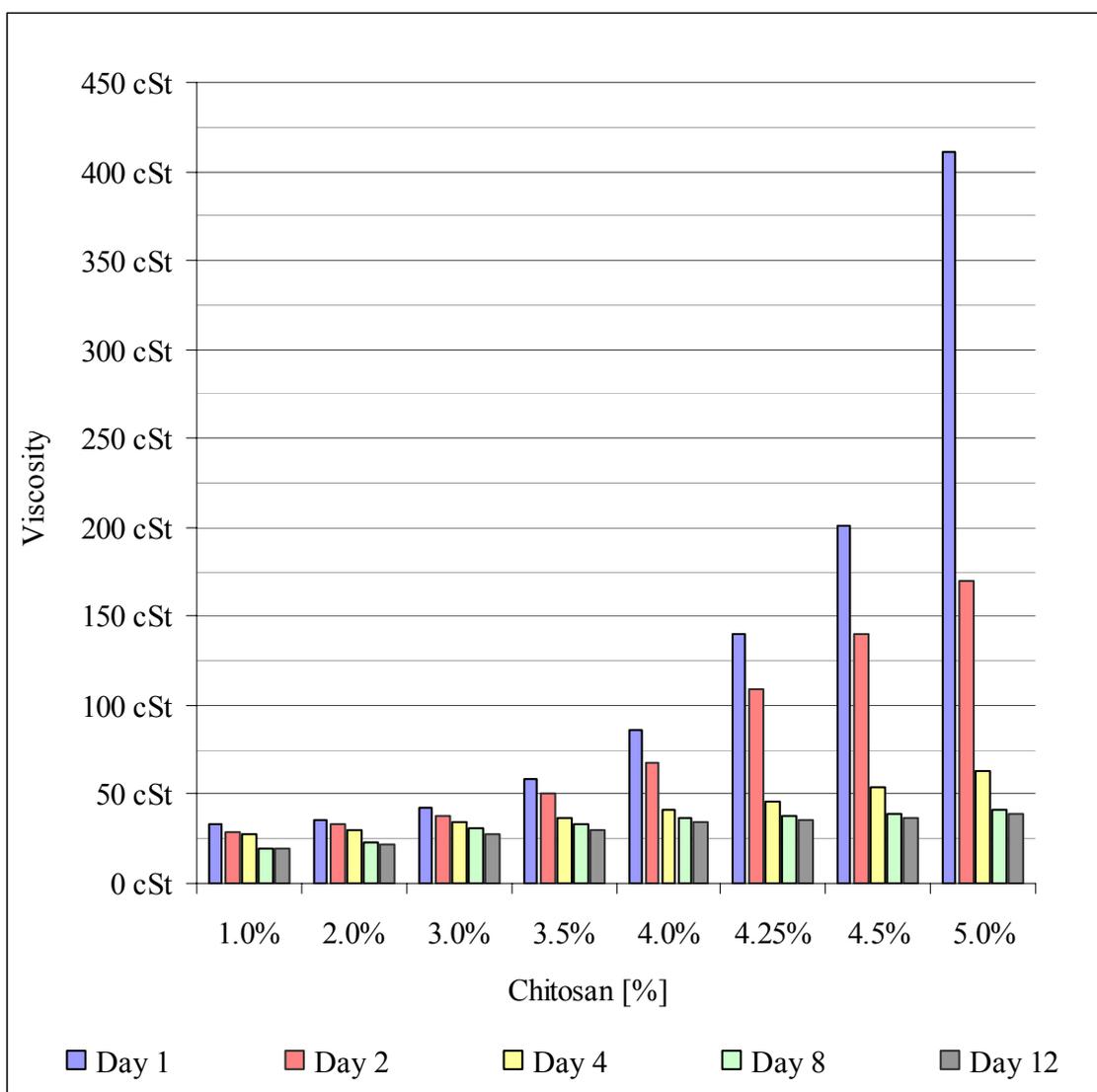


Figure 15: Viscosity change for increasing chitosan ratios over time

As stated, the solution viscosity decreased with time. It is well established in chitosan research that the organic acid in which the chitosan is dissolved usually changes the viscosity with time. The viscosity of the solutions where acetic acid was the solvent changed more rapidly than the viscosity of chitosan solutions with other acids (Uragami and Tokura, 2006).

### Effect of acetic acid on viscosity

Data described in the previous section (Figure 15) demonstrates that viscosity changes occur more between 4 and 5 percent chitosan than they do below 4 %. Further investigation was conducted into the effect of acetic acid concentration for chitosan concentrations at 4, 4.5 and 5 %. The actual formulae are demonstrated in Table 7, sorted by nominal chitosan concentration, then by nominal acid concentration

**Table 7: Ratio of solution A1 to D3**

Solution	Nominal [g] Chitosan per 100 ml solution	Nominal Acetic acid ratio in solution	Formula		
			Total solution volume	Chitosan	Acetic acid
A1	4.0	3.0 %	250 ml	10.002 g	7.5 ml
B1	4.0	4.0 %	250 ml	10.00 g	10.0 ml
C1	4.0	5.0 %	250 ml	9.998 g	12.5 ml
D1	4.0	8.0 %	250 ml	10.00 g	20.0 ml
A2	4.5	3.38 %	250 ml	11.251 g	8.44 ml
B2	4.5	4.5 %	250 ml	11.250 g	11.25 ml
C2	4.5	5.62 %	250 ml	11.250 g	14.05 ml
D2	4.5	9.0 %	250 ml	11.252 g	22.5 ml
A3	5.0	3.75 %	250 ml	12.499 g	9.38 ml
B3	5.0	5.0 %	250 ml	12.50 g	12.5 ml
C3	5.0	6.26 %	250 ml	12.501 g	15.65 ml
D3	5.0	10.0 %	250 ml	12.50 g	25.0 ml

The changes of viscosity over time for the mixtures described in the previous table are shown in Table 8. Figure 16 depicts this entire set of results in graphical form. Figures 17, 18 and 19 separate the data into different sets for each percentage chitosan.

**Table 8: Viscosity mean converted from Zahn cup data**

<b>Solution</b>	<b>Day 1</b>	<b>Day 2</b>	<b>Day 4</b>	<b>Day 8</b>	<b>Day 12</b>
A1	55.74 cSt SD 0.85cSt	37.35 cSt SD 1.35 cSt	38.13 cSt SD 1.35 cSt	34.66 cSt SD 0.09 cSt	33.35 cSt (a <sub>1</sub> ) SD 0.05 cSt
B1	53.82 cSt SD 0.4 cSt	37.71 cSt SD 1.03 cSt	39.54 cSt SD 1.11 cSt	35.42 cSt SD 0.03 cSt	34.61 cSt (b <sub>1</sub> ) SD 0.41 cSt
C1	53.10 cSt SD 1.84 cSt	38.19 cSt SD 1.25 cSt	42.77 cSt SD 0.79 cSt	36.06 cSt SD 0.52 cSt	34.37 cSt (b <sub>1</sub> ) SD 0.29 cSt
D1	55.63 cSt SD 0.32 cSt	36.66 cSt SD 0.13 cSt	39.06 cSt SD 0.09 cSt	34.86 cSt SD 0.03 cSt	33.65 cSt (a <sub>1</sub> , b <sub>1</sub> ) SD 0.18 cSt
A2	63.64 cSt SD 0.9 cSt	42.29 cSt SD 0.7 cSt	42.20 cSt SD 2.2 cSt	38.95 cSt SD 0.1 cSt	36.87 cSt (a <sub>2</sub> ) SD 0.03 cSt
B2	62.49 cSt SD 0.94 cSt	39.28 cSt SD 0.64 cSt	42.80 cSt SD 1.01 cSt	39.02 cSt SD 0.06 cSt	37.49 cSt (a <sub>2</sub> ) SD 0.54 cSt
C2	61.01 cSt SD 0.86 cSt	40.74 cSt SD 0.28 cSt	45.76 cSt SD 0.69 cSt	39.34 cSt SD 0.13 cSt	37.95 cSt (a <sub>2</sub> , b <sub>2</sub> ) SD 0.35 cSt
D2	57.95 cSt SD 0.10 cSt	40.80 cSt SD 0.04 cSt	44.00 cSt SD 0.92 cSt	38.97 cSt SD 0.05 cSt	39.34 cSt (b <sub>2</sub> ) SD 1.02 cSt
A3	67.80 cSt SD 2.28 cSt	43.23 cSt SD 0.99 cSt	44.98 cSt SD 2.12 cSt	40.47 cSt SD 0.33 cSt	40.53 cSt (a <sub>3</sub> ) SD 0.03 cSt
B3	67.40 cSt SD 0.73 cSt	44.96 cSt SD 0.81 cSt	46.01 cSt SD 1.87 cSt	42.05 cSt SD 0.03 cSt	41.11 cSt (b <sub>3</sub> ) SD 0.03 cSt
C3	68.23 cSt SD 0.1 cSt	45.51 cSt SD 0.47 cSt	45.53 cSt SD 0.89 cSt	41.91 cSt SD 0.31 cSt	41.92 cSt (c <sub>3</sub> ) SD 0.04 cSt
D3	64.57 cSt SD 0.91 cSt	44.53 cSt SD 1.08 cSt	47.70 cSt SD 0.22 cSt	41.33 cSt SD 0.02 cSt	39.62 cSt (d) SD 0.04 cSt

It can be seen from Figure 16 that the viscosity appears to fall, then peak in day 4 and then fall again. This increase in viscosity is most likely attributable to the fact that the viscosity had to be measured using Zahn cups with different range and gradation. The higher viscosities (days 1 and 2) were measured using a Zahn cup 2, whose range is from 39 to 238 cSt. The next measurements were taken using a Zahn cup 1, whose range is between 15 to 78 cSt.

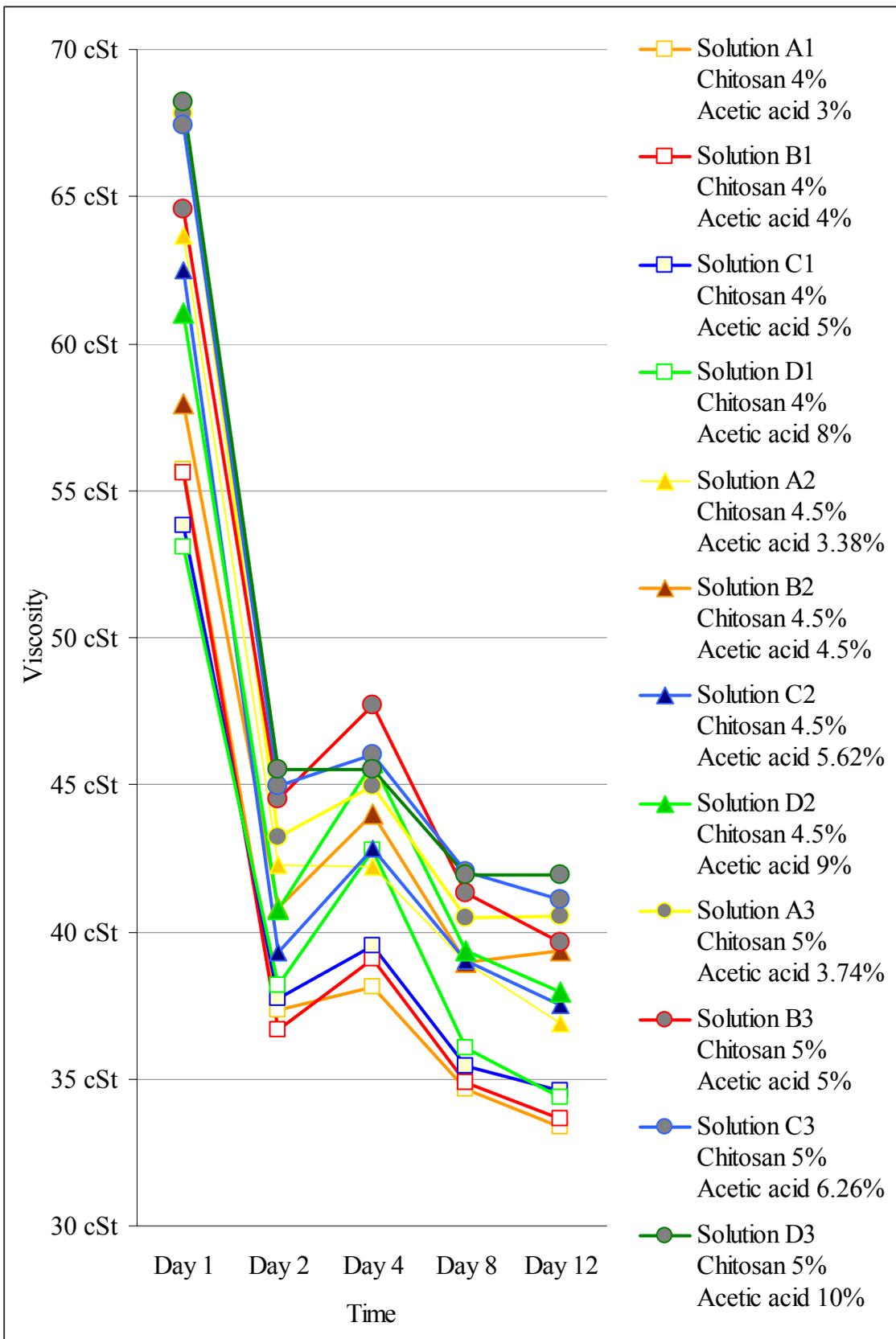
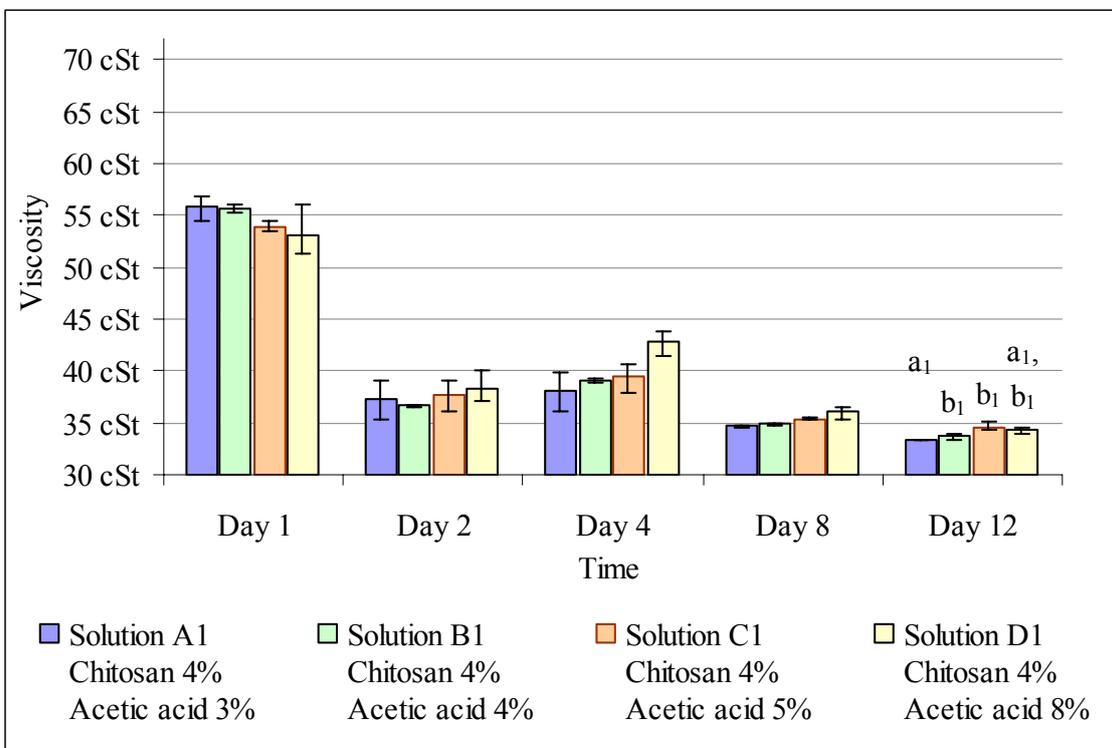


Figure 16: Solutions with different acid and chitosan ratio

The largest single drop in viscosity (2.14 cSt) for the data was between day 1 and day 2 for the 4.5 % chitosan solution. This difference, in Zahn cup 2 efflux times, is approximately 0.4 seconds. The smallest measure-to-measure variation decreased to 0.67 cSt for 5 % chitosan solutions between Day 8 and day 12. This viscosity variation of 0.67 cSt is equal to 0.3 seconds of Zahn cup 1 flux time.

These changes in time are too high to be due to random variation, since the standard deviation between measurements was around 0.15 seconds of flux time. In order to better explore the relationship between the amount of chitosan and acid solvent, the mean of each amount of chitosan and the SD of each point in the change of 12 days is shown in Figures 17 to 19.



**Figure 17: Change of the viscosity for 4 % chitosan solution with different acid ratios**

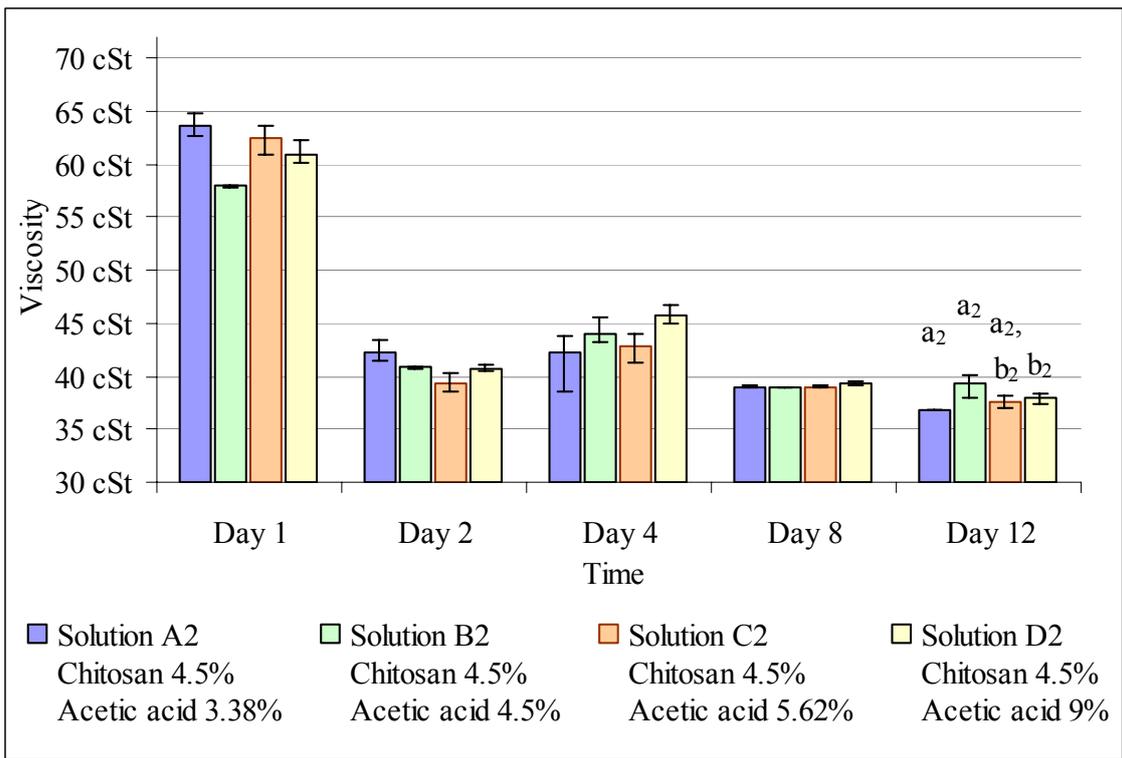


Figure 18: Change of the viscosity for 4.5 % chitosan solution with different acid ratios.

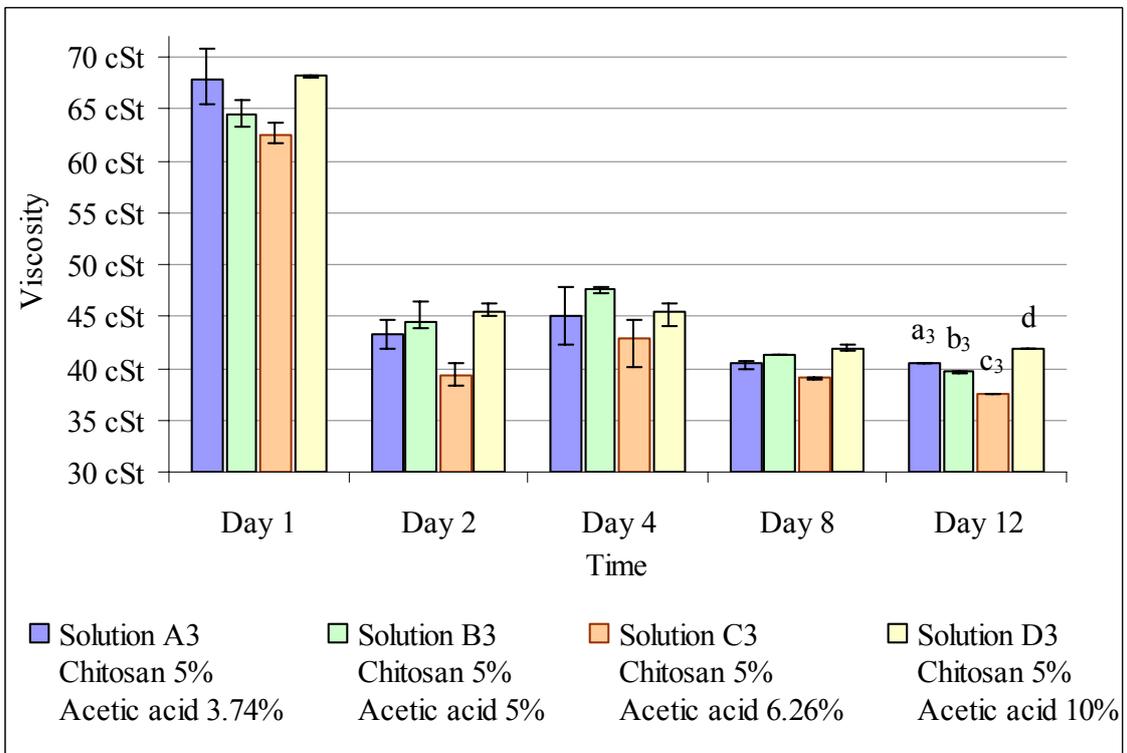


Figure 19: Change of the viscosity for 5 % chitosan solution with different acid ratios.

Generally, 80 % of the total viscosity change happens between day 1 and day 2. The biggest difference is seen in the first two days. After day 4, the viscosity changes level out, and at day 12, there is little difference between the viscosities of the different solutions. The differences between the coatings in viscosity at day 12 has been proven to be statistically significant in several cases, noted by the placement of letters showing statistically grouped values in Figures 17, 18 and 19. However, these viscosity differences amount to less than one second on a no. 2 Zahn cup. Viscosity differences at these levels would not be considered to be practically different in the industry.

It appears that the influence of acetic acid percentage only appears in the first 24 hours after the mixing. The effect was observed by a decrease in the time it took to attain a homogeneous solution with the higher percentage of acetic acid. It is unknown why acetic acid affects the viscosity only during the first 24 hours.

Based on these results, it was decided to perform coating experiments 4 days after mixing the coating solutions to allow enough time for the viscosity to stabilize. The viscosities of each solution with different acid ratio were nearly the same after 12 days.

### **Viscosity of solutions with ethanol**

For gravure roll coating, a higher volume of coating solution is required. The formulae used are shown in Table 9. The volumes of solutions made were around 4000ml. This high volume was made in smaller batches to maintain accuracy of mixture. The tested liquid was separated and stored in a closed container.

**Table 9: Ratio of solution with the wetting agent ethanol**

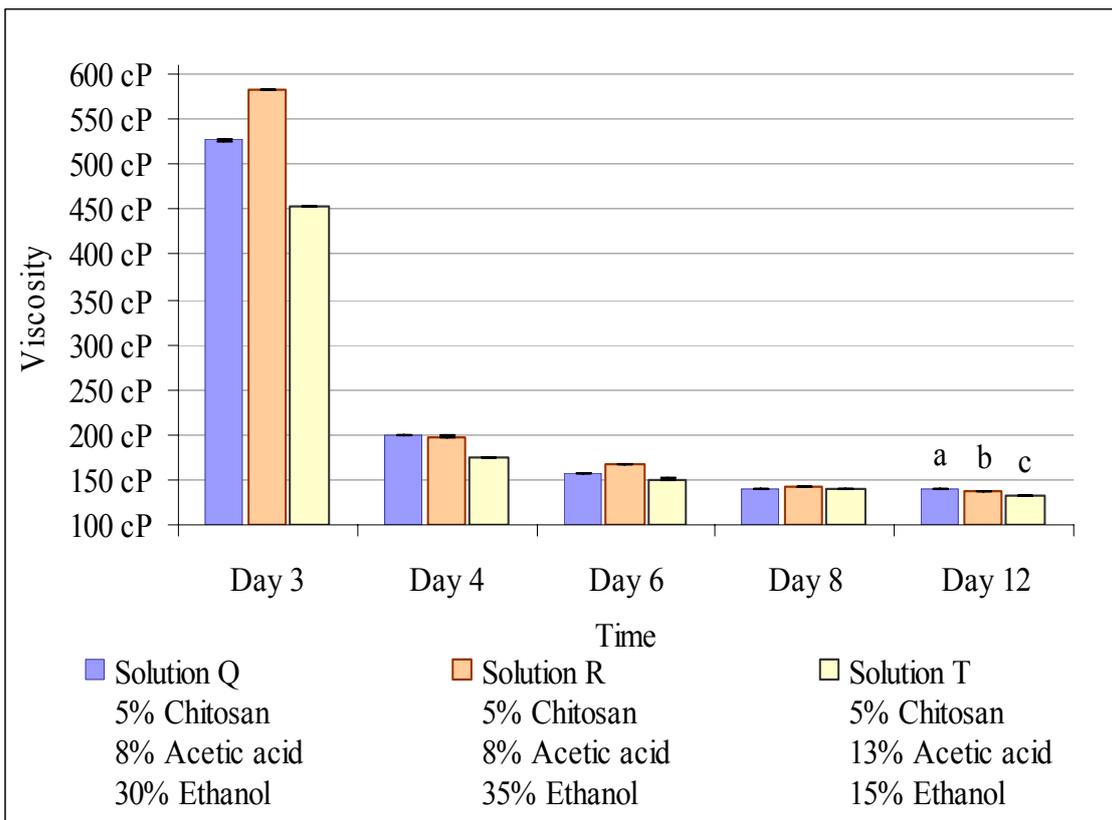
<b>Solution</b>	<b>Chitosan</b>		<b>Ethanol</b>		<b>Acetic acid water solution</b>
Solution R	5 %	200g	35 %	1400ml	8 % acid in 2400ml
Solution Q	5 %	200g	30 %	1200ml	8 % acid in 2600ml
Solution T	5 %	200g	15 %	600ml	13 % acid in 3200ml

The viscosities of solutions with the wetting agent ethanol were measured using a Brookfield viscometer. The reason for this change to a Brookfield instrument is that the viscosity was too high for both the Zahn cup 1 and Zahn cup 2. Measurement with the Brookfield started at the third day because the viscosity was out of the range of the available spindles for the Brookfield instrument too.

The viscosity was measured in centipoises (cP). The test results of the viscosity of the solution and the standard deviations of the measurements are shown in the Table 10. The standard deviation were too low (less than 2.5 cP) to show in Figure 20.

**Table 10: Viscosity of solution with ethanol**

<b>Time</b>	<b>Solution R</b>	<b>Solution Q</b>	<b>Solution T</b>
Day 01	Out of range	Out of range	Out of range
Day 02	Out of range	Out of range	Out of range
Day 03	581.5 cP SD 0.20 cP	526.7 cP SD 2.36 cP	453.0 cP SD 0.28 cP
Day 04	197.9 cP SD 0.84 cP	198.7 cP SD 0.25 cP	175.0 cP SD 0.16 cP
Day 06	167.9 cP SD 0.19 cP	158.0 cP SD 0.16 cP	151.0 cP SD 0.65 cP
Day 08	142.7 cP SD 0.47cP	140.5 cP SD 0.25 cP	139.0 cP SD 0.16 cP
Day 12	137.8 cP (a) SD 0.28 cP	138.7 cP (b) SD 0.09 cP	132.0 cP (c) SD 0.28 cP



**Figure 20: Change of the viscosity of solution with an ethanol ratio**

As can be seen in Figure 20, ethanol-containing mixtures exhibit similar viscosity changes as those discussed for earlier coatings without ethanol. Also, after several days, the solutions went to nearly to the same viscosity levels, as was observed earlier. Solutions Q, R and T exhibited the highest change rate of viscosity between days 3 and 4, although the fact those days 1 and 2 were “out of range” suggests that the rest of the curve may be similar.

The viscosities for solutions Q, R and T at day 12 were tested for statistical differences. The three values were statistically different. The Brookfield viscometer is even more precise than the Zahn cups described in previous sections, so that small viscosity differences could be detected. While statistically different, these viscosity differences of only 7 cP would again be considered negligible in the industry.

Solutions Q and R had nearly the same viscosity. The explanation for this small difference was in the formulas of solutions Q and R. The viscosity differences between each solution decreased more and more in time. The ratio of solution R has 5 % more ethanol than solution Q but the viscosities of both solutions show a similar graph on about the fifth day. The higher ratio of ethanol in solution R was tested to study the drying dependence on ethanol percentage.

Solution T had 5 % more acid than solutions R and Q. It also showed nearly 100 cP lower viscosity at the third day, even though the ratio of ethanol was 15 to 20 % lower. At the sixth day the three solutions went to nearly the same viscosity level. The same affect was observed by solutions without ethanol. This suggests that the amount of chitosan has the main influence on the viscosity.

## **6.2. Percent solids of the chitosan solutions**

Percent solids were tested on some of the chitosan solutions made for this research. Each solution was tested once, so statistical analysis was not conducted. The data in Table 11 show that the percent solids increased with time and with percent chitosan. These data were collected for solutions with a fixed one percent acetic acid and an increasing amount of chitosan. An increase of the percent solids was also detected in solutions with a variation of acid as shown in Table 12.

**Table 11: Effect of Chitosan concentration on percent solid**

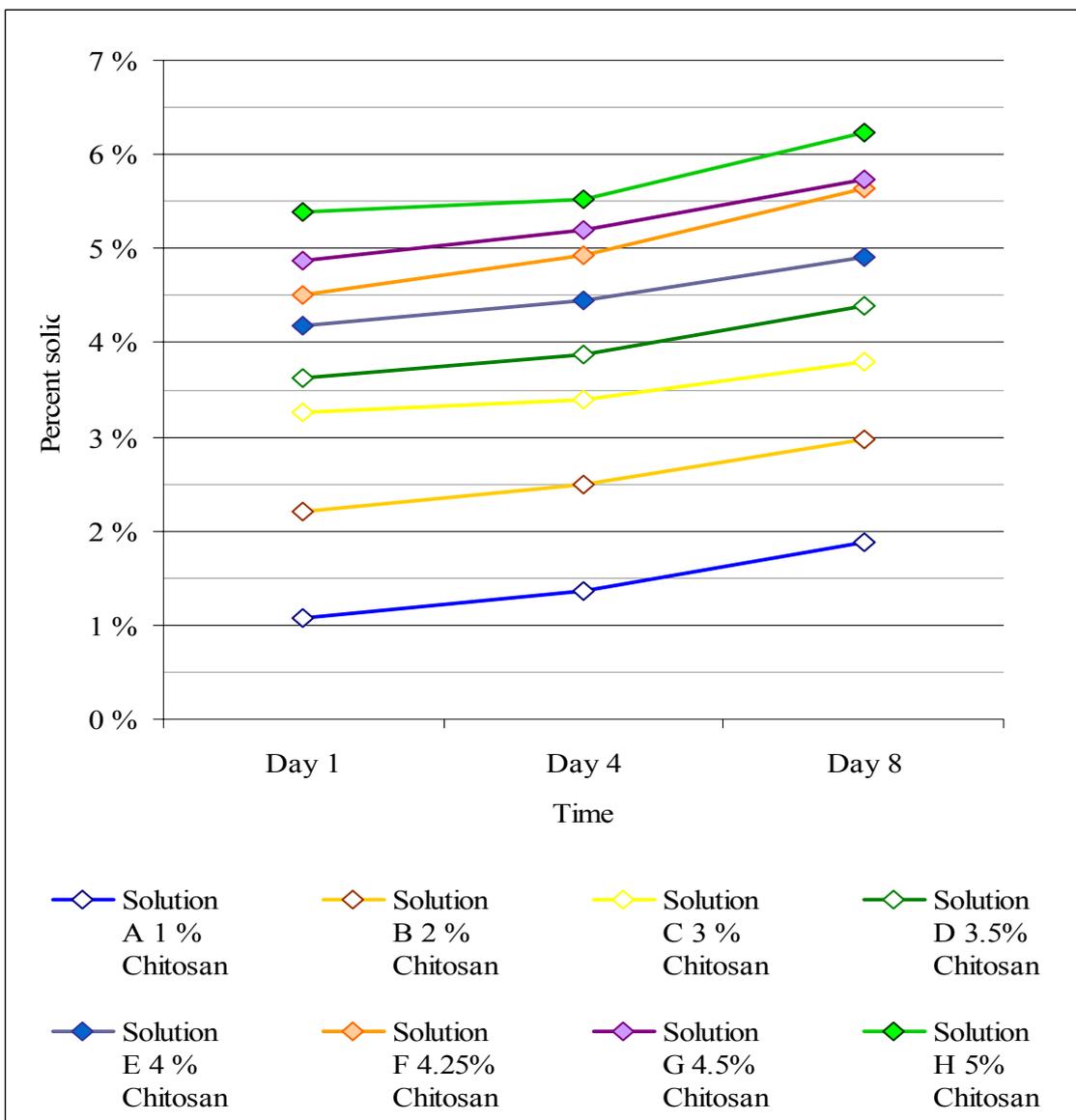
<b>Solution No.</b>	<b>% Solid Day 1</b>	<b>% Solid Day 4</b>	<b>% Solid Day 8</b>
A 1 %	1.08 %	1.36 %	1.89 %
B 2 %	2.21 %	2.48 %	2.97 %
C 3 %	3.26 %	3.40 %	3.80 %
D 3.5 %	3.63 %	3.88 %	4.39 %
E 4 %	4.19 %	4.46 %	4.91 %
F 4.25 %	4.52 %	4.93 %	5.63 %
G 4.5 %	4.88 %	5.21 %	5.74 %
H 5 %	5.39 %	5.53 %	6.23 %

**Table 12: Effect of acetic acid concentration on percent solid**

<b>Solution No.</b>	<b>% Solid Day 1</b>	<b>% Solid Day 2</b>	<b>% Solid Day 8</b>	<b>% Solid Day 12</b>
A1-4.0 %	4.14 %	4.18 %	4.75 %	5.37 %
B1-4.0 %	4.19 %	4.38 %	4.44 %	4.92 %
C1-4.0 %	4.04 %	4.09 %	4.79 %	5.30 %
D1-4.0 %	4.09 %	4.13 %	4.50 %	4.91 %
A2-4.5 %	5.19 %	5.20 %	5.57 %	6.08 %
B2-4.5 %	5.01 %	5.18 %	5.12 %	5.96 %
C2-4.5 %	4.66 %	4.68 %	5.46 %	6.38 %
D2-4.5 %	4.76 %	4.80 %	5.23 %	6.34 %
A3-5.0 %	5.36 %	5.39 %	6.12 %	6.64 %
B3-5.0 %	5.55 %	5.79 %	5.84 %	6.70 %
C3-5.0 %	5.29 %	5.35 %	6.06 %	6.74 %
D3-5.0 %	5.12 %	5.15 %	5.72 %	6.84 %

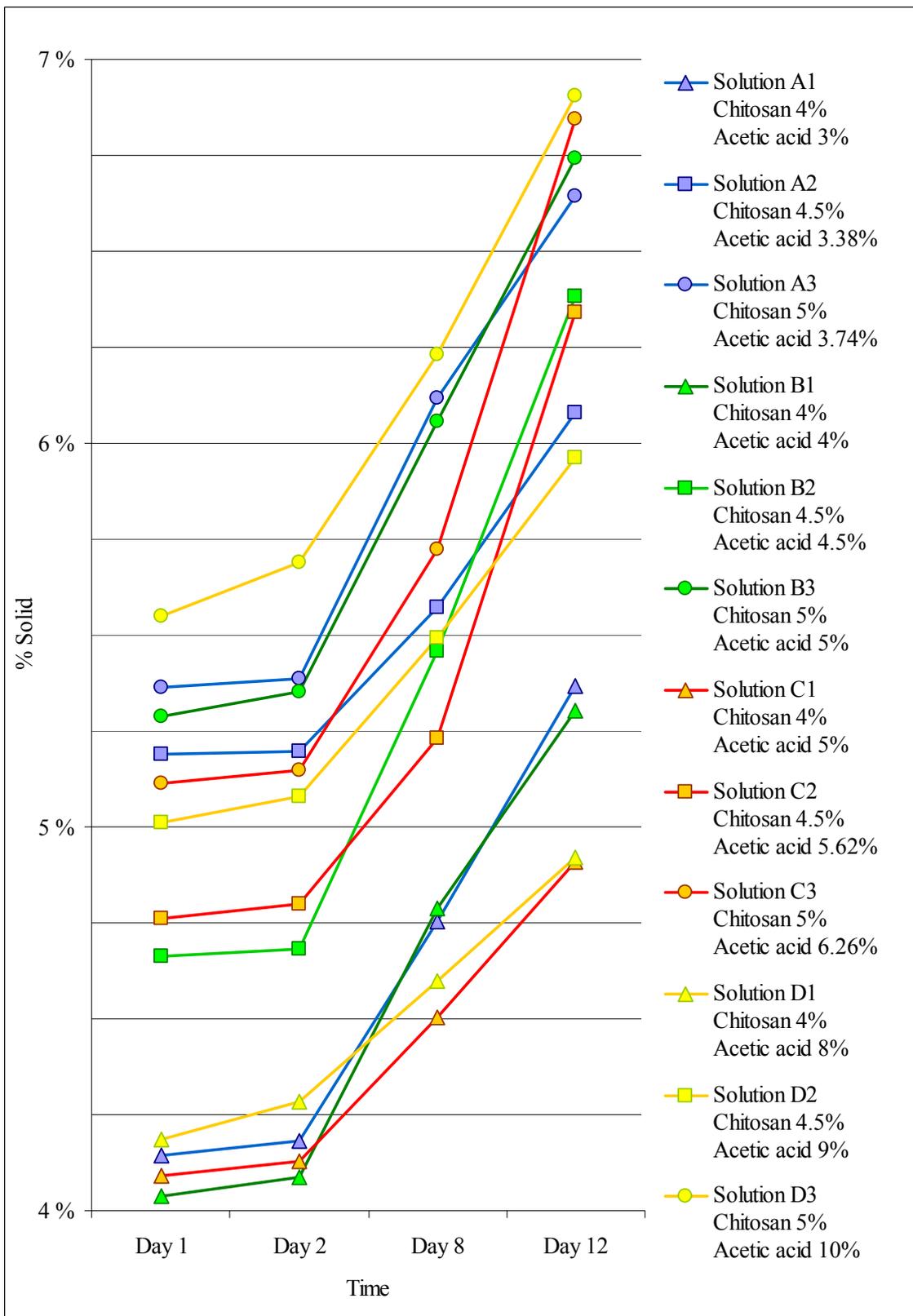
The average change in the percent solids of the solutions in 8 days was  $0.80 \pm 0.15$  % for the 1 % acid solutions. The change in percent solids remained constant independent of the chitosan % in the solution. It is unlikely that evaporation was a factor, since the containers with the test solutions were only opened for the testing.

The change rate increased more between days 4 and 8 than between days 1 and 4, as can be seen in Figure 21 and to a higher degree in Figure 22. Figure 22 shows percent solids change versus time for several acid concentrations at three different chitosan percentages. Data points drawn with a circle are 5 % chitosan solutions, squares represent 4.5 % and triangles represent 4 % chitosan. This chart suggests that the solids percentages change with acid content and chitosan content.

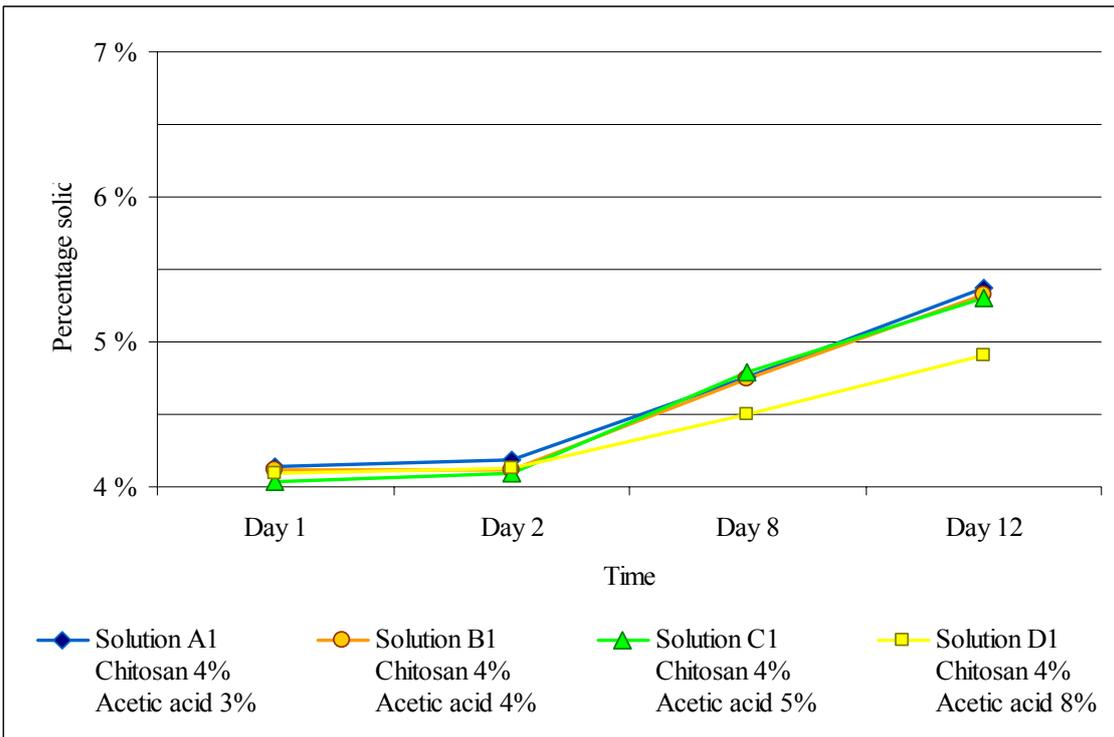


**Figure 21: Percent solids of Solution A-H**

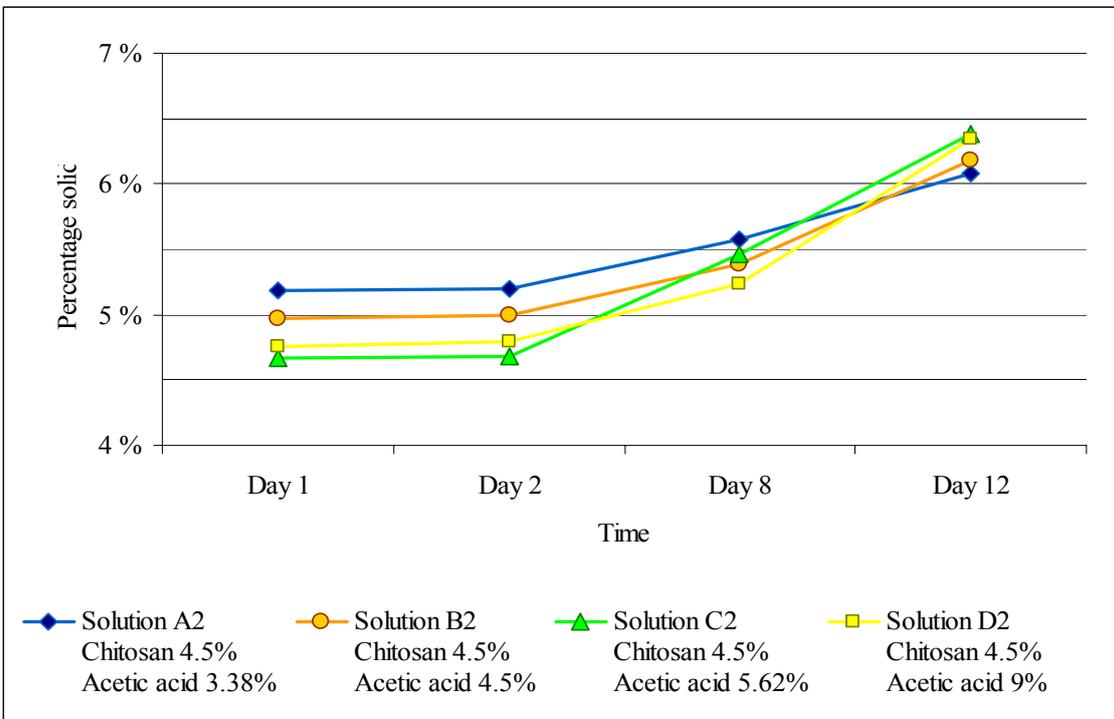
The same data are presented in Figures 23, 24 and 25 for easier viewing. Solutions with higher acid ratio (Table 12) show variation up to  $1.30 \pm 0.13$  % of the percentage of solid in 12 days.



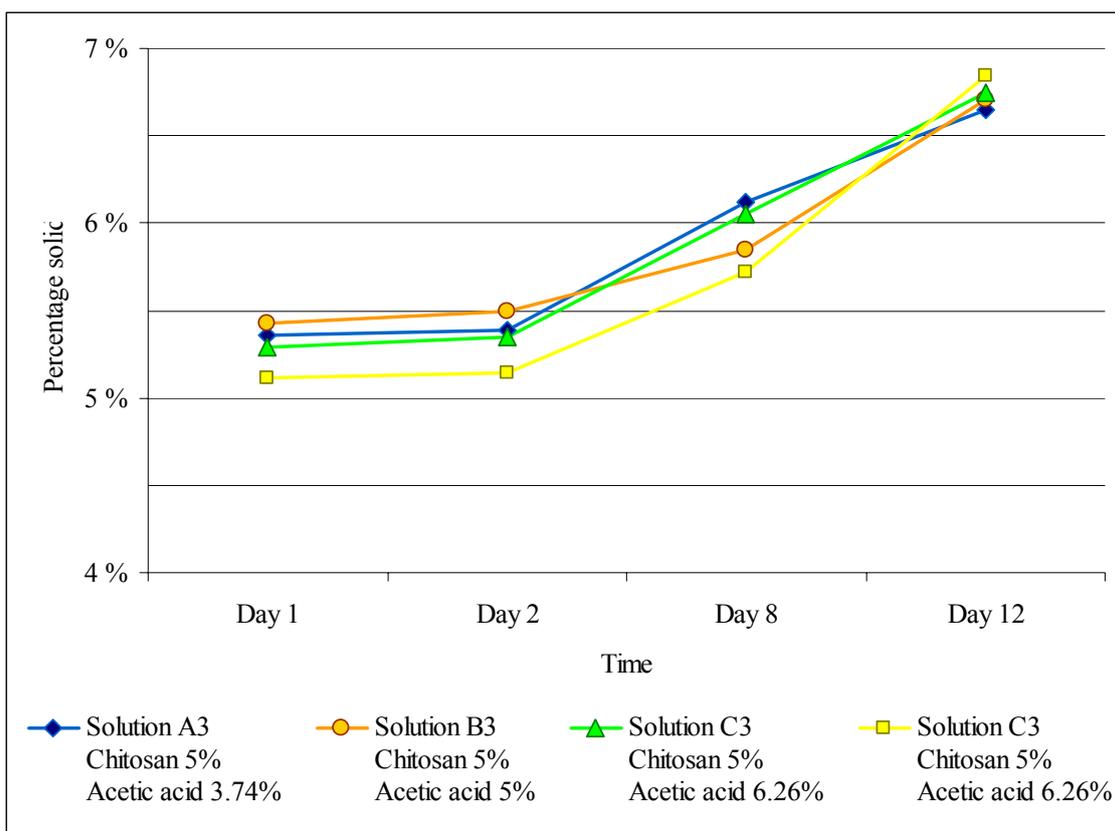
**Figure 22: Change in percent solids with varying acetic acid concentration at three different chitosan percentages**



**Figure 23: Percent solids change over time for 4 % chitosan solutions**



**Figure 24: Percent solids change over time for 4.5 % chitosan solutions**



**Figure 25: Percent solids change over time for 5 % chitosan solution**

Possible reasons for this effect can be that water or acid volatilized to the headspace air in the jar, up to the saturation point. When the jar was opened for the testing this headspace escaped. It might also be possible that the gas phase in the headspace escaped when the jar was closed.

It is also possible that the chitosan takes up and holds more mass of the solvent blend in its “matrix”, so that the percent solids would increase. If chitosan holds some percentage of the solvent, it is possible that the test solutions were drying to a different end ratio. The acetic acid did not completely dry out, the odor held for weeks. It is known that chitosan swells with a certain amount of taking up moisture (Uragami and Tokura 2006), but it is not known if this process reverses by drying.

This could explain the difference in the data but not increase in percent solids after day 2. If the increase in the percent solids suggests that the chemical reaction between chitosan and the acid solution are still in process after 8 days, then why would the viscosity stabilize after this period?

It is possible that this increase in percent solids is not an issue for the industry, because percent solids varies in gravure coating by similar or larger degrees due to evaporation of solvents. This effect was expected and detected for the coating process during this research when the ethanol solutions were used. Measurements of the solid weight before and after the machine run show the results of this evaporation. The change of percent solids due to evaporation during the coating process (around 4 hours) are shown in Table 13. Table 14 shows the percent solids data for the same solutions which were stored separately in closed jars.

**Table 13: Increasing % solid by evaporation during the coating process**

<b>Measurement start at day 4</b>	<b>Solution Q run 1</b>	<b>Solution Q run 2</b>	<b>Solution R</b>	<b>Solution T</b>
% Solid beginning of the run	5.85 %	6.01 %	5.16 %	5.81 %
% Solid end of the run	6.01 %	7.10 %	6.53 %	6.68 %

**Table 14: Increasing % solid by storage of the solution in a closed jar**

<b>Time</b>	<b>Solution Q</b>	<b>Solution R</b>	<b>Solution T</b>
Day 1	5.85 %	5.16 %	5.81 %
Day 2	6.04 %	5.88 %	6.55 %
Day 8	6.89 %	6.80 %	7.02 %
Day 12	8.18 %	8.11 %	8.56 %

### 6.3. Mayer rod coating

The coatability of chitosan solutions was tested by drawdown with several Mayer rods (Numbers 12, 20, 30 and 40). Coatings formulated without ethanol did not wet out the treated LDPE film. As a result of this, ethanol was added as a wetting agent to all of the solutions discussed in this section. The formula variations can be seen in Table 15. The percentage of acetic acid given is the v/v ratio contained in water. The percentage of chitosan is the w/v ratio to the acetic acid / water solution. The ethanol percentage is the volume percentage (v/v) of ethanol in the final solution.

**Table 15: Tested solution formulae**

<b>Solution No.</b>	<b>Total Volume</b>	<b>Ethanol</b>	<b>Acetic acid water solution</b>	<b>Chitosan</b>
A	100 ml	10 %	1,0 %	0,5 %
B	100 ml	15 %	1,0 %	0,5 %
C	100 ml	20 %	1,0 %	0,5 %
D	100 ml	25 %	1,0 %	0,5 %
E	100 ml	30 %	1,0 %	0,5 %
F	100 ml	35 %	1,0 %	0,5 %
G	100 ml	34,5 %	2 %	1,0 %
H	100 ml	35,2 %	6,0 %	3,0 %
I	100 ml	36,3 %	4,0 %	2,0 %
J	100 ml	38,0 %	4,0 %	2,0 %
K	100 ml	33,5 %	3,0 %	1,5 %
L	100 ml	31,5 %	6,0 %	1,5 %
M	100 ml	29,5 %	9,0 %	1,5 %
O	100 ml	37,1 %	4,02 %	2,0 %
P	100 ml	35,4 %	4,02 %	2,0 %

Three samples were produced with each Mayer rod for the surface area test. The percent coverage area was measured for each sample using the staining and scanning procedure outlined in the Materials and Methods chapter. Three

measurements of the coating coverage were taken from each sample of each Mayer rod. The mean and the standard deviation of the percent coverage results can be seen in Table 16. Results labeled “no wetting” define samples on which the coated and stained substrate showed no real wetting of the surface. Tables 15, 16 and 17 are comprehensive and somewhat difficult to interpret, so these data have been excerpted in Tables 20 through 28.

**Table 16: Results of the Mayer rod drawdown in percent coverage with different solutions and rods.**

<b>Solution</b>	<b>Meyer Rod 12</b>	<b>Meyer Rod 20</b>	<b>Meyer Rod 30</b>	<b>Meyer Rod 40</b>
A to C	No wetting	No wetting	No wetting	No wetting
D Mean D SD	No wetting	No wetting	No wetting	4.96 % SD 1.722 %
E Mean E SD	No wetting	No wetting	5.07 % SD 1.8676 %	5.02 % SD 1.5895 %
F Mean F SD	No wetting	No wetting	5.19 % SD 3.7529 %	7.73 % SD 1.7913 %
G Mean G SD	No wetting	17.93 % SD 2.7009 %	30.32 % SD 0.8259 %	41.98 % SD 2.4696 %
H Mean H SD	13.44 % SD 3.3352 %	30.56 % SD 0.7766 %	54.96 % SD 2.8733 %	77.32 % SD 2.1304 %
I Mean I SD	7.83 % SD 1.6214 %	36.00 % SD 2.4439 %	51.84 % SD 4.9133 %	72.18 % SD 1.3677 %
J Mean J SD	12.95 % SD 2.4763 %	35.19 % SD 3.3968 %	57.41 % SD 2.5707 %	79.72 % SD 1.1248 %
K Mean K SD	11.25 % SD 3.1598 %	41.28 % SD 2.3204 %	48.34 % SD 2.0744 %	69.03 % SD 3.9397 %
L Mean L SD	26.20 % SD 0.7789 %	69.47 % SD 2.9907 %	77.86 % SD 1.5094 %	92.20 % SD 1.5160 %
M Mean M SD	18.92 % SD 3.7219 %	75.53 % SD 3.0912 %	91.88 % SD 2.3518 %	97.38 % SD 0.8425 %
O Mean O SD	11.00 % SD 1.3491 %	35.08 % SD 0.8411 %	54.51 % SD 2.7590 %	74.80 % SD 2.5665 %
P Mean P SD	5.01 % SD 0.7483	30.79 % SD 0.6693 %	51.35 % SD 1.0654 %	71.53 % SD 0.4110 %

### Characterization of the coated surface

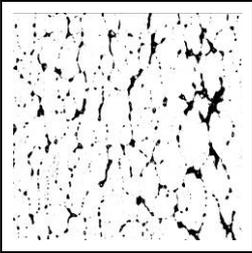
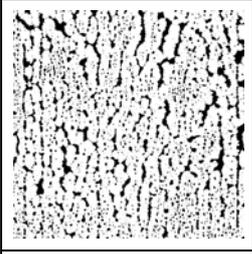
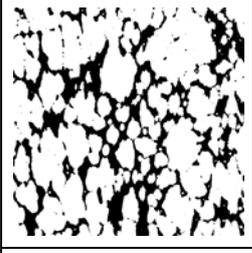
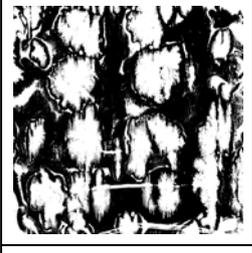
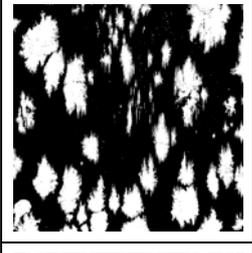
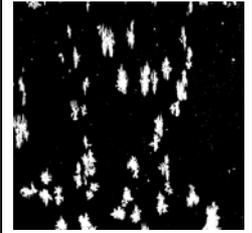
The percentage coverage of the coated substrate has significant variation, so it is important to describe the surface in qualitative terms as well as quantitatively. So a qualitative, visual examination was also conducted on each stained sample. The visual evaluation of spots and fisheyes, which reduce the coverage surface, was subjective, but offers insight into the percent coverage data. The classification of the coated surface for each solution and rod are presented in Table 17.

**Table 17: Visual evaluation of spots, border and fisheyes**

<b>Solution</b>	<b>Mayer Rod 12</b>	<b>Mayer Rod 20</b>	<b>Mayer Rod 30</b>	<b>Mayer Rod 40</b>
A to F	No wetting	No wetting	No wetting	No wetting
G	Spotty	Small border	Small border	Small border
H	Fine spotty	Small border	Small border	Big fisheyes
I	Spotty	Small border	Small border	Big fisheyes
J	Fine spotty	Small border	Big fisheyes	Fisheyes
K	Spotty	Small border	Small border	Big fisheyes
L	Small border	Small fisheyes	Small fisheyes	Small fisheyes
M	Fine spotty	Small fisheyes	Small fisheyes	Some spots
O	Fine spotty	Small border	Small border	Some spots
P	Fine spotty	Small border	Small border	Big fisheyes

A visual key of these descriptions is provided in Table 18. Sometimes, surface irregularities of the coating, such as fisheyes and spots were caused by dust particles in the coating, which changed the surface energy enough to break the coating surface.

**Table 18: Characterization of the coating surfaces**

Sample image	Name	Characterization
	No wetting	Coating beaded up immediately
	Spotty	The surface energy was too high to wet more than small areas, some areas had no coating. The coating solution retracted to a few drops in the drying process
	Fine spotty	The surface energy was too high to wet areas but the size and the distance between the drops was smaller. More and more drops joined together.
	Small border between fisheyes	Most drops were connected and built a kind of net structure, but the coating surface looked more like a grid. The size of the fisheyes varied greatly.
	Big fisheyes	The coated surface was broken by areas without wetting; the shape of the fisheyes had a fairly clear border, often surrounded by a second ring gap. The size of the fisheyes was variable.
	Fisheyes	The coated surface was broken by areas without wetting, the shape of the fisheyes were fissured, transitioning to the coated areas. There were broad as opposed to sharp borders around the fisheyes.
	Small fisheyes or spots	The shape of the fisheyes looked corrugated. Some of the fisheyes were caused by dust or particles which broke the surface tension of the coating

The drawdown of all solutions was done with rods no. 12, 20, 30 and 40, but the stained coatings with rods 12 and 20 showed mostly irregular spotty or small border drawdown. Therefore, samples coated with rods 12 and 20 were excluded from further interpretation or work. The results of Mayer rods 30 and 40 showed a more regular and complete coverage.

### **Limits of ethanol and acetic acid in the solutions**

In defining the research scope, limits were applied to the amount of ethanol and acetic acid that would be utilized in the research. Ethanol in the solution becomes flammable (flash point) at 40 % ethanol concentration in water (v/v) and 26°C (79°F) reported by the NFPA (National Fire Protection Association) (Spacer and Colonna, 2002). The critical ethanol ratio for good wetting was found to be around 35 %.

A ratio of acetic acid to water of around 15 % of acid was utilized as a limit, given by the acid resistance of the equipment such as some component of the gravure roll coating machine.

### **Influence of the ethanol concentrations**

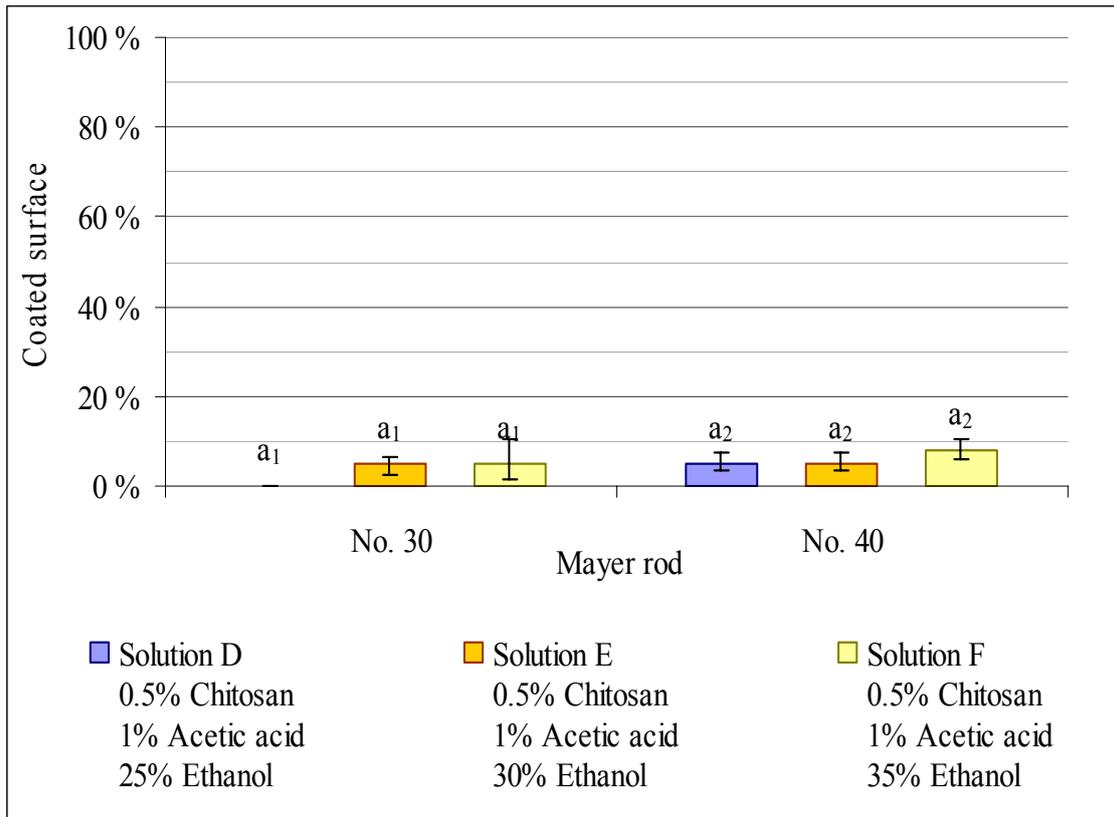
Since tests without a wetting agent such as ethanol exhibited a failure to wet the film surface, tests were designed to find the ratio of ethanol required to wet the surface. This was tested with a coatings formulated from 10 to 35 % ethanol with 0.5 % chitosan and 1 % acetic acid water solution as shown on Table 19. The drawdowns were done with rods 12, 20, 30 and 40.

**Table 19: Formulations of solutions A to F**

<b>Solution No.</b>	<b>Total Volume</b>	<b>Ethanol</b>	<b>Acetic acid water solution</b>	<b>Chitosan</b>
A	100 ml	10 %	1,0 %	0,5 %
B	100 ml	15 %	1,0 %	0,5 %
C	100 ml	20 %	1,0 %	0,5 %
D	100 ml	25 %	1,0 %	0,5 %
E	100 ml	30 %	1,0 %	0,5 %
F	100 ml	35 %	1,0 %	0,5 %

Only solutions D, E and F resulted in a measurable coating and these are presented in Figure 26. In these cases, the surfaces were not really wetted out by the coating. The coating results were spotty, with large drops and only about 10 % coating coverage. The variations of the drawdowns were too high and not reproducible. None of these solutions wet the substrate surface with Mayer rods 12 and 20 either. Coatings A to F did not result in sufficient wettability to merit further investigation.

Solutions with 0.5 % chitosan and 1 % acetic acid were not useful to coat the treated PE surface. An increase of the ratio to 35 % of ethanol did not give better results. Mayer rods 12 and 20 never gave an acceptable result of drawdowns. Only rods 30 and 40 showed some partial wetting of the substrate. The stained coatings show an irregular spotty drawdown with several big drops. Statistics showed no discernable difference in percent coverage between the three coating formulations with either Mayer rod 30 or rod 40.



**Figure 26: Percent coverage for solutions D, E and F with an increasing ethanol ratio**

**Influence of ethanol ratio with a higher concentration of chitosan and acetic acid**

It was not expected that increasing of the ethanol ratio up to 40 % would give much better results, so the chitosan and acid ratios were adjusted. Drawdowns were conducted on coating solutions with 2 % chitosan dissolved in a 4 % acetic acid water solution, with ethanol ratios between 35.5 % and 38 %. The percent coverages for each rod are presented in Table 19. The graphic presentations of these data are shown in Figure 24 and the qualitative characterizations of the stained coating surface are shown in Table 20.

**Table 20: Formulations of solution P, I, O and J**

<b>Solution No.</b>	<b>Total Volume</b>	<b>Ethanol</b>	<b>Acetic acid water solution</b>	<b>Chitosan</b>
P	100 ml	35,4 %	4,02 %	2,0 %
I	100 ml	36,3 %	4,0 %	2,0 %
O	100 ml	37,1 %	4,02 %	2,0 %
J	100 ml	38,0 %	4,0 %	2,0 %

**Table 21: Percentage coverage of solution P, I, O and J with different rods.**

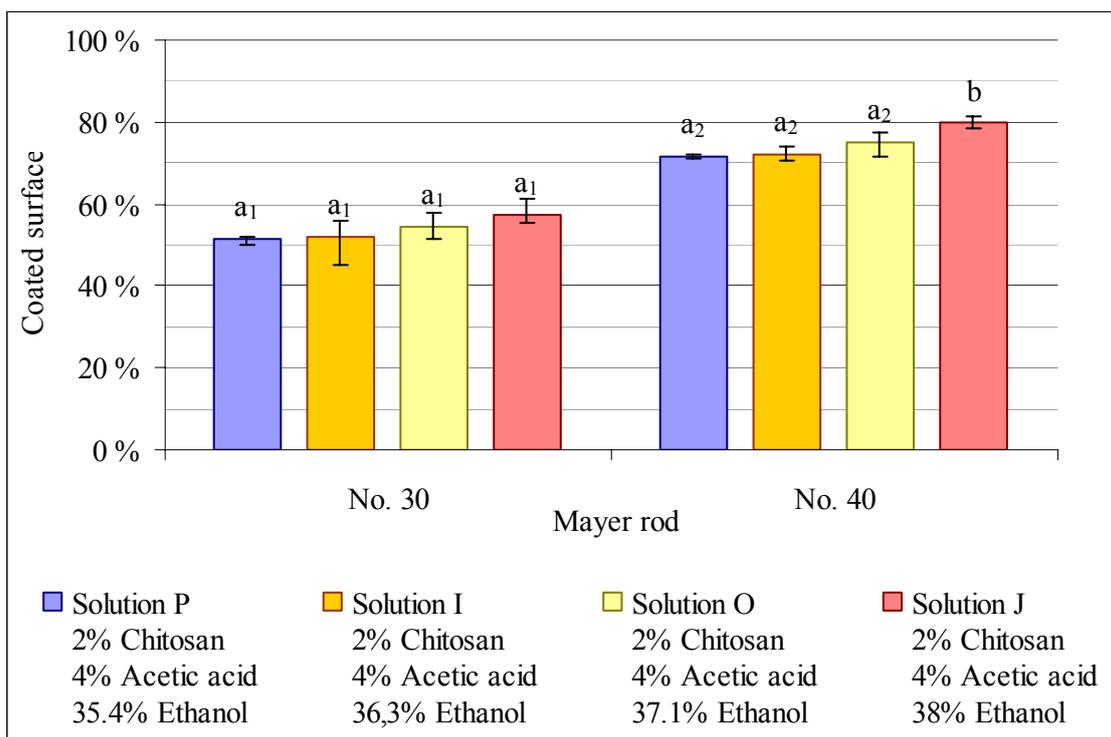
<b>Meyer rod</b>	<b>Solution P</b>	<b>Solution I</b>	<b>Solution O</b>	<b>Solution J</b>
No. 30	51.35 % (a <sub>1</sub> ) SD 1.0654 %	51.84 % (a <sub>1</sub> ) SD 4.9133 %	54.51 % (a <sub>1</sub> ) SD 2.7590 %	57.41 % (a <sub>1</sub> ) SD 2.5707 %
No. 40	71.53 % (a <sub>2</sub> ) SD 0.4110 %	72.18 % (a <sub>2</sub> ) SD 1.3677 %	74.80 % (a <sub>2</sub> ) SD 2.5665 %	79.72 % (b) SD 1.1248 %

**Table 22: Visual characterization of the drawdowns of solution P, I, O and J**

<b>Mayer rod</b>	<b>Solution P</b>	<b>Solution I</b>	<b>Solution O</b>	<b>Solution J</b>
No. 30	Small border	Small border	Small border	Big fisheyes
No. 40	Big fisheyes	Big fisheyes	Some spots	Fisheyes

Solutions P, O, J and I increased the percent coverage up to 80 %. The higher content of chitosan and acid (by a factor of four) was the cause for the increase in coverage. The increase of ethanol between these formulae of around 3 % appears to give an 8 % higher percentage of the coating area, but this is not supported by the statistics in each case. For Mayer rod 30, the 4 ethanol concentrations are not significantly different from each other. For Mayer rod 40, only the highest ethanol concentration (solution J) is statistically different from the rest.

This suggests that the influence of ethanol is dependent on the chitosan and acid ratios. The doubling of the amounts of chitosan and acid gave the first viable options for coating and increased the coated area up to 80 %.



**Figure 27: Percent coverage of the coated surface for solutions P, I, O and J**

It was again observed that the variation in the percent coverage decreased when the amount of applied coating (Mayer rod number) increases. This verified that a higher rod number gave a better coating. An improvement of roughly 20 % coverage was observed between rods 30 and 40.

### **Influence of the ratio of chitosan and acetic acid solution**

The ratio between the volume of the chitosan/acetic acid solution and the ethanol were studied for their effect on percent coverage. The influence of the chitosan and acid ratio was tested by raising the amount of acetic acid solution and chitosan. The chitosan ratio was varied from 1 % to 3 %. The w/v ratio of 1:2 between chitosan and acetic acid solution was maintained at a constant. The ratio of ethanol was nearly constant between 35 %  $\pm$ 0.5 %. The target was to find the threshold

volume of the chitosan and acid ratio. The ratios of the solution mixed are shown in Table 23. The results, sorted by the ratio of acid are presented in Table 24, with visual characterization presented in Table 25.

**Table 23: Formulation of solutions G, K, P and H**

<b>Solution No.</b>	<b>Total Volume</b>	<b>Ethanol</b>	<b>Acetic acid water solution</b>	<b>Chitosan</b>
G	100 ml	34,5 %	2 %	1,0 %
K	100 ml	33,5 %	3,0 %	1,5 %
P	100 ml	35,4 %	4,02 %	2,0 %
H	100 ml	35,2 %	6,0 %	3,0 %

**Table 24: Percent coverage of solutions G, K, P and H with different rods**

<b>Meyer rod</b>	<b>Solution G</b>	<b>Solution K</b>	<b>Solution P</b>	<b>Solution H</b>
No. 30	30.32 % (a <sub>1</sub> ) SD 0.8259 %	48.34 % (b <sub>1</sub> ) SD 2.0744 %	51.35 % (b <sub>1</sub> , c <sub>1</sub> ) SD 1.0654 %	54.96 % (c <sub>1</sub> ) SD 2.8733 %
No. 40	41.98 % (a <sub>2</sub> ) SD 2.4696 %	69.03 % (b <sub>2</sub> ) SD 3.9397 %	71.53 % (b <sub>2</sub> ,c <sub>2</sub> ) SD 0.4110 %	77.32 % (c <sub>2</sub> ) SD 2.1304 %

**Table 25: The characterization of the drawdown of solution G, K, P and H**

<b>Mayer rod</b>	<b>Solution G</b>	<b>Solution K</b>	<b>Solution P</b>	<b>Solution H</b>
No. 30	Small border	Small border	Small border	Small border
No. 40	Small border	Big fisheyes	Big fisheyes	Big fisheyes

The Figures 28 and 29 show the change between the ratio of chitosan and the percent coverage. A fairly large increase of coverage appears to be a result of going from 1 % chitosan (formula G) to 1.5 % chitosan (formula K), and further increases in chitosan offer less dramatic improvement. This is supported by the statistics as shown by statistical grouping in the figures.

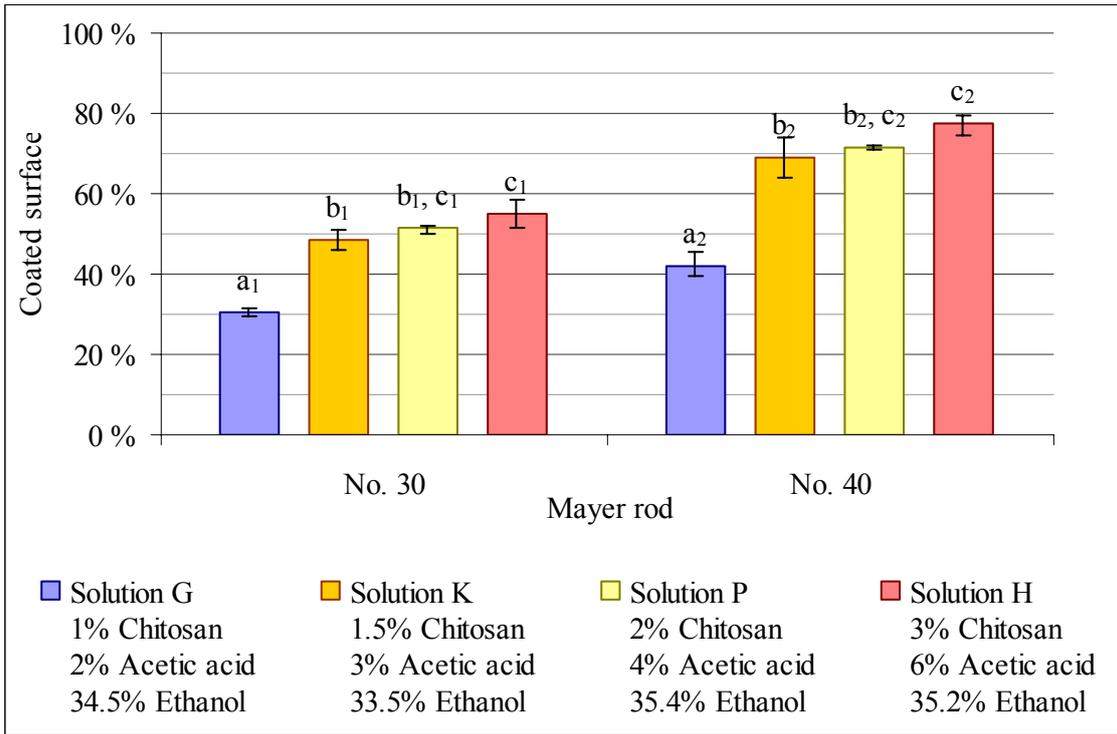


Figure 28: Percent coverage for solutions G, K, P and H with an increasing chitosan acid ratio

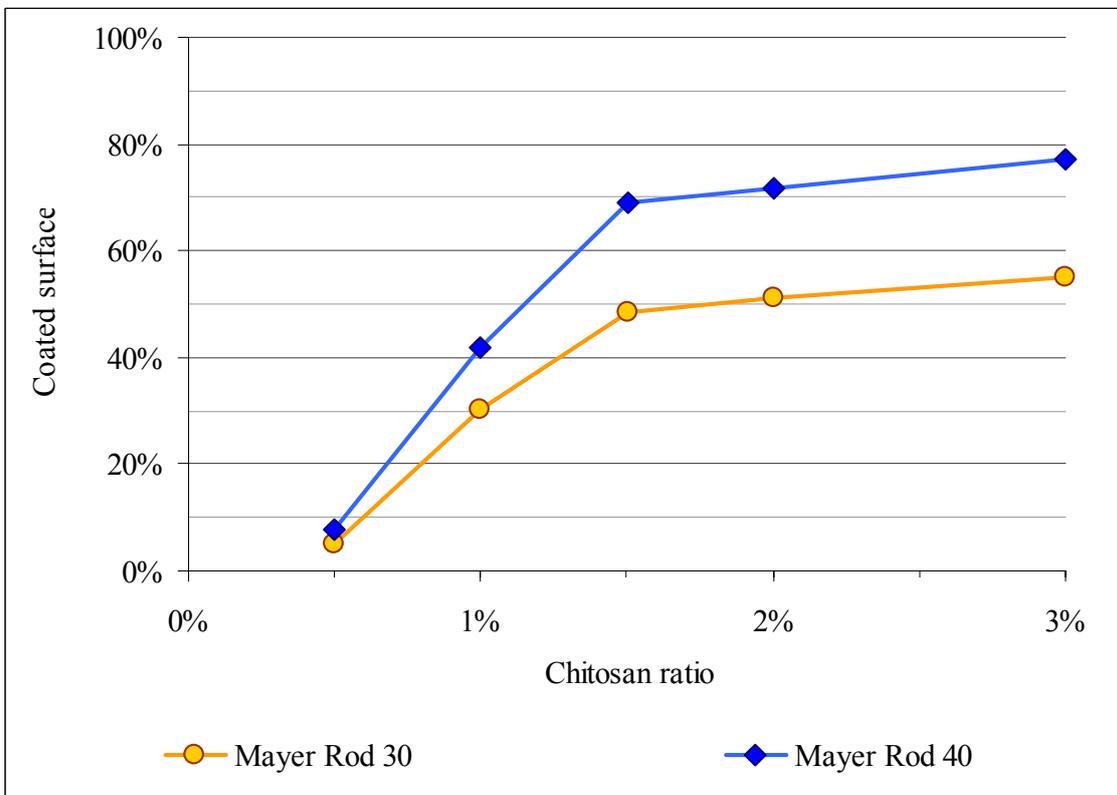


Figure 29: Percent coverage related to the chitosan amount

### **Influence of the balance between acetic acid and ethanol**

With a constant chitosan percentage of 1.5 %, formula adjustments were made to increase the acetic acid ratio and decrease the ethanol volume (Table 26). These results are shown in Table 27 and 28. The ratio of acid in the acid water solution varied between 3 % and 9 %, while the concentration of ethanol was decreased at three values between 33.5 % and 29.5 %.

**Table 26: Formulations of solution K, L, und M**

<b>Solution No.</b>	<b>Total Volume</b>	<b>Ethanol</b>	<b>Acetic acid water solution</b>	<b>Chitosan</b>
K	100 ml	33,5 %	3,0 %	1,5 %
L	100 ml	31,5 %	6,0 %	1,5 %
M	100 ml	29,5 %	9,0 %	1,5 %

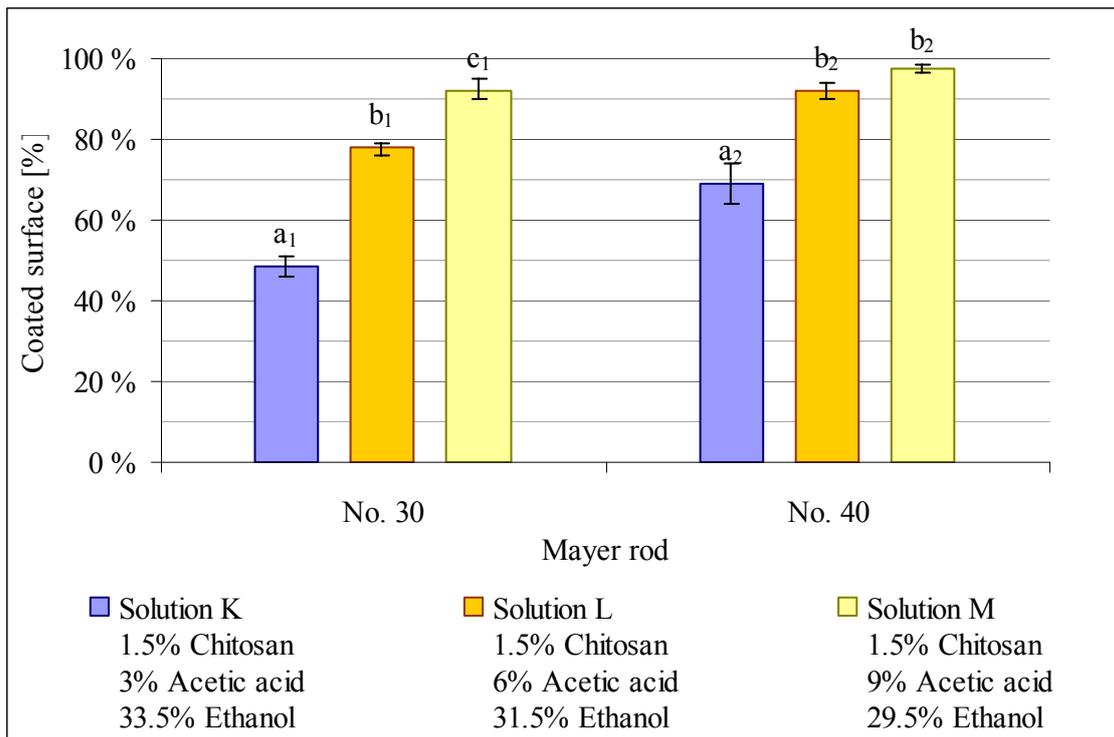
**Table 27: Percent coverage with solutions K, L and M**

<b>Meyer rod</b>	<b>Solution K</b>	<b>Solution L</b>	<b>Solution M</b>
No. 30	48.34 % (a <sub>1</sub> ) SD 2.0744 %	77.86 % (b <sub>1</sub> ) SD 1.5094 %	91.88 % (c <sub>1</sub> ) SD 2.3518 %
No. 40	69.03 % (a <sub>2</sub> ) SD 3.9397 %	92.20 % (b <sub>2</sub> ) SD 1.5160 %	97.38 % (c <sub>2</sub> ) SD 0.8425 %

**Table 28: Visual classification of solutions K, L and M**

<b>Mayer rod</b>	<b>Solution K</b>	<b>Solution L</b>	<b>Solution M</b>
No. 30	Small border	Small fisheyes	Small fisheyes
No. 40	Big fisheyes	Small fisheyes	Some spots

Figure 27 shows the percent coverage changes with respect to increasing acid to ethanol ratios and with coating weight (Mayer rod). From the graph, it can be seen that, within the range tested, the ethanol to acetic acid ratio affects the percent coverage, although with higher coating weights, the effects become less pronounced.



**Figure 30: Coated Ratio between ethanol and acetic acid**

#### 6.4. Gravure roll coating

All gravure roll coatings were applied to the treated LDPE side of the PET/LDPE laminations. Since the gravure coating system requires different coating properties from those required for Mayer rod coating, additional formulations were made specifically for gravure coating. The formulae for solutions Q, R and T can be seen in the Table 29.

**Table 29: Formulations for solutions Q, R and T**

<b>Solution</b>	<b>Chitosan</b>	<b>Ethanol</b>	<b>Acetic acid water solution</b>
Solution R	5 %	35 %	8 % acid in 2400ml
Solution Q	5 %	30 %	8 % acid in 2600ml
Solution T	5 %	15 %	13 % acid in 3200ml

The line or web speeds were varied from 25 to 200 feet per minute, depending on the coating conditions. The temperatures reported in this work were the dryer set point temperatures, since measurements of the real web temperature are difficult and exhibited high variation. The percent coverage and visual observations of the coating quality for each run are shown in Tables 30 to 33.

**Table 30: Gravure roll parameter and coating condition for solution Q and 85Q**

<b>Run No.</b>	<b>Roll [Q]</b>	<b>Test solution</b>	<b>Dryer air pressure</b>	<b>Dryer 1 setting</b>	<b>Dryer 2 setting</b>	<b>Web speed</b>	<b>Coating Condition</b>
Q01	85	Q	22 psi	175°F	180°F	25 fpm	Dry
Qx1	85	Q	22 psi	175°F	180°F	50 fpm	Wet
Qx2	85	Q	22 psi	180°F	195°F	50 fpm	Wet
Qx3	85	Q	22 psi	195°F	200°F	50 fpm	Wet
Qx4	85	Q	22 psi	195°F	200°F	35 fpm	Wet
Q02	85	Q	22 psi	175°F	200°F	25 fpm	Dry
Q03	85	Q	22 psi	175°F	200°F	35 fpm	Dry

Solution Q: 5% Chitosan; 30% ethanol; 8% acetic acid solution

**Table 31: Gravure roll parameter and coating condition for solution Q and 150Q**

<b>Run No.</b>	<b>Roll [Q]</b>	<b>Test solution</b>	<b>Dryer air pressure</b>	<b>Dryer 1 setting</b>	<b>Dryer 2 setting</b>	<b>Web speed</b>	<b>Coating condition</b>
Q04	150	Q	22 psi	175°F	180°F	25 fpm	Dry
Q05	150	Q	22 psi	175°F	180°F	35 fpm	Dry
Q06	150	Q	22 psi	175°F	180°F	50 fpm	Dry
Q07	150	Q	22 psi	175°F	200°F	75 fpm	Dry
Qx8	150	Q	22 psi	175°F	180°F	100 fpm	Wet
Q09	150	Q	22 psi	175°F	180°F	75 fpm	Wet

Solution Q: 5% Chitosan; 30% ethanol; 8% acetic acid solution

**Table 32: Gravure roll parameter and coating condition for solution R and 200Q**

<b>Run No.</b>	<b>Roll [Q]</b>	<b>Test solution</b>	<b>Dryer air pressure</b>	<b>Dryer 1 setting</b>	<b>Dryer 2 setting</b>	<b>Web speed</b>	<b>Coating Condition</b>
R01	200	R	12 psi	175°F	200°F	25 fpm	Dry
R02	200	R	12 psi	175°F	200°F	50 fpm	Dry
R03	200	R	12 psi	175°F	200°F	75 fpm	Dry
R04	200	R	12 psi	175°F	200°F	100 fpm	Dry
R05	200	R	12 psi	175°F	200°F	150 fpm	Dry
Rx1	200	R	12 psi	175°F	200°F	200 fpm	Wet
Rx2	200	R	12 psi	175°F	200°F	175 fpm	Wet
Rx3	200	R	12 psi	200°F	200°F	175 fpm	Wet

Solution R: 5% Chitosan; 35% ethanol; 8% acetic acid solution

**Table 33: Gravure roll parameter and coating condition for solution T and 200Q**

<b>Run No.</b>	<b>Roll [Q]</b>	<b>Test solution</b>	<b>Dryer air pressure</b>	<b>Dryer 1 setting</b>	<b>Dryer 2 setting</b>	<b>Web speed</b>	<b>Coating Condition</b>
T01	200	T	12 psi	175°F	200°F	25 fpm	Dry
T02	200	T	12 psi	175°F	200°F	75 fpm	Dry
T03	200	T	12 psi	175°F	200°F	100 fpm	Dry
T04	200	T	12 psi	175°F	200°F	50 fpm	Dry

Solution T: 5% Chitosan; 15% ethanol; 8% acetic acid solution

### **Overview of the results with gravure roll coating**

The tests of the percent coverage on the gravure coated samples follow the same steps as those used for the Mayer rod coated substrates. Table 34 presents the mean results for each solution and gravure roll / or run. Table 34 is comprehensive and somewhat difficult to interpret, so these data have been excerpted in Tables 20 through 41. In Table 34 are some runs not tested the reason is explained in the next pages.

**Table 34: All results for dry coating condition**

<b>Run No.</b>	<b>Roll [Q]</b>	<b>Web speed</b>	<b>Coating weight</b>	<b>Tape test Average Load</b>	<b>Percent coverage</b>
Q01	85	25 fpm	0.626 lb/ream	not tested	not tested
Q02	85	25 fpm	0.676 lb/ream	9.8061 N	99.99 %
Q03	85	35 fpm	0.692 lb/ream	9.6734 N	100 %
Q04	150	25 fpm	0.284 lb/ream	8.2132 N	99.15 %
Q05	150	35 fpm	0.274 lb/ream	8.3027 N	98.80 %
Q06	150	50 fpm	0.248 lb/ream	8.0240 N	95.53 %
Q07	150	75 fpm	0.256 lb/ream	8.3686 N	92.47 %
R01	200	25 fpm	0.190 lb/ream	8.4776 N	99.47 %
R02	200	50 fpm	0.160 lb/ream	8.2646 N	99.53 %
R03	200	75 fpm	0.190 lb/ream	7.6462 N	98.40 %
R04	200	100 fpm	0.160 lb/ream	8.3350 N	97.93 %
R05	200	150 fpm	0.173 lb/ream	8.3542 N	97.70 %
T01	200	25 fpm	1.148 lb/ream	8.6500 N	not tested
T02	200	75 fpm	1.496 lb/ream	7.4141 N	not tested
T03	200	100 fpm	0.462 lb/ream	9.6225 N	not tested
T04	200	50 fpm	1.142 lb/ream	9.5865 N	not tested

Solution Q: 5% Chitosan; 30% ethanol; 8% acetic acid solution;

Solution R: 5% Chitosan; 35% ethanol; 8% acetic acid solution;

Solution T: 5% Chitosan; 15% ethanol; 8% acetic acid solution

### **Effect of the gravure roll engraving on applied weight**

The effect of the gravure roll engraving was studied with respect to the applied coating weight. These tests were run with solution Q and the 85 and 150Q cylinders. As expected, the 85Q cylinder applied more weight and had slightly higher variability than the 150Q cylinder. These results are shown in Tables 35 and 36. The results for the coating weight of run R and T with a 200Q gravure roll shown in Table 37 and 38.

**Table 35: Coating weight in lb/ream for solution Q, (gravure roll 85Q)**

<b>Run no.</b>	<b>Gravure roll</b>	<b>Solution</b>	<b>Mean</b>	<b>Std dev</b>
Q01	85Q	Q	0.626 lb/ream	0.108 lb/ream
Q02	85Q	Q	0.676 lb/ream	0.038 lb/ream
Q03	85Q	Q	0.692 lb/ream	0.052 lb/ream

Solution Q: 5% Chitosan; 30% ethanol; 8% acetic acid solution

**Table 36: Coating weight in lb/ream for solution Q, (gravure roll 150Q)**

<b>Run no.</b>	<b>Gravure roll</b>	<b>Solution</b>	<b>Mean</b>	<b>Std dev</b>
Q04	150Q	Q	0.284 lb/ream	0.039 lb/ream
Q05	150Q	Q	0.274 lb/ream	0.022 lb/ream
Q06	150Q	Q	0.248 lb/ream	0.019 lb/ream
Q07	150Q	Q	0.256 lb/ream	0.033 lb/ream

Solution Q: 5% Chitosan; 30% ethanol; 8% acetic acid solution

**Table 37: Coating weight in lb/ream for solution R, (gravure roll 200Q)**

<b>Run no.</b>	<b>Gravure roll</b>	<b>Solution</b>	<b>Mean</b>	<b>Std dev</b>
R01	200Q	R	0.190 lb/ream	0.022 lb/ream
R02	200Q	R	0.160 lb/ream	0.022 lb/ream
R03	200Q	R	0.190 lb/ream	0.022 lb/ream
R04	200Q	R	0.160 lb/ream	0.014 lb/ream
R05	200Q	R	0.173 lb/ream	0.017 lb/ream

Solution R: 5% Chitosan; 35% ethanol; 8% acetic acid solution

**Table 38: Coating weight in lb/ream for solution T, (gravure roll 200Q)**

<b>Run no.</b>	<b>Gravure roll</b>	<b>Solution</b>	<b>Mean</b>	<b>Std dev</b>
T01	200Q	T	1.148 lb/ream	0.557 lb/ream
T02	200Q	T	1.496 lb/ream	0.855 lb/ream
T03	200Q	T	0.462 lb/ream	0.553 lb/ream
T04	200Q	T	1.142 lb/ream	0.629 lb/ream

Solution T: 5% Chitosan; 15% ethanol; 8% acetic acid solution

Some runs were not included in this analysis. As can be seen in Tables 35, 36 and 38, some of the combinations of speed, drying temperature, cylinders and formulae resulted in coatings that were not sufficiently dry or were too variable to be usable. For example, the standard deviation for the coating weight for run Q01 was 17 % of the mean value. The coating weight standard deviations for all trials using T were around 50 % of the mean values. In the case of solution Q, a coating that wets out pretty well, the source of the high variability was due to drying. For solution T, a coating that dried well, the low percentage of ethanol prevented sufficient wetting. These combinations were excluded from further analysis.

#### **Effect of web speed / dryer residence time**

The residence time in the dryer on a coating line is related to the web speed (fpm) and the length of the drying oven (drying area). At low speeds, the coated web spends more time in the drying oven, and thus has more opportunity to dry. The status of the drying from these experiments is shown in Table 39. From this Table, the speed at which each solution / gravure roll combination resulted in sufficient residence time could be ascertained. The speed of 35 fpm was not tested for solution R and T but it can be surmised that if the coating was sufficiently dry at higher speeds, then 35 fpm would have been sufficient to dry.

**Table 39: Web speed [fpm] and dry / wet border**

<b>Solution</b>	<b>Q</b>	<b>Q</b>	<b>R</b>	<b>T</b>
Gravure roll size	85Q	150Q	200Q	200Q
Dryer air pressure	22 psi	22 psi	12 psi	12 psi
Dryer 1/2 temperature	175/200°F	175/180°F	175/200°F	175/200°F
Coating with 25 fpm	Dry	Dry	Dry	Dry
Coating with 35 fpm	Dry	Dry	Dry	Dry
Coating with 50 fpm	Wet	Dry	Dry	Dry
Coating with 75 fpm	Wet	Wet	Dry	Wet
Coating with 100 fpm	Wet	Wet	Dry	Wet
Coating with 150 fpm	Wet	Wet	Dry	Wet
Coating with 175 fpm	Wet	Wet	Wet	Wet

Solution Q: 5% Chitosan; 30% ethanol; 8% acetic acid solution;  
Solution R: 5% Chitosan; 35% ethanol; 8% acetic acid solution;  
Solution T: 5% Chitosan; 15% ethanol; 8% acetic acid solution.

These results are not directly comparable, because of the change of solutions, temperature and gravure rolls. However, the minimum residence time for a certain gravure cylinder and temperature can be determined. Also, it appeared that the coated material may have fitness for use under real conditions such as up to 150 feet per minute. This showed promise, from a commercial standpoint, which the hand-dried Mayer rod system could not demonstrate.

### **Effect of “line speed” on percent coverage for solution Q**

Table 40 and Figure 31 demonstrate the relationship between web speed and coating surface percent coverage for solution Q with gravure rolls engraved at 150Q. The same analysis was conducted for the 85Q roller and is displayed in Table 41 and Figure 31.

**Table 40: Machine settings and coverage of solution Q (150Q) with different line speed**

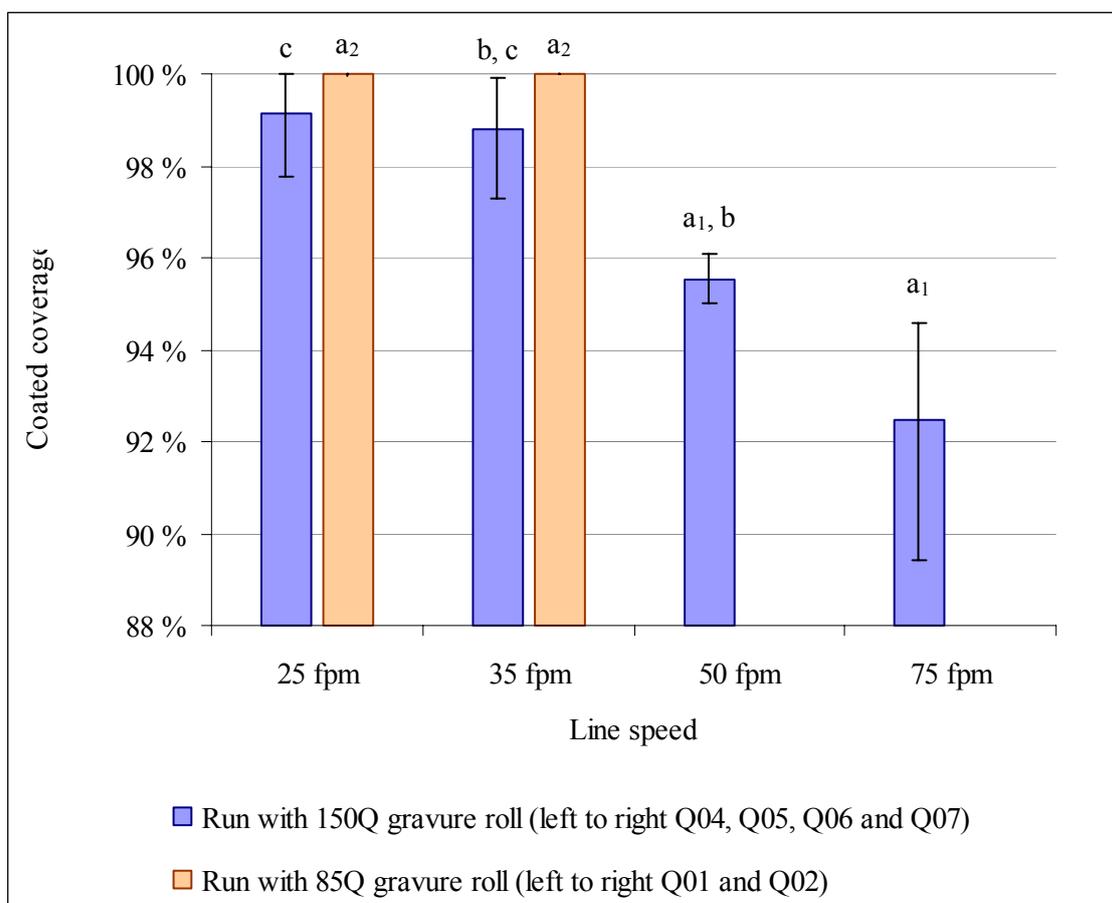
Run no.	Gravure roll	Dryer air pressure	Dryer 1 setting	Dryer 2 setting	Web Speed	Coated Coverage mean	Coated Coverage SD
Q04	150Q	22 psi	175°F	180°F	25 fpm	99.15 % (c)	0.9827 %
Q05	150Q	22 psi	175°F	180°F	35 fpm	98.80 % (b, c)	1.0985 %
Q06	150Q	22 psi	175°F	180°F	50 fpm	95.53 % (a, b)	0.4497 %
Q07	150Q	22 psi	175°F	200°F	75 fpm	92.47 % (a)	2.2231 %

Solution Q: 5% Chitosan; 30% ethanol; 8% acetic acid solution

**Table 41: Machine settings and coverage of solution Q (85Q) with different line speed**

Run no.	Gravure roll	Dryer air pressure	Dryer 1 setting	Dryer 2 setting	Web Speed	Coated Coverage mean	Coated Coverage SD
Q01	85Q	22 psi	175°F	200°F	25 fpm	99.99 % (a)	0.01 %
Q02	85Q	22 psi	175°F	200°F	35 fpm	100,00 % (a)	0.01 %

Solution Q: 5% Chitosan; 30% ethanol; 8% acetic acid solution

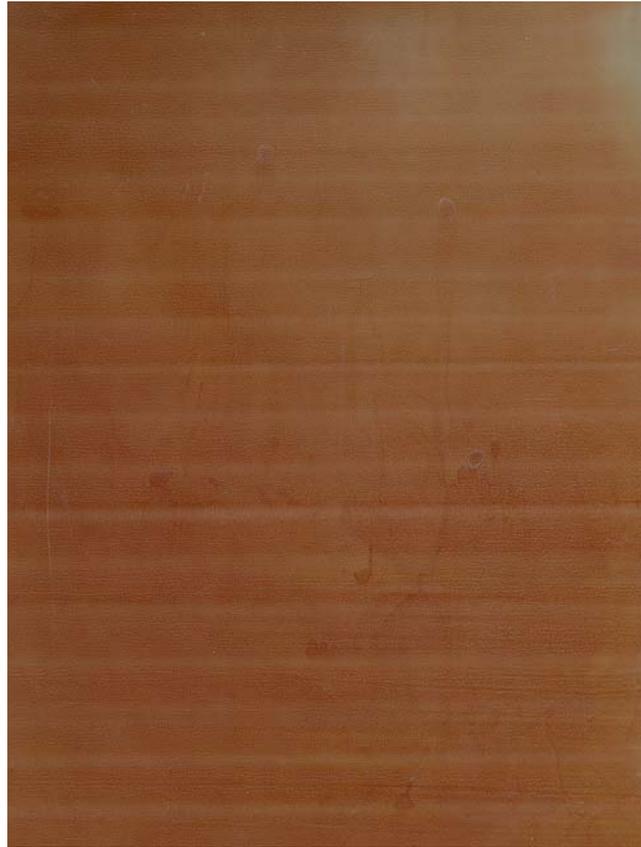


**Figure 31: Percent coverage vs. line speed with solution Q**

The variation of the percent coverage in run Q01 and Q02 was negligible. A run with 85Q gravure roll and a higher line speed than 35 fpm was never successful due to drying issues. Different temperature combinations were tested up to 225°F without completely drying the coating.

Runs between 25 and 75 fpm with the 150Q cylinder showed statistical differences between the maximum and minimum speeds, although the intermediate speeds show less definite differences. The variation in the percent coverage of run Q07 with 75 fpm was close to double the variation at 25 or 35 fpm. Perhaps the coating was not totally dry, but the stained film test showed another reason. The dryers utilize both temperature and air flow to get a dry coating. For samples, it appears that the air pressure in the dryer “pushed” the wet coating away from the point where the air contacts the surface. While there was not enough air pressure to move all of the coating, it could produce thick and thin spots of coating. This is demonstrated in Figure 32.

This effect could be reduced by changing the machine parameters. The drying temperature was increased in the second dryer to 200°F and the air-pressure was reduced to 12 psi, the lowest possible level for both dryers, for the subsequent runs. The effect could also be reduced by the line speed, altering the relation between the time that the air pressure has to push the coating and the total time that the coating has to dry.



**Figure 32: Excerpt of a with 150Q gravure roll, 75 fpm and solution Q coated substrate**

### **Effect of line speed on percent coverage with solution R**

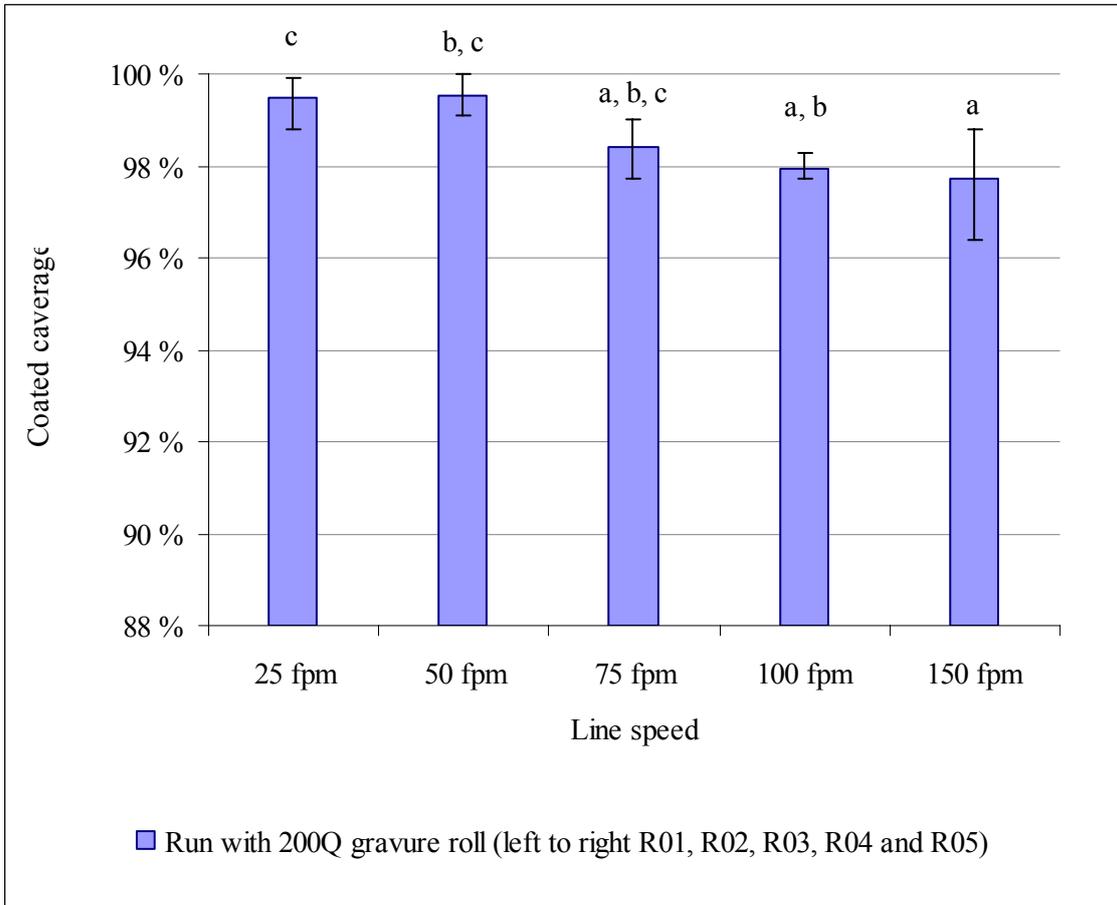
The stripe effects discussed above were shown by all other runs, but by reducing of the line speed the variation was decreased. A test was run to see if the stripe effect could be decreased or eliminated by increasing the ratio of ethanol, as tested with solution R. To get a thinner coating, the 200Q gravure roll was chosen. The relationship between line speed and percent coverage for solution R with a 200Q roll is presented in Table 42 and Figure 33.

**Table 42: Machine settings and coverage of solution R with different line speeds**

<b>Run no.</b>	<b>Gravure roll</b>	<b>Dryer air pressure</b>	<b>Dryer 1 setting</b>	<b>Dryer 2 setting</b>	<b>Line speed</b>	<b>Coated coverage mean</b>	<b>Coated Coverage SD</b>
R1	200 Q	12 psi	175°F	200°F	25 fpm	99.47 % (c)	0.4784 %
R2	200 Q	12 psi	175°F	200°F	50 fpm	99.53 % (b, c)	0.3682 %
R3	200 Q	12 psi	175°F	200°F	75 fpm	98.40 % (a, b, c)	0.5354 %
R4	200 Q	12 psi	175°F	200°F	100 fpm	97.93 % (a, b)	0.2625 %
R5	200 Q	12 psi	175°F	200°F	150 fpm	97.70 % (a)	0.9899 %

Solution R: 5% Chitosan; 35% ethanol; 8% acetic acid solution

Again, the percent coverage is shown in Figure 33 to be dependent on the line speed, as the minimum and maximum line speeds show to be statistically different. The differences are very small however. It was also noticed that, at the highest line speed (150 fpm), the variability was again significantly higher. It is important to note that the data for solution R showed slightly less than 100 percent coverage. This can be explained by the procedure of the measurement. Very thin coatings are more sensitive to the influence of the stain process. Smallest mistakes such dust, surface contact, touching (like fingerprints) and small variations in the stain process resulted in variations in the scanned samples. Coating defects such as fisheyes were not evident in the samples analyzed with solution R. Visual observation of these samples showed that the existing variation of around 98 %  $\pm$  2 % percent coverage demonstrated an even, smooth coating with very high coverage. This is contrast to the fisheyes and other visual defects seen and discussed in the previous sections regarding Mayer rod coating. Figure 33 present the average and the variation of the coverage surface of each run with solution R.



**Figure 33: Percent coverage vs. line speed with solution R**

That the line speed has an influence on the quality of the coating is demonstrated in the tests of both solutions Q and R. The difference between test runs Q02-Q05 and R01-R05 was a 5 % higher ethanol ratio and that the gravure roll has 50 lines more per inch. The coating is, on the average of 0.09 lb/ream thinner, but the standard deviation is nearly the same (0.0142 lb/ream for run Q02-Q05 and 0.0134 lb/ream for R01-R05). With these data, it cannot be concluded whether the effect of striping was reduced by the lower weight or the addition of ethanol.

### Effect of line speed on drying

Coating weight and line speed are often inter-related. Higher coating weights can be dried by running more slowly. Lower coating weights can be dried at higher speed. In this process, drying issues are often manifested as a coating that was physically wet to touch. However, it was noted during the running that, before this point was reached, coating quality and applied weights increased in variability. Using this observation and the data in Table 39, a maximum speed was developed for each gravure cylinder. Figure 34 shows the maximum speeds at which the coating was effectively dried.

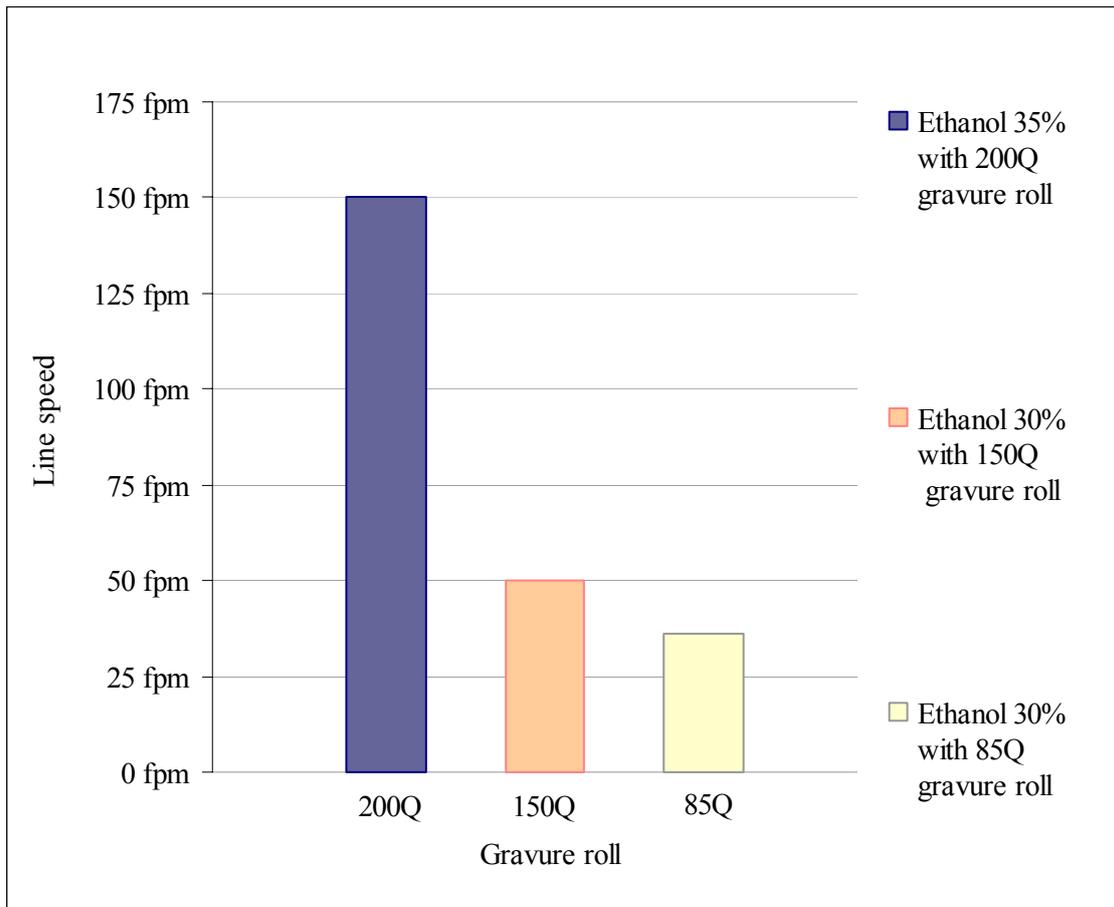


Figure 34: The different line speed in relation to the coating condition

Since, the ethanol percentage used at 200Q with up to 150 fpm was different; it is not possible to state conclusively that applied weight is the only factor. However, it is common knowledge in the converting industry that the time needed to dry depends on the volume (mass) that has to evaporate.

### **Drying process**

Coverage of the substrate with the Mayer rod was not comparable to the gravure roll samples. The reasons for this included the difference in the application of the solution and the drying process.

The manual drawdown gave the coating solution much more time to bead up before the drying process was started. The drying process with the gravure roll coating machine started drying just seconds after the application, depending on the line speed.

The distance between the applying the coating with the gravure roll and the first dryer unit was 6 feet. This is around 7 seconds for the coating solution to bead up at a 50 fpm line speed. In manual coating with Mayer rods, many more steps and much more time (around 20 seconds) existed between coating and drying.

Another difference existed in the drying process. On the coating machine used, the dryer blower had air circulation and the web did not need to be held down to prevent curling. Also, the dryer air on a coating line is in close contact with the web surface, which is not the case with manual coating and drying systems.

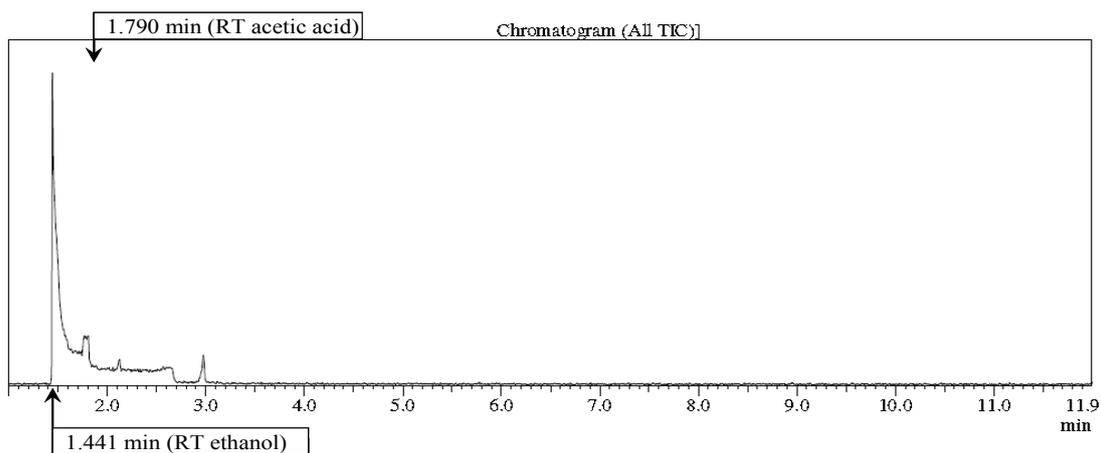
**Table 43: Line speed vs. drying time**

<b>Line speed</b>	<b>Time from the coater to the dryer</b>	<b>Dryer residence time</b>
25 fpm	14,4 sec	7,2 sec
35 fpm	10,3 sec	5,1 sec
50 fpm	7,2 sec	3,6 sec
75 fpm	4,8 sec	2,4 sec
100 fpm	3,6 sec	1,8 sec
150 fpm	2,4 sec	1,2 sec
175 fpm	2,1 sec	1,0 sec

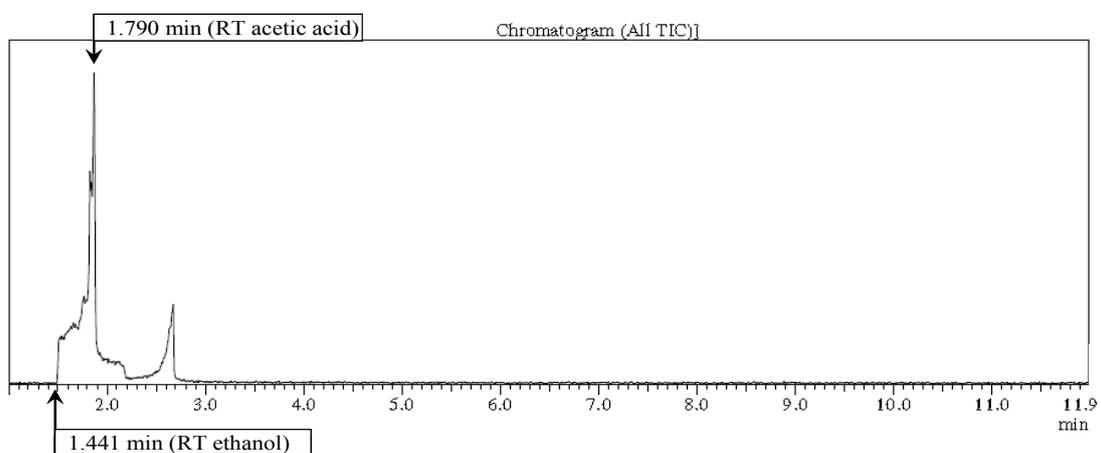
### **Testing the dry coating for retained ethanol**

To test for the presence of ethanol after drying in the gravure roll coating, the coated films were analyzed with a Gas Chromatograph Mass Spectrometer (GS-2010 SHIMADZU). Applied coating of each solution (Q and R) and the liquid samples of solutions Q and R were tested. The coating itself (five samples which an area 7 in<sup>2</sup>) was washed off of the film surface with 0.8 ml acetic acid solution (50 % v/v). The coating washed off was diluted in 99 % deionized distilled water. The volume of the GC injection was 2 ml. All tests of the dried coating showed little retention with respect to retained ethanol. The ethanol was sufficiently evaporated with the drying at the gravure roll coater. The test Chromatograms are shown in Figures 35 to 37.

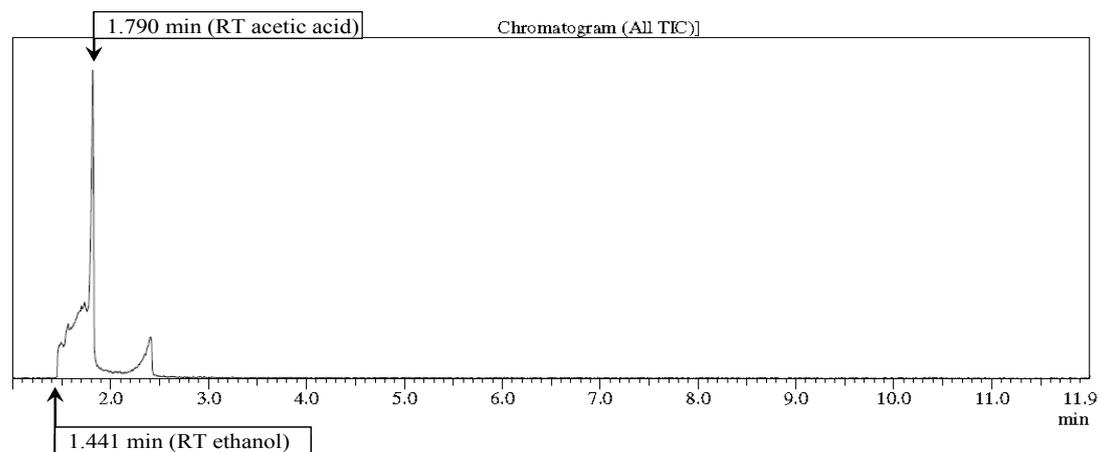
At the x-axis show the time in minutes and the y- axis the total ion count. The measured retention time (RT) for ethanol is 1.441 minutes and for acetic acid is 1.790 minutes, both marked in the follow Figures with an arrow.



**Figure 35: Test solution with ethanol 30 % and acid water solution 5 % without chitosan**



**Figure 36: Run Q02 with solution Q and gravure roll 85Q (85Q the highest coating amount for solution Q)**



**Figure 37: Run R01 with solution R and gravure roll 200Q (200Q the highest coating amount for solution R)**

### Adhesion- Tape test Scotch <sup>TM</sup> 610 (ASTM F2252)

All coated substrates passed this test with no removal of the coating. The force to remove the tape strip was measured in a second test in order to define a numerical value that the coating adhesion exceeds.

**Table 44: Tape test and the measurements of the force it needs to take the tape off**

Run no.	Tape test ASTM F2252	Average Load	Average Load
Q13	Passed	0.9999 Kgf	9.8061 N
Q14	Passed	0.9864 Kgf	9.6734 N
Q02	Passed	0.8375 Kgf	8.2132 N
Q03	Passed	0.8466 Kgf	8.3027 N
Q04	Passed	0.8182 Kgf	8.0240 N
R01	Passed	0.8645 Kgf	8.4776 N
R02	Passed	0.8428 Kgf	8.2646 N
R03	Passed	0.7797 Kgf	7.6462 N
R04	Passed	0.8499 Kgf	8.3350 N
R05	Passed	0.8519 Kgf	8.3542 N

Solution Q: 5% Chitosan; 30% ethanol; 8% acetic acid solution;  
Solution R: 5% Chitosan; 35% ethanol; 8% acetic acid solution;  
Solution T: 5% Chitosan; 15% ethanol; 8% acetic acid solution.

The adhesion of the dry coating was high, i.e. all tape tests showed that the coating never separated from the surface. This was the reason to test the force which was needed to remove the tape at a 180° angle. After the tape tests, the coating continuity was tested with staining of the coating.

The iodine stain separated internally, but remained on both surfaces, indicating that the solution was adhered to the surface. It was observed that a few samples showed a separation of the adhesive from the tape to the coating. There was no evidence of blocking (adhesion between wraps) in the rolls of chitosan coated films.

### **Heat seal strength of chitosan coated substrate**

All chitosan coated substrates showed no ability to heat seal. The separation started after sealing with no added force. The tested jaw temperatures were 180°F to 260°F, jaw pressure 40 psi and dwell times between 1 to 5 seconds. All chitosan coated samples (gravure roll and Mayer rod) failed to seal. It was impossible to measure any strength due to this.

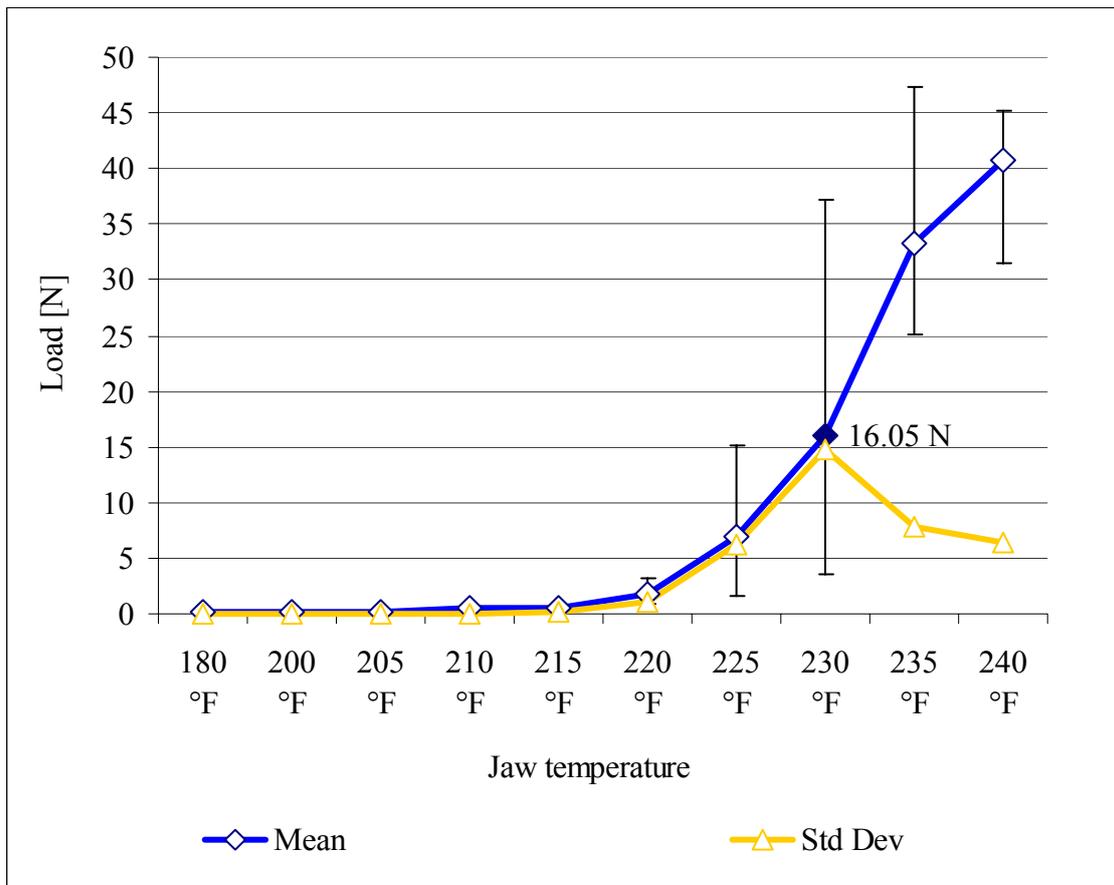
### **Heat seal strength of uncoated substrate**

The heat seal curves for the corona treated lamination were done with one second dwell times and a temperature range between 180°F and 240°F. The jaw pressure was 30 lbs. The seal jaw used was a flat, one inch wide bar, 10 inches long.

For samples sealed above 225°F, the strength layer (PET) broke and the seal layer (PECOEX) stretched by elongation. The curve (Figure 38) of the standard deviation showed that the SD increased when the force was due only to the elongation of the PE COEX layer, (after the PET layer broke).

**Table 45: Sealing temperature vs. load**

Sealing temperature	Load mean	Std. dev	Maximum load	Minimum load
180 °F	0,205 N	0,022 N	0.227 N	0.178 N
200 °F	0,247 N	0,044 N	0.308 N	0.181 N
205 °F	0,247 N	0,040 N	0.319 N	0.204 N
210 °F	0,464 N	0,040 N	0.513 N	0.412 N
215 °F	0,474 N	0,153 N	0.777 N	0.368 N
220 °F	1,749 N	1,033 N	3.199 N	0.853 N
225 °F	7,016 N	6,274 N	15.092 N	1.529 N
230 °F	16,048 N	14,797 N	37.244 N	3.646 N
235 °F	33,333 N	7,873 N	47.259 N	25.045 N
240 °F	40,669 N	6,483 N	45.253 N	31.501 N



**Figure 38: Heat seal curve of corona treated and uncoated lamination with a 1 sec dwell time**

## **CONCLUSION**

### **Corona treatment on LDPE**

- Without raising the surface energy of the substrate it was not possible to wet the surface with the chitosan solutions developed.
- Coating with the chitosan solutions was not possible with a corona treatment less than 46 dyne/cm, the coating built a film and skinned off.
- Coating with ethanol as a wetting agent initially wetted the film surface well if the treatment level was around 50 dyne/cm, but at this level, the coating beaded up with time.
- With a corona treatment of about 52 dyne/cm, good wetting occurred with chitosan coatings containing ethanol as a wetting agent.

### **Viscosity**

- The viscosity decreased in time (12 days) and most solutions developed converged to about the same viscosity level. The rate of change of viscosity decreased with time, after 4 days the viscosity change was incremental.
- It was observed that the change in the first day was dependent on the acetic acid ratio. Higher ratios also reduced the time to get the solution to the point that it was filterable.

### **% solids**

- Based on single measurements utilized for % solids measurement, it appeared that the % solids increased over time.
- The increasing % solid variation started after 24 hours.

- This effect has been reported by others for solutions with a low evaporation point such as water/ethanol or water/acetic acid solutions.
- The increasing of the % solids in process may have been due to evaporation, but it is also likely that some sort of absorption into the chitosan may have been contributing.

### **Coating process (Mayer rod)**

- The coatability, as measured by percent coverage, was tested by drawdown with Mayer rod no. 12, 20, 30 and 40. The best results were achieved with rods 30 and 40. With Mayer rod coating, higher amounts of coating gave better results with respect to percent coverage
- Higher chitosan levels exhibited a significant effect on the surface coverage when coating with Mayer rods.

### **Solution & percent coverage**

- All testing of solutions without the wetting agent ethanol failed to wet the surface. However, higher ethanol concentration at low chitosan concentrations did not produce good percent coverage.
- Higher levels of chitosan in the solution resulted in higher percent coverage, possibly because the solution beaded up more slowly due to a somewhat higher viscosity.
- Small changes in ethanol percentage gave small or no improvement of surface wetting in cases where the chitosan percentages were higher.

- The concentration of ethanol was not the only factor affecting wetting, the ratio of acetic acid also affected wetting. The relative combinations of chitosan, acetic acid and ethanol also showed influence.
- Formulations with chitosan lower than 1.5 % were not effective to get a good percent coverage.
- The ratio of acetic acid to chitosan needed to be 2 or higher to support good coverage ability, as well as to get the chitosan into solution.

### **Gravure roll vs. Mayer rod**

- Two coating formulations, coded Q and R, were successfully machine coated on a gravure coater. Maximum speeds reached were 150 fpm. The speed limitation was at least partially related to drying.
- The gravure system showed better results in general, partly due to the fact that the Mayer rod process used for this research was done manually and the gravure application was performed on an automated machine.
- The web speed and the drying were found to be related. Manual drawdown has more steps between the application and drying.

### **Drying**

- The drying process had a direct influence on the coating quality. The sooner the drying process was begun, the better the percent coverage became, as long as the coating was completely dried.
- If the coating was not completely dry, lower quality of coating (percent coverage) was observed.

- Each solution resulted in a different optimum condition set (between coating weight, speed and temperature).
- Incompletely dry coatings were more sensitive for handling, scratched during the stain process exhibited more coating weight variation.

### **Sealing**

- All tests showed that there was no seal between chitosan coated films, independent from temperature, dwell time and pressure of the flat bars.
- The amount of the coating did not have an influence of the sealing property.
- For sealing, an area has to be free from chitosan coating.

### **Adhesion to the surface of the substrate**

- The bonding between the coating and the substrate were successful as long as the material was sufficiently dry. All samples with a dried coating passed the tape test (ASTM F2252).
- The coating may be strong enough to carry a heat seal coating or to coat partially to get sealability.

## **RECOMMENDATIONS FOR FUTURE STUDY**

Further study involving coating and sealing of flexible material with chitosan should be conducted.

### **Solution properties**

In this work, a viscosity change was measured and noted. Coatings were not applied until the solution had stabilized for at least 4 days. However, it is possible that the properties of the coating may also be changing. In future work, coatings should be applied during this viscosity change and reviewed for property differences.

It was noted that the properties changed with the levels of chitosan, acetic acid and ethanol. There is a need to optimize the balance between these components using statistical design of experiments to find the optimum levels of these ingredients.

Only acetic acid was studied in this work as the “solvent” for chitosan. Only ethanol was studied as a wetting agent. In both cases, there are many other options that may improve the coating quality and therefore need to be studied.

In this work, it appears that the % solids over time increases. However, the tests were not conducted with replication, so there are no statistics to verify this appearance. Additional work should be conducted to verify this effect, and studies should be designed to understand the mechanism behind this.

### **Coating process**

Further tests should be conducted using a patterned gravure cylinder to verify that the chitosan coating could be pattern-applied. This would allow for leaving an open area of LDPE for sealing. Other options that should be evaluated include dot

coating or strip coating with the chitosan. Such testing would allow the evaluation of some seal strength as a function of percent coverage.

### **Sealing**

It is of interest to test if other sealing techniques, such ultrasonic sealing or a serrated heat seal bar, would create enough stress on the chitosan to break through it and allow a seal.

It also possible to envision placing a pattern-applied heat seal coating on the chitosan. Testing would need to include adhesion testing, seal testing, and the effects of humidity, time and other environmental conditions to a chitosan coating covered with a heat seal coating.

### **Drying process**

This work noted some that drying is an important factor in chitosan coating quality. To get an absolutely even coating, there is more work to be done. The continuous drying process of the gravure coating machine eliminated most of the variation, but more work may need to be done get the optimum adjustment for the dryer. The gravure rolls, speed and dryer adjustment all exhibit influence on the results/qualities of the coating surface.

### **Chitosan coatings general view**

This work has found a method for machine-applied chitosan coating. However, the efficacy of chitosan coated in this manner needs to be evaluated. Have the steps of coating manufacture, application and drying had any effect on the

antimicrobial properties? Does the efficacy change along with the viscosity and percent solids changes? Will the coating adhesion be affected by the packaging liquid materials such as brine or vinegar? Will the properties be affected by hot fill or other thermal processes?

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