



Application of Cationic Tapioca to Unmodified Pearl Corn Starch – A Papermaking Handsheet Study

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Authors' contributions

This work was carried out in collaboration among all authors. Author KD supervised the study, wrote the final draft and approved the final manuscript. Authors EP and JK managed the analyses of the study and wrote the first draft of the manuscript.

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ABSTRACT

An handsheet study was performed to compare the application of unmodified pearl corn starch and cationic tapioca starch on 100% recycled paperboard. To analyze the benefits tensile index, Canadian Standard Freeness, and starch retention was measured. The results found that cationic tapioca starch had the highest tensile index at 61.36 N*m/g for a dosage rate of 16 lbs./ton at a comparable dosage for unmodified pearl corn starch at 48 lbs./ton the tensile index was 56.11 N*m/g. Tests of the Canadian Standard Freeness showed that the unmodified pearl corn starch had the lowest freeness at 34.3 ml. The cationic tapioca starch had a freeness of 53.5 ml. For starch retention, more starch was retained in the sheet with cationic tapioca starch, with only 0.0065 grams ending up in the filtrate, compared to 0.015 grams of filtrate for the sheet containing unmodified pearl corn starch.

Keywords: *Starch; cationic; tapioca; tensile index; Canadian standard freeness.*

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1. INTRODUCTION

Renewable hardwood and softwood materials including recycled paper materials are today common materials used to manufacture paper [1]. Recycling paper products have improved the environmental footprint of the paper industry in the past decades [2].

Ever rising production cost for paper and board products and their application demand new solution of utilizing raw materials for the production process [3,4].

To become more eco-efficient the paper industry is increasing their efforts to become more sustainable, biodegradable and eco-efficient. In addition, environmental regulations demand an increasing use of sustainable chemical and additives. This will result in an increasing use of renewable materials and additives, which can replace less environmentally friendly additives in the future [3,4].

Starch is based on polymeric chains of sugar monomers [5] and is a common and crucial bio-additive to papermaking and paper conversion [6]. Starch application range from dry strength agents, coating binders, retention aids in wet end applications and as adhesives in converting operations [5]. Behind biomass fibers and fillers, starch is the third leading component by weight in paper [5,7]. Starch is considered a low-cost and sustainable product, as it is naturally abundant and biodegradable [8]. In addition, starch provides impressive strength and surface benefits to a variety of different paper grades, including packaging paper and cardboard grades [9].

Various starch products find a place in the industrial process of papermaking, because starch can play a variety of different roles, where it can gel, thicken, and form to create optimal sheet construction [10]. Due to starch's substantial use in the paper industry, there are a variety of different products on the market, with major sources ranging from corn and potato to waxy maize, wheat and tapioca [6].

Starch applied at the wet-end mixing systems is in most times modified to cationic, anionic or amphoteric cationic or amphoteric [5,11].

Uncharged and unmodified pearl corn starch is a widely utilized additive to the pulp and paper industry, specifically as a binder and laminate in

corrugated board processes [12]. This specific additive is incredibly useful within the industry because it aids in the promotion of inter-fiber bonds, at dosages of up to 20% of the sheet. To influence inter-fiber bonding, the nonionic starch gels cross-link with the fibers within the sheet. Once the gel forms closer contact with the fibers, it can increase and improve formation, influence efficiency in draining on the machine and bind sheets in the corrugation process [9]. This unmodified starch often has limitations, since it is high solids and high viscosity, requiring increased water usage and difficulty in make-down [13]. In addition, this type of starch is often used as a glue between sheets rather than an additive for strength [14]. Therefore, cationic starches are often utilized over unmodified starches in the paper industry.

Since these cationic starches are utilized in abundance over unmodified starches, there are several different types including tapioca, maize, and potato [15]. Studies comparing these types of starches have found that cationic starches perform better than native starches in tensile, tear, and burst [10]. These cationic starches provide several benefits on the wet-end of the machine including increased fiber and ash retention, improved process runnability, better dewatering behavior, and cost-effectiveness [16]. Cationic starch is also preferred on the dry-end because the positive charge that gets introduced on the chain forms an electrostatic bond with the negative cellulosic fibers of the biomass [14]. This bonding is strong, which provides strength and formation benefits in the final sheet [8]. In addition, these modified starches coat the fillers and fiber to create better retention of chemistries within the paper, which promotes better paper performance and cost savings [17].

This study is looking to exploring the potential strength and economic benefits of utilizing cationic tapioca starch over uncharged and unmodified pearl corn starch. To properly examine various strength benefits, tensile index tests were performed on handsheets with varying additions of tapioca starch and the unmodified and uncharged pearl corn starch. In addition, Canadian Standard Freeness Testing was analyzed to determine the effects of starch addition on paper machine drainage.

2. MATERIALS AND METHODS

This section describes the materials, procedures, and standardized test methods of the Technical

Association of the Pulp and Paper Industry (TAPPI), used for this study. Repeatability of the results stayed in between the allowable margins of the TAPPI testing standards.

2.1 Materials

The materials used for this study included an Uncharged and Unmodified Pearl Corn Starch (UUCS) and an Cationic Tapioca Starch (CTA). As fiber material recycled fibers from the wet-end of a board mill were obtained and used for the handsheet preparation.

2.2 Starch Make Down

The starch solutions were prepared as described below and then added to the fiber suspension based on handsheet oven dry weight.

2.2.1 Uncharged and unmodified corn starch

Uncharged unmodified pearl corn starch was obtained from an industrial starch cooking process at 13% consistency prior to handsheet making.

2.2.2 Cationic tapioca starch

Cationic tapioca starch was prepared as described by Doelle et al. [18] at a temperature of 48.9°C (120°F). In a 500 ml beaker 291 ml of distilled water was added at a temperature of 20°C (68°F), followed by adding 9 g cationic tapioca starch powder under constant stirring to reach a 3% solids content. The solution was then heated to 48.9°C (120°F) and stirred for one minute after reaching the temperature. To prevent water evaporation during starch cooking, the flask containing the starch solution was covered with an aluminum foil.

2.3 Vacuum Filtration

Vacuum filtration was used to determine the starch retention at a dosage of 12 lbs./ton. A Büchner funnel set up was used as described in TAPPI testing method T 218 sp-06 "Forming handsheets for reflectance testing of pulp-Büchner funnel procedure" [19]. The filtrate from the handsheet forming with filter paper was recovered and analyzed for solids content.

2.4 TAPPI Methods

Handsheets for physical testing were prepared accordance with T 205 sp-06 [20]. The method

was followed exactly except for the handsheet basis weight, pressing and drying of the pearl and tapioca starch containing handsheets. For the basis weight 3.0 g instead of 1.2 g of recycled pulp were used to produce a board handsheet with 150 g/m² instead of 60 g/ m². Drying was completed in one step using a Labtech Speed Dryer at 86.6°C (188°F), to simulate the drying process at the paper machine and to gelatinize the unmodified pearl starch. The ash content was measured in accordance to T 211 0m-02, "Ash in wood pulp, paper and paperboard: Combustion at 525°C" [21]. T 218 sp-06 "Forming handsheets for reflectance testing of pulp-Büchner funnel procedure" [19] was followed for handsheet forming to determine starch retention. Physical testing of handsheets was performed in accordance to T 220 sp-06, "Physical testing of pulp handsheets" [22]. The freeness of pulp was measured as Canadian Standard Freeness (CSF) according to T 227 om-09 "Freeness of pulp (Canadian standard method)" [23]. Conditioning of the paper samples was done according to T 402 sp-08, "Standard conditioning and testing atmospheres for paper, board, pulp handsheets, and related products" [24]. Tensile strength was performed following T494 om-06, "Tensile properties of paper and paperboard (using constant rate of elongation apparatus)" [25].

2.5 Testing

The main goal of this handsheet study was to determine strength benefits between uncharged pearl starch and cationic tapioca starch. First, 150 g/m² TAPPI handsheets were created without any starch as a control, in addition to addition rates of the tapioca starch at 4 lbs./ton (0.2 grams of starch), 12 lbs./ton (0.6 grams of starch), and 16 lbs./ton (0.8 grams of starch), and addition rates of pearl starch at 12 lbs./ton (0.1385 grams of starch), 36 lbs./ton (0.4154 grams of starch), and 48 lbs./ton (0.5538 grams of starch). Weights for the starch additions were computed based on the solids content in the make-down, which was 3% for cationic tapioca starch and 13% for unmodified pearl starch. The addition rates for comparison of the two starches was three times higher for the pearl starch because tapioca starch is three times as costly. In addition, the addition rates for the tapioca starch are between 4 lbs./ton - 16 lbs./ton in industry, whereas the addition rates for pearl starch can be much higher, at rates up and above of 80 lbs./ton depending on the product produced.

While strength analyzation was the major purpose for conducting this experiment, other measures were also examined including drainage and retention of the starch in the sheets. Drainage was considered because too much starch could cause issues with drying of the sheet, if drainage is too slow, the CSF number will be low, and the sheet will not be dry enough by the time it reaches the dryers. This would require an increase of vacuum suction, thus an increase of energy usage and operational cost. Therefore, TAPPI CSF tests were computed with the addition of starch in the pulp. Retention of starch in the sheet is also a necessary factor to be tested because when the starch passes through the sheet it ends up in the process water, creating food for bacteria and increase in biological activity. Starch was added to pulp and filtered through a vacuum filtration set-up, then the water sucked through the sheet was analyzed through ash content to analyze the amount of starch that did not remain in the sheet.

3. RESULTS AND DISCUSSION

3.1 Light Microscope Imaging

Microscope images were taken to compare unmodified pearl corn starch and cationic tapioca starch at a 40 times magnification. Fig. 1 shows the unmodified pearl corn starch had more of a crystalline structure, compared to the cationic tapioca starch shown in Fig. 2 which had more of a spherical structure. Therefore, cationic starches are often utilized over unmodified starches in the paper industry.

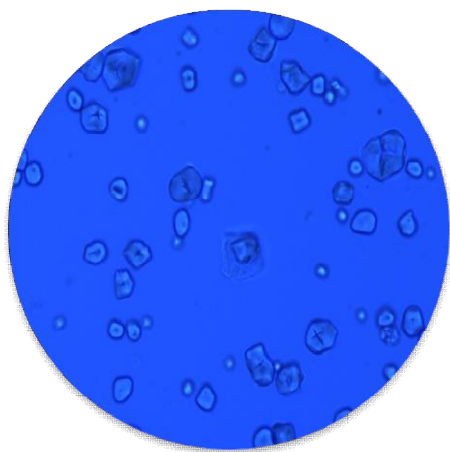


Fig. 1. Light microscope image of unmodified pearl corn starch at a magnification of forty times

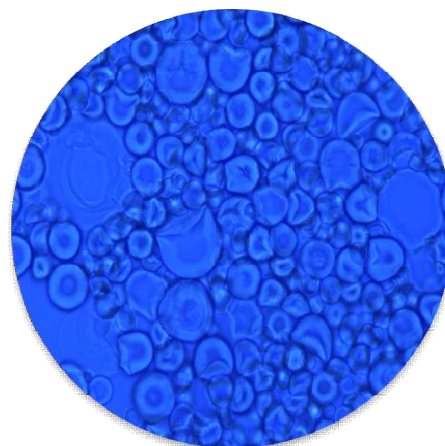


Fig. 2. Light microscope image of cationic tapioca starch at a magnification of forty times

3.2 Tensile Index

Fig. 3 shows the computed tensile index for various dosages of cationic tapioca starch and unmodified pearl corn starch compared to tensile index of handsheets with no starch addition. The handsheets with no starch performed at the lowest tensile index of 20.30 N*m/g and a low standard deviation of 0.25. At dosages of 4 lbs./ton of cationic tapioca starch and 12 lbs./ton of unmodified pearl corn starch, the tensile index was 51.29 N*m/g with a standard deviation of 13.5 and 35.60 N*m/g with a standard deviation of 12.9, respectively, representing a 44.07% increase. At dosages of 12 lbs./ton of cationic tapioca starch and 36 lbs./ton of unmodified pearl corn starch, the tensile index was 54.80 N*m/g with a standard deviation of 3.5 and 42.82 N*m/g with a standard deviation of 8.1, respectively, representing a 27.98% increase. At dosages of 16 lbs./ton of cationic tapioca starch and 48 lbs./ton of unmodified pearl corn starch, the tensile index was 61.36 N*m/g with a standard deviation of 11.8 and 56.11 N*m/g with a standard deviation of 10.6, respectively, representing a 9.36% increase.

A similar study found that at a dosage rate of 0.8% of the sheet cationic tapioca starch had a tensile index of 44.0 N*m/g and cationic corn starch had a tensile index of 40 N*m/g [8]. In addition, the dosage of 12 lbs./ton makes up 0.6% of the sheet. Cationic starches are also made to perform higher strength benefits, therefore if the pearl corn starch had not been cationic, the tensile index would have been lower than 40 N*m/g.

3.3 Canadian Standard Freeness

The CSF testing, shown in Fig. 4, found that the pulp with no starch had the highest freeness, at an average of 153.90 ml with a standard deviation of 9, followed by cationic tapioca starch at 53.50 ml with a standard deviation of 9, and the unmodified pearl corn starch had the lowest freeness at 34.30 ml with a standard deviation of 9. The freeness test determines machine retention and drainage in a lab setting. The higher the freeness value, often the lower the machine retention and the quicker the drainage. The cationic tapioca starch had a significantly

lower CSF than the unmodified pearl starch and the test with no starch, meaning that there could be issues with drainage on the machine if the cationic tapioca starch is introduced. While this testing variable is not a guarantee, it should be considered when introducing the cationic tapioca starch to the machine. A recommendation would be to increase vacuum power if issues with drainage speeds do begin to occur, but if increased retention is desired, the addition of cationic tapioca starch could be of great benefit to the paper making process. This could result in higher retention of starch on the machine and less energy used in the white-water system.

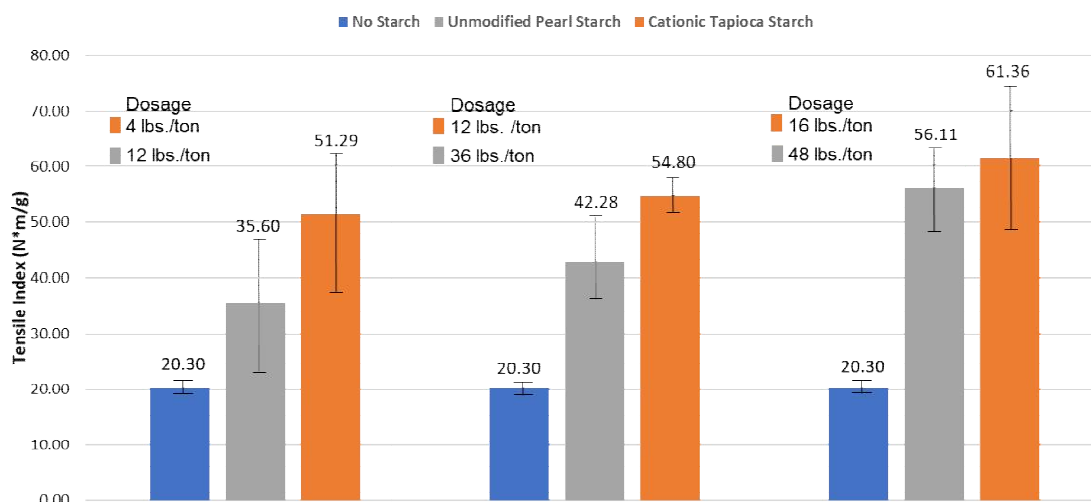


Fig. 3. Tensile index (N*m/g) of handsheets with no starch, unmodified pearl starch and cationic tapioca starch

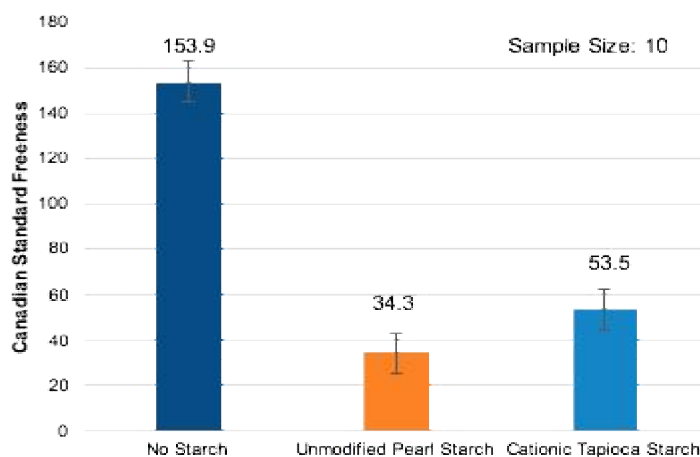


Fig. 4. Canadian standard freeness comparing no starch, unmodified pearl starch, and cationic tapioca starch

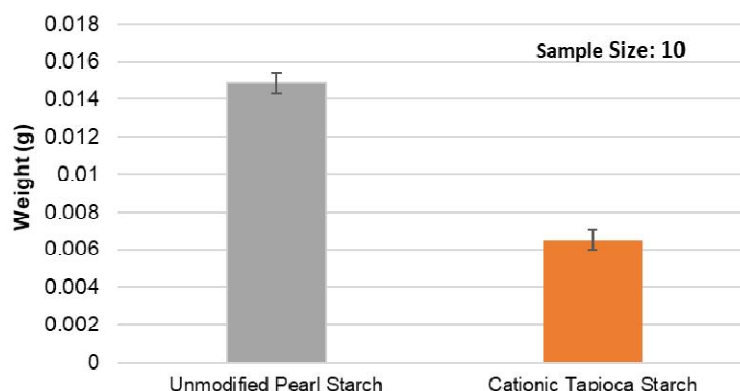


Fig. 5. Starch not retained in sheet comparing unmodified pearl starch and cationic tapioca starch

3.4 Handsheet Starch Retention

Starch retention in the handsheet is shown in Fig. 5. The handsheet weight was highest for the cationic tapioca starch, because after ash content testing the weight of leftover solids in the filtrate was only 0.0065 grams with a standard deviation of 0.0005, compared to 0.015 grams, or 2.31 times lower for the unmodified pearl corn starch with a standard deviation of 0.0005. The successful retention of starch in the sheet is important because when the starch passes through the sheet it ends up in the white-water system. The starch acts as a food for bacteria and increases biological activity, creating need for higher usage of biocide chemistries and other resources. Therefore, the change to the cationic tapioca starch could decrease the need for biocide chemistries in the mill, as well as issues with cleaning the white-water system.

4. CONCLUSION

Handsheets made with various dosages of cationic tapioca starch and unmodified pearl corn starch at a ratio of 1:3 show that the highest tensile index improvement of 44.07% was achieved for a dosage of 4lbs./ton achieving a tensile index of 51.29 N*m/g versus 12 lbs./ton achieving a tensile index of 20.30 N*m/g for cationic tapioca starch and unmodified pearl corn starch respectively. Higher starch dosages of 12lbs. versus 36 lbs./ton and 16lbs. versus 48lbs./ton revealed a tensile index increase of 27.98% and 9.36% with a maximum tensile index at 54.80 N*m/g and 56.11 N*m/g respectively.

The pulp with cationic tapioca starch application resulted in a CSF of 53.50 ml and the unmodified

pearl corn starch resulted in a CSF of 34.30 ml compared to the pulp with no starch with a CSF of 153.90 ml.

Starch retention in the handsheet was highest for the cationic tapioca starch was 2.31 times higher than the unmodified pearl corn starch based on solids content measurement of the handsheet filtrate water.

Application of cationic tapioca starch could result in economic benefits regarding less storage needs due to a lower volume usage as well as lower shipping and handling costs. In addition, better retention could yield a lower retention chemical usage. However, to assess the above results in more detail a pilot paper machine study should be conducted.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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