Synthesis, Characterization, and Evaluation of Chitosan-Complexed Starch Nanoparticles on the Physical Properties of Recycled Paper Furnish

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ABSTRACT: The objectives of the current research were to synthesize and characterize chitosan-complexed starch nanoparticles and examine their effect on the physical performance of recycled pulp, specifically old corrugated containerboard (OCC). This new approach provides a uniquely renewable and useful approach to enhance mechanical properties of pulp while maintaining environmental compatibility, industrial compatibility, and paper qualities. The starch nanoparticles used for the research were prepared from cooked cornstarch gel with ethanol and reacted with diethylenetriamine penta-acetic acid (DTPA) in the presence of sodium hypophosphite. Thereupon, the DTPA-modified starch nanoparticles (SNs) were complexed with chitosan as part of a general chemical strategy to improve their incorporation into an OCC matrix and increase interfiber bonding. Spectral characterization of the SNs was done using TGA, DSC, FT-IR, and SEM to analyze their composition and structure. Approximately 2% chitosan-complexed starch nanoparticle derivatives by mass (SNX/C) of OCC-based slurry were thoroughly mixed before manufacturing a two-dimensional sheet for physical testing. The tensile and burst strength of the modified OCC pulp sheet increased 50 and 49%, respectively, albeit having a decreased tear strength compared to the control sample. However, when the OCC pulp sheet was coated with a 1% SNX/C by mass solution, the tensile and burst strength increased 120 and 70%, respectively, while also providing significantly increased gloss, decreased roughness, and tear strength. Because the mechanical properties are the most critical property facing the recyclability of OCCs, the tremendous gains afforded by the starch nanoparticle−DTPA−chitosan proposed give the system enormous potential applicability as a viable dry strength agent for paper substrates.

KEYWORDS: starch nanoparticles, chitosan, complexation, OCC pulp, mechanical properties
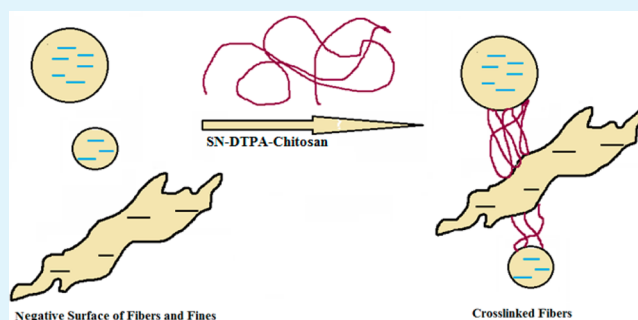
1. INTRODUCTION

Starch is a carbohydrate-based polymer that is widely abundant and readily available in a number of commercial forms. It typically occurs as semi-crystalline granules composed of amylopectin and amylose.[1] Its multihydroxyl chemical make-up offers a number of derivatization opportunities for the chemical community, in addition to also being the primary feedstock for cyclodextrin manufacture. The low cost, commercial availability, and chemical derivatization opportu-nities of starch in the market not surprisingly attract a number of researchers attempting to develop new functional starch derivatives for industrial applications. Chemical modification of a paper surface in the pulp and paper arena is currently a common practice for improving printing quality, surface gloss, surface sizing, and calendaring. Typically and especially for printing- and writing-grade papers, starch is used for surface sizing, with the main goal of improving paper surface resistance (to uneven penetration and flow of inks/liquid media) and printability.[2] Recycling is a very visible and highly important conceptual framework in any effort to address environmental concerns, reduce expanding landfills, and reduce the need for virgin fiber manufacture with the concomitant expenditure of energy and resources. Hence, it is a highly sustainable approach that demands increased research efforts for future success. For old corrugated containerboard (OCC) paper, a major component of the recycled market, the market is primarily concerned with improving mechanical strength because of the compromised nature of the fibers utilized. OCC pulp is a category of pulp fibers which have previously passed through at least two recycling processes. As a result, its fibers are much more degraded (shorter and/or thinner) and weaker than the original fibers. The bonding between these shorter fibers is significantly weaker which leads to very poor quality in terms of paper strength, such as burst strength, tear strength, and tensile strength. OCC also carries a significant amount of anionic trash which causes strength agents to lose their efficiency.[3,4]

Approximately 70 million tons of paper and paperboard are used per year in the United State (2011 MSW Characterization Reports). The utilization rate of waste fiber (OCC) for recycled containerboard in 1963 was reported to be 21.1% in the US, whereas in 2001 it was 67% with a concomitant recovery rate of approximately 70%.[5] Recently, the American Forest & Paper Association (AF&PA) released a 2011 recovery rate for Old Corrugated Containers (24.1 million tons recovered) which has reached a new high of 91.2%. Therefore, much research in this area attempts to improve the strength of OCC because waste fibers are typically mechanically inferior to their virgin equivalents. Early research work identified several types of chemical treatments that yielded measurable improvements in the bonding strength of recycled sheets.[6,7] A few innovative studies have shown that chemical derivatization of fiber surfaces can sometimes prevent strength losses from occurring,[8,9] while refining and chemical treatments improved the mechanical properties of OCC pulp.[3] The papermaking industry is currently using existing commercial dry strength agents such as cationic starch, polyacrylamide, and glyoxylate polyacrylamide to address potential improvements in the strength of OCC, but strength improvement is still very low relative to that of virgin pulp despite the current efforts.[10,11]

Meanwhile, nontraditional approaches for strength improvements in such materials as OCC are available. For example, nanomaterials offer a promising alternative to tackling the issue of low OCC strength because of the nanometric size effect compared to conventional bulk fillers even at low filler content. Nanofillers have strong reinforcing effects, and studies have also shown their positive impact in barrier packaging. However, for decades studies have been conducted with nonrenewable inorganic fillers and a petroleum-based matrix for a number of applications including packaging, a high value sector of the pulp market.[12] Increasing environmental concerns have led to, for example, developing new flexible barrier bio-based packaging materials and investigating the potential uses of renewable resources for such applications.[12]

The present study therefore focuses on the application of a novel nanomaterial system for improving the critically important mechanical properties of OCC: starch nanoparticles (versus bulk cationized starch, a traditional commercial product) that have been modified with diethylenetriamine pentaacetic acid sodium salt in the presence of sodium hypophosphate (SHP) and later complexed with chitosan. The chemical modification of OCC pulp fibers currently presented a means for preparing materials with unique properties that can increase the ultimate value and utility of these biopolymers. Additionally, it is suggested that the stronger bonding afforded by the current system will allow enhanced wet web formation at the paper machine and after mechanical pressing and steam drying allow for improved paper runnability (less opportunity for paper breaks). The present research will therefore focus on their characterization and provide a review of their application in paper furnishes.

2. EXPERIMENTAL METHODS

2.1. Materials. The OCC pulp was furnished by AzkoNobel Pulp and Performance Chemicals, Marietta, GA. Corn starch (S) was supplied by Cargill Incorporated, Minneapolis, MN. Chitosan (C), CAS no. 9012-76-4, was purchased from Sigma-Aldrich. Chemicals of reagent grade utilized were sodium hypophosphate (SHP), CAS registry number 123333-67-5, sodium hydroxide, CAS registry number 1310-73-2, and diethylenetriamine pentaacetic acid (X), CAS no. 67-

43-6. Thyl alcohol denatured and acetic acid were purchased from Fisher Scientific, Fair Lawn, NJ. Deionized water was used for all experiments that required water as the medium.

2.2. Extraction of Starch Nanoparticles (SNs). Corn starch (8 g) was added into 150 mL of distilled water. The mixture was heated at 90°C with constant stirring for 1 h for the complete gelatinization of corn starch, and then 150 mL of ethanol was added dropwise to the solution of gelatinized starch solution with constant stirring. The resultant nanoparticle suspensions were cooled to room temperature; another 150 mL of ethanol was added drop-wise for 50 min with constant stirring. The suspensions were centrifuged at 5300 rpm for 20 min, and the settled SNs were washed using ethanol to remove the water. After complete washing, the SNs were dried at 50 °C to remove ethanol.[13]

2.3. Chemical Modifications of the Starch Nanoparticle (SN). Into 20 mL of sodium hydroxide solution (pH 11) in a 50 mL Petri Dish were dissolved 10 g of diethylenetriamine pentaacetic acid (X) and 2 g of SHP. Starch nanoparticles (SNs, 10 g) were combined with diethylenetriamine pentaacetic acid (X) solution and manually mixed vigorously with a glass rod. The mixture was placed in an air oven at 130 °C for 4 h. Reaction products were washed with water and filtered several times to remove unreacted materials. The product obtained was modified starch nanoparticles (SNXs) that were air dried at 50 °C in an air oven overnight.[14]

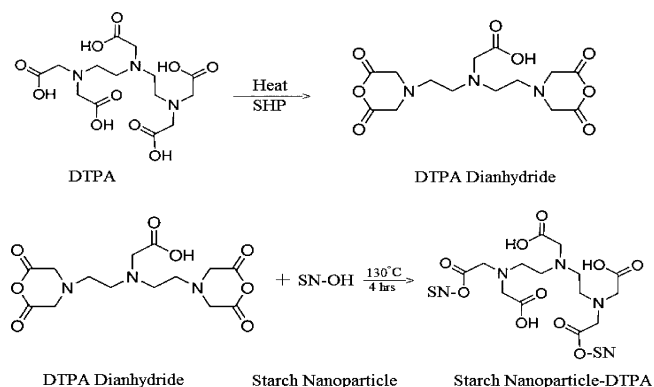The proposed reaction scheme of interest is shown in Figure 1.

Figure 1. Esterification reaction of starch nanoparticles (SN) with DTPA.

2.4. Polyelectrolyte Complexation. Chitosan (C, 1 g) was dissolved into 50 mL of 1.5 % acetic acid solution. Modified starch nanoparticles (1 g) were also dissolved with 50 mL of water and then added to a 50 mL chitosan solution in a 250 mL round-bottom flask. The reaction mixture was stirred using a magnetic stirrer at 80 °C for 90 min.[15] The proposed reaction scheme is shown in Figure 2.

2.5. Preparation of the OCC Pulp Sheet. An amount of 0.6 g of the additive was properly mixed with 10 L of the OCC pulp slurry (0.3% consistency) in a plastic bucket and then stirred (400 rpm) for 10 min. The additive mixed pulp slurry temperature was 30 °C with pH 5.4–5.8. The sheet was prepared using a 600 mL pulp slurry (1.8 g of OCC having a freeness of 400 CSF, an empirical measure of the
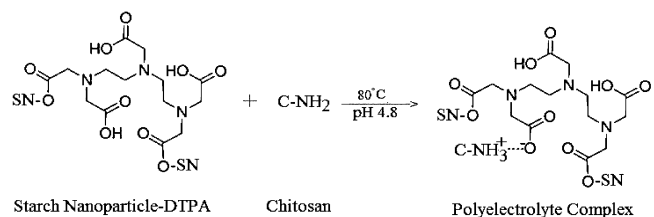

Figure 2. Polyelectrolyte complexation of starch nanoparticle (SN)-DTPA with chitosan.

total volume of water not absorbed in a sample, i.e., higher value, less adsorption) with or without additives in a sheet molder machine. The pulp slurry was also diluted with 10 L of white water into the sheet molder (diluted pulp slurry pH was 6.3−6.8) to produce a uniform sheet. The sheet was dried in a condition room and subsequently cured at 105 °C for 1.0 h.

2.6. Coating of OCC. The OCC sheet was immersed into a 1% SNX/C solution and passed through a laboratory sizing press machine. The sheets were then dried in a condition room and then cured at 105 °C for 1 h for further characterization.

2.7. Testing Methods. *2.7.1. Determination of Carboxyl Content.* A known amount of starch nanoparticle derivative was dissolved in 0.1 N NaOH and hydrolyzed for one hour. The remaining excess amount of NaOH was determined by titration with 0.1 N HCl using phenolphthalein as an indicator,[16] and the carboxyl content in milliequivalents of acidity per 100 g was calculated as follows:

$$\text{Carboxyl Content (meq)} = \frac{(V_2 - V_1) \times N \times 100}{W}$$

N = Normality of HCl
V_2 = Volume of HCl without sample
V_1 = Volume of HCl with sample
W = Weight of Sample

2.7.2. Determination of Degree of Esterification and Degree of Substitution. The starch nanoparticle derivative was dissolved in DMSO in a conical flask for 10 h, and then excess 0.1 N NaOH was added to the solution to saponify the ester over 2 h. The excess NaOH was determined by titration with 0.1 N HCl[17,18] to determine the percent esterification and the degree of substitution shown below:

$$\text{Degree of Esterification (\%)} = \frac{6.005(V_2 - V_1) \times N}{W}$$

N = Normality of HCl
V_2 = Volume of HCl without sample
V_1 = Volume of HCl with sample

$$\text{Degree of Substitution} = \frac{162 \times A\%}{100M - (m - 1)A\%}$$

A % = Degree of esterification
W = Weight of sample
M = Molecular weight of crosslinking agent
m = Molecular weight of the crosslinking part of crosslinking agent

2.7.3. Gloss Testing. The gloss of OCC pulp hand sheet was tested with a GLOSSMETER tester according to the TAPPI T 480 test method.

2.7.4. Roughness Testing. The roughness of the OCC pulp hand sheet was tested with an L&W roughness tester according to the TAPPI T 538 test method.

2.7.5. Tensile Strength. The tensile of OCC pulp hand sheet strength was tested with an ALWETRON TH1 tester according to the TAPPI T 220 test method.

2.7.6. Burst Strength. The burst strength of OCC pulp hand sheet was tested with a MULLEN tester according to the TAPPI T 810 test method.

2.7.7. Tear Strength. The tear strength of the OCC pulp hand sheet was tested with an L & W tester according to the ASTM D 689 test method.

2.8. Characterization. *2.8.1. ATR Analysis.* IR spectra of all starch-based nanoparticle samples were recorded with a Perkin Elmer FT-IR spectrophotometer. All the spectra were obtained by accumulation of 8 scans, with a resolution of 4 cm^{-1}, at 400−4000 cm^{-1}.[19]

2.8.2. Thermal Gravimetric Analysis (TGA). The thermogravimetric analyzer used in this study was a TGA Q500. A nitrogen atmosphere was used. The temperature range and heating rate were 30−600°C and 5°C/min, followed by isothermal heating at 600 °C.[20]

2.8.3. Differential Scanning Calorimeter (DSC). A differential scanning calorimeter DSC Q100 was used with a Hermetic pan (T 090127). Samples were subjected to a 2 °C/min temperature ramp from 30 to 200 °C followed by isothermal heating at 200 °C for 15 min. An empty pan was used as the reference.[21]

2.8.4. Scanning Electron Microscope (SEM). Morphological characterization of modified starch nanoparticle/chitosan derivative-treated OCC pulp hand sheets was performed on images acquired using a scanning electron microscope (SEM), Hitachi S-3200N.[14]

2.8.5. Contact Angle. Dynamic contact angle measurements were performed with a Phoenix 300 Contact Angle Analyzer (Seo Co., Ltd., Korea) on starch derivative/chitosan-treated OCC pulp hand sheets. Deionized water was used as the probe fluid.[16]

3. RESULTS AND DISCUSSION

3.1. Characterization of Starch Nanoparticles. *Morphology and Surface Chemical Changes.* The SEM image of extracted starch nanoparticles had the form of coagulates that displayed a particle size length and width of 386.52 and 222.38 nm, respectively (Figure 3). In general, starch nanoparticles
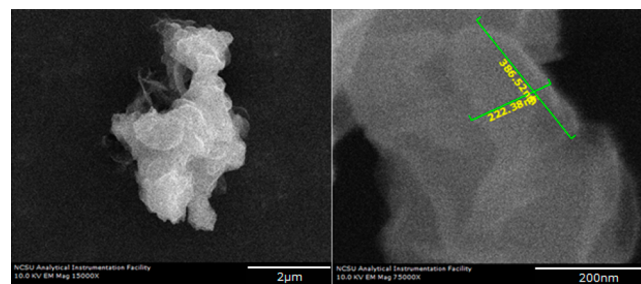

Figure 3. SEM photomicrographs of coagulated starch nanoparticles (the images have length scales of 2 μm (left) and 200 nm (right), respectively.

possess a surface covered with reactive hydroxyl groups that allow for surface decoration (for a specific functionality) using the appropriate chemical reaction strategy. The reaction pathway that was chosen for the particular functionality (mechanical strength improvement of OCC) in this work has already been shown in Figures 1 and 2.

The carboxyl content of the starch nanoparticles increased from 0.0 meq/100 g to 452 meq/100 g. To further clarify the changes that occurred after the surface modification, the DS (degree of substitution) and percent esterification were explicitly employed and determined by titration. For this study, the monomer formula weight and number of hydroxyls per starch monomer unit that were used in the calculations were 162 Da and 3. Thus, the degree of substitution and percent esterification were calculated to be 0.2 and 38%. The intrinsic viscosities of the 1 M CED dissolved starch nanoparticle and starch nanoparticle−DTPA were determined at 25 °C with an Ubbelohde-type viscometer to ascertain molecular weight.[17] Depending on the specific viscosity measured, typical molecular weights of starch nanoparticles and starch nanoparticle−DTPA were found to be 10 190 and 14 623 Da, respectively.

Thermal Behavior. The thermogravimetric behavior of the starch nanoparticle derivatives was evaluated with a 5 °C/min heating ramp under nitrogen and shown in Table 1. For several samples, a weight loss below and around 100 °C was attributed to water evaporation.[22] However, the weight loss above 100 °C was caused by the thermal decomposition of the starch nanoparticles/derivatives themselves.[23] DTPA had a single

Table 1. Thermal Analysis of Starch Nanoparticles and Derivatives

Sample	TGA maximum (DTG) degradation temp (°C)	Residual char at 600 °C (%)	DSC melting point (°C)
DTPA	280.26	25.10	199.2
SN	300.12	10.4	117.0
SNX	283.26	27.9	170.5
SNX/C	285.85	30.5	175.3
Chitosan	290.0	26.0	269.0

sharp decomposition peak at 280.26 °C, whereas the starch nanoparticles have a single weight loss peak at 300.12 °C; however, all derivatives of the starch nanoparticle have a decrease in the maximum weight loss temperature and a concomitant significantly higher residual mass after heating to 600 °C. This may be explained by the fact that the starch surface-modifying agents have a lower decomposition temperature, that the layer of this material is on the surface of the starch nanoparticles, and that the materials derived from the esterification have a lower temperature of degradation as previously shown for starch citrate and xylan citrate.[16,17] From this past work, it was shown that citric acid can be bonded to xylan (another polysaccharide), a compound containing multiple carboxylic acid groups, in a similar respect to DTPA. In addition, agents such as citric acid or DTPA both possess maximum degradation temperatures that are lower than that of the substrate (SN, chitosan).[16]

The thermal behavior obtained from a differential scanning calorimetric analysis of the starch nanoparticle derivatives was evaluated with a 2 °C/min heating ramp up to 200 °C under nitrogen as shown in Table 1. DTPA displays a very sharp melting point at 199.2°C, whereas for the starch nanoparticles an endothermic peak was observed at 117.0 °C. The melting points all increased for the reaction products as illustrated in Table 1. The increase in the melting points may be from changes in chemical composition due to increased hydrogen bonding and plasticization as well as the more robust molecular organization obtained from the esterification reaction.[16]

ATR Analysis. The ATR spectra of the starch nanoparticles (A) and starch nanoparticle−DTPA/chitosan are shown in

Figure 4. The spectrum of the starch nanoparticle shows a prominent peak at 3306.43 cm^{-1} which arises from the hydroxyl groups, whereas there is no peak over the region of 1700−1800 cm^{-1}, reflecting that there are no carbonyl groups on the starch nanoparticles. However, when the starch nanoparticles reacted with the DTPA and further complexed with chitosan, peaks appeared at approximately 1732.39 cm^{-1} that were attributable to the carbonyl group of the ester functionality and at 1638.38 cm^{-1} when chitosan was reacted with the starch nanoparticle−DTPA derivatives that were attributable to the carbonyl groups in the amide bond of starch nanoparticle−DTPA derivatives. Thus, the appearance of amide bands increased after the starch nanoparticle−DTPA derivatives were reacted with chitosan first by a complexation reaction that was then followed by an amide reaction (arising from the pressure/heat of the sheet formation), strongly pointing to the conclusion that starch nanoparticle−DTPA was linked to chitosan via a coupling reaction between the amino groups of chitosan and the carboxylic groups of starch nanoparticle−DTPA derivatives.[14]

3.2. Starch Nanoparticle Derivatives Applications. *Effect of Starch Nanoparticle Derivatives on OCC Pulp Paper Strength Properties.* Mechanical resistance is one of the most important properties of generic paper substrates. These substrates need to have sufficient resistance in applications that require packaging, wrapping, or sealing. In general, such gross resistance can be attributed at the molecular level to the adequate development of hydrogen bonds. Also, it depends on the quantity and area of bonding sites. In recycling, fibers irreversibly damage, and this damage can affect final paper resistance properties. Figure 5 shows the tensile strength of OCC recycled pulp hand sheet that results after the addition of either virgin (nonrecycled) pulp or starch nanoparticle derivatives.

Virgin pulp in theory has a much higher mechanical resistance because the fibers have not been damaged from previous use. The control for these studies was the base OCC recycled pulp which is a collection of fibers and broken fibers or fines (CSF = 400). Defibrillated or nondefibrillated virgin soft wood kraft pulp (revolutions = 5000, CSF = 530) was blended
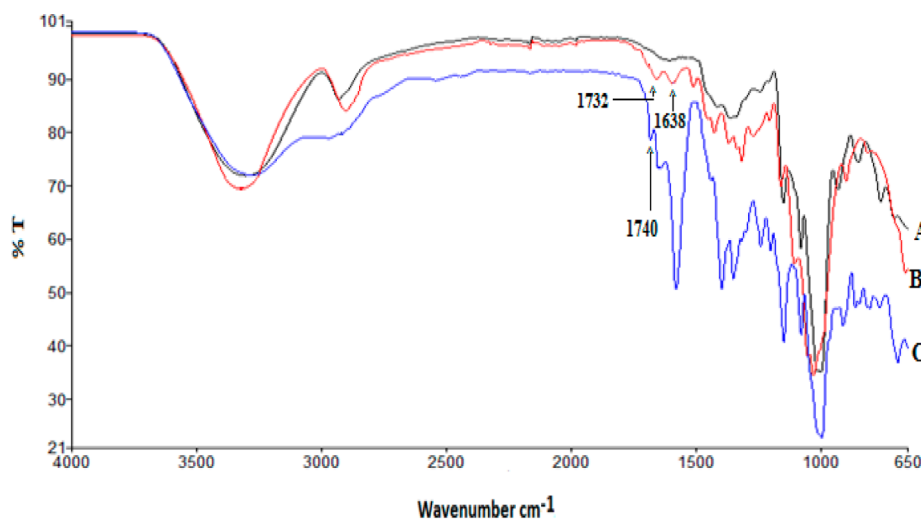

Figure 4. ATR spectra of starch nanoparticle (A), starch nanoparticle−DTPA−chitosan (B), and starch nanoparticle−DTPA (C). As shown in the spectrum, the 1732 cm^{-1} band can be attributed to the ester carbonyl stretch (from the DTPA attachment), whereas the 1638 cm^{-1} band can be attributed to the carbonyl stretch in the amide bond of starch nanoparticle−DTPA derivatives.
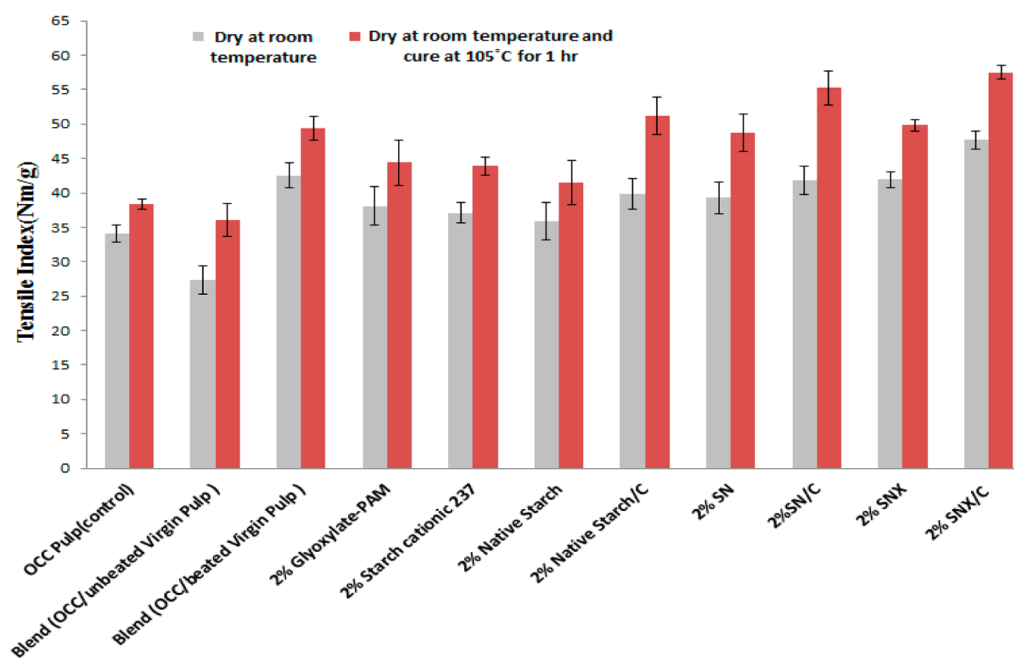
Figure 5. Effect of starch nanoparticle derivatives on the tensile index of OCC recycle pulp samples.
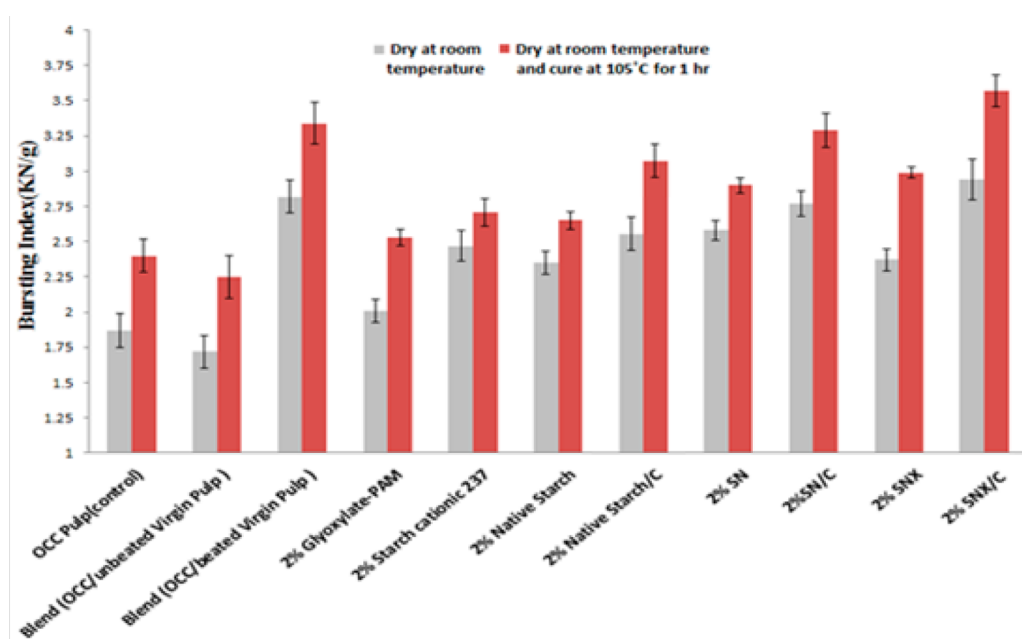

Figure 6. Effect of starch nanoparticle derivatives on the burst index of OCC recycle pulp samples.

with OCC recycle pulp (50:50) to increase the ultimate strength properties. In tandem, 2% starch nanoparticle derivatives (based on the mass of dried pulp) were also mixed with the OCC pulp slurry separately. As a result, the nondefibrillated virgin pulp sample had a decreased tensile index, but the defibrillated virgin pulp blend sample had a significantly increased tensile index compared to the control sample (Figure 5). This may happen due to a significant decrease in the fiber size and an increase in the bonded area at the high revolutions (for defibrillation of fibers) introduced to the virgin pulp. The tensile index of the starch nanoparticle (SN) and its derivative-treated OCC pulp samples such as SNX, SN/C, and SNX/C were found to be 27, 30, 44, and 50% higher than the control sample. The result was also significantly

higher than what has been found for commercial dry strength additives such as glyoxylate polyacrylamide, cationic starch, and native corn starch. This may be because of the very high surface area/volume ratio (very small size) of the starch nanoparticles and the resultant strong bonding that is generated among the OCC pulp fibers through the high quantity of carboxyl and amino groups on the nanoparticles. During the formation of the sheets, i.e., the drying and curing (heating) of hand sheets, the starch nanoparticles and its derivatives can deform into very thin films and distribute within the fibers/fibrils/fines. Consequently, more hydrogen bonds can be formed among the fibers (including the fines) and starch nanoparticle derivatives via the increased generation of contact areas. Additionally, the starch nanoparticles−DTPA/chitosan poly-
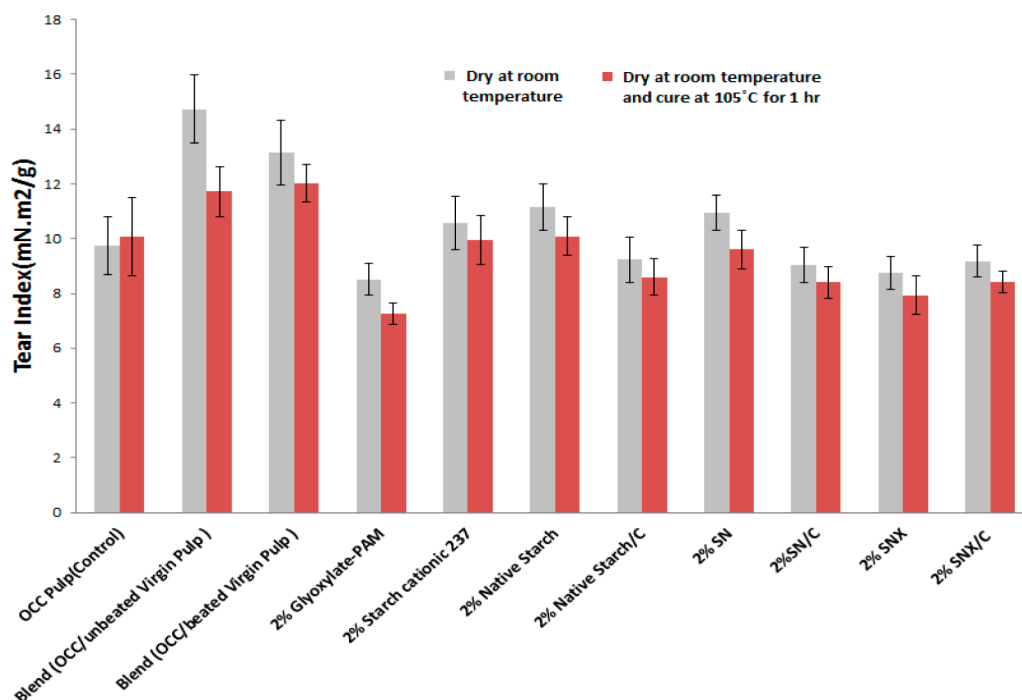
Figure 7. Effect of starch nanoparticle derivatives on the tear strength of OCC recycle pulp samples.
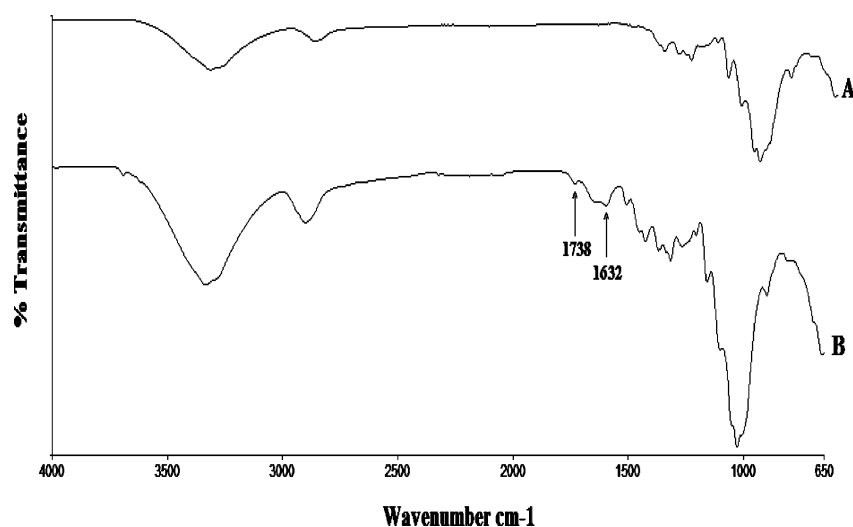

Figure 8. ATR spectra of control pulp sheet (A) and starch nanoparticle−DTPA−chitosan pulp sheet (B).

electrolyte complex became bonded (amide bond)[23] and had the opportunity to bond more liberally to the fiber hydroxyl groups; the free carboxyl groups of starch nanoparticle−DTPA also contributed to interfiber bonding and thus increased the paper strength.[24,25] However, the density of the starch nanoparticles−DTPA/chitosan-treated sample increased approximately 30% which is also one of the causes for the increases in the strength.[26]

In contrast, the tensile index of 2% SN/C and SNX/C derivative-treated OCC pulp samples was also more improved than defibrillated virgin pulp blends (Figure 5). Similarly, a burst index of SN, SNX, SN/C, and SNX/C treated samples increased 22, 24, 37, and 49%, respectively, compared to the control sample, and all the test cases provided better results compared to the commercial dry strength additive (Figure 6). It is also observed from Figure 7 that the tear index of SN, SNX,

SN/C, and SNX/C treated OCC pulp samples was less than the control sample but slightly higher than the commercial glyoxylate polyacrylamide-treated sample.

3.3. Bond Formation with OCC Recycle Pulp. The basic groups $(-NH_2)$ on every ring in starch nanoparticle−DTPA−chitosan derivatives develop positive charges when they are in a sufficiently acidic medium and may thus form ionic or covalent bonds with the negatively charged cellulosic in paper fibers during the paper making process.[27] In addition, the DTPA in starch nanoparticle−DTPA−chitosan derivatives contains a number of free carboxyl groups which can also engage in ionic bonds with the fiber surface of pulp and also increase the relative bonded area between fibers. The combined interactive effects attributable to the carboxyl and amine groups for increasing bonding between fibers during sheet formation also contributed to an increase in tensile strength.[28]
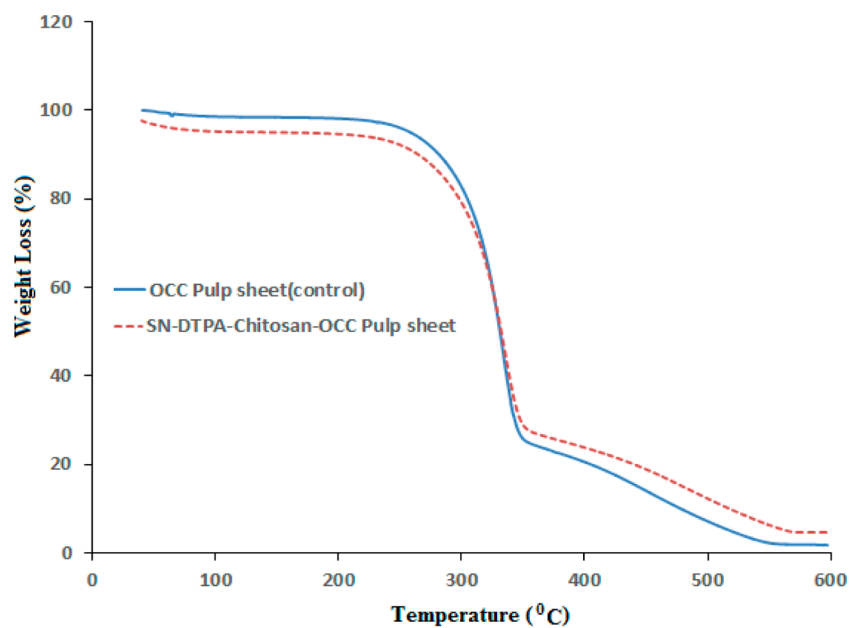
Figure 9. Thermogravimetric analysis of the OCC pulp sheet (blue line) and starch particle−DTPA−chitosan-treated OCC pulp sheet (dashed line).
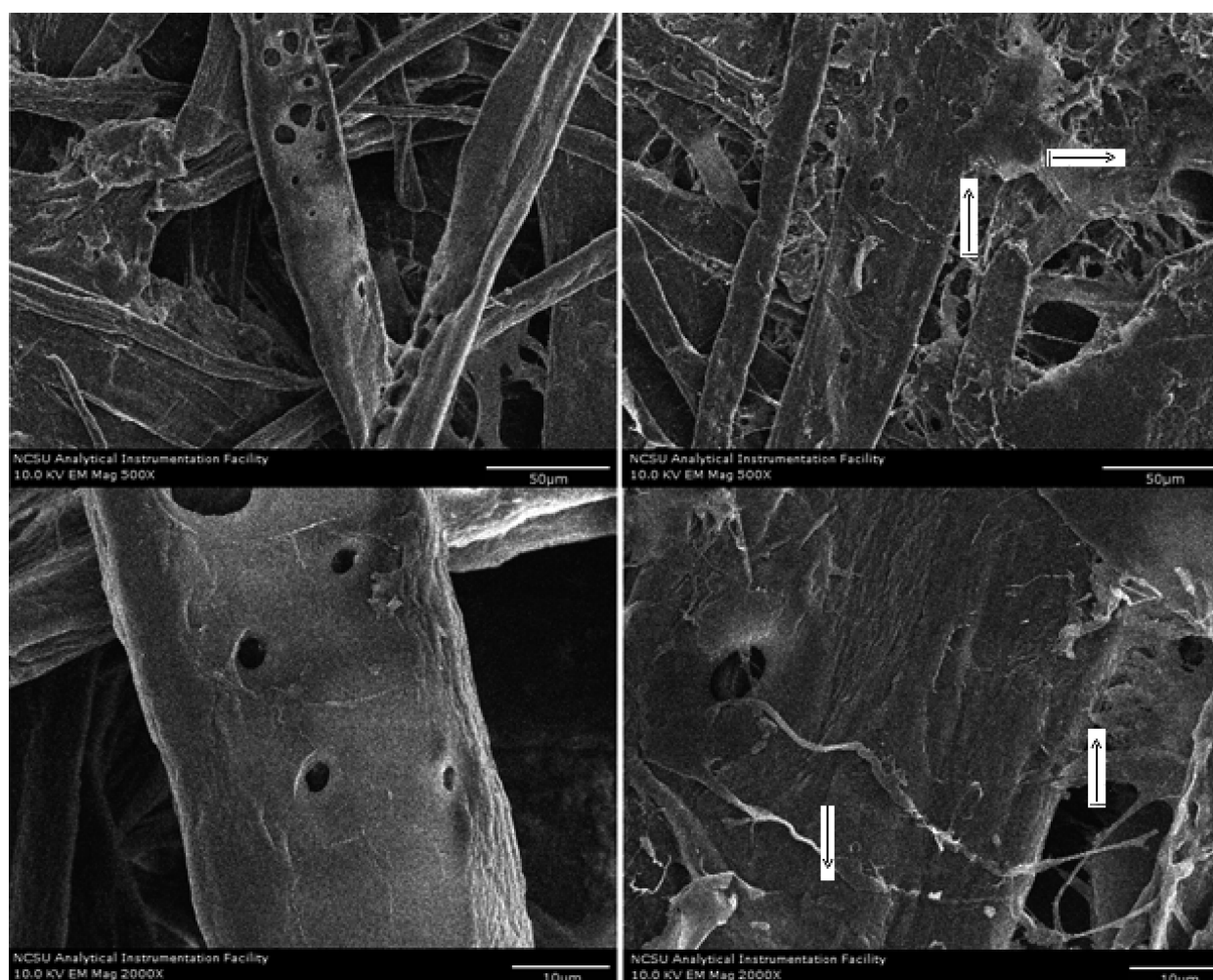

Figure 10. SEM photomicrograph of OCC recycle pulp sample (left) and 2% SNX/C derivative-treated OCC pulp samples (right). Top and bottom images have length scales of 50 and 10 mm, respectively. The arrows on the right images point to the smaller fiber fragments and fibrils that partially account for the enhanced mechanical properties.

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dx.doi.org/10.1021/am403261d | *ACS Appl. Mater. Interfaces* 2013, 5, 11029−11037

Table 2. Results of Starch Nanoparticle Derivative-Based Coating on OCC Pulp Samples[a]

OCC starch nanoparticle derivatives	tensile			brightness index	gloss	roughness	contact angle (20 s)
	tensile index (Nm/g)	burst index (KN/g)	tear index (mN·m²/g)				
-	38.35	2.44	9.28	20.91	10.43	11.14	80
SN	45.80	2.86	7.30	20.56	11.50	10.27	50
SN/C	62.30	3.92	5.93	18.50	36.20	9.40	95
SNX/C	84.38	4.15	4.81	18.20	53.10	9.0	100

[a]Conditions: 1% starch nanoparticle derivative solution, coated with laboratory paper machine, and cured at 105 °C for 1 h.

It can also be observed from Figure 8 that the starch nanoparticle−DTPA−chitosan derivatives-treated pulp sheet has a large band at 3400 cm^{-1} compared to the control pulp sheet. This large band can be attributed to the hydrogen bonding interactions arising among the hydroxyl groups within the chitosan, starch nanoparticles, and DTPA moieties. However, a large new peak observed at 1632 cm^{-1} is present from the polyelectrolyte complex of starch nanoparticle−DTPA−chitosan derivatives that is attributed to an amide linkage when the pulp sheet was dried at high temperature.[23] In addition, a high residual char (4.5%) value was observed in the starch nanoparticle−DTPA−chitosan-treated pulp sheet compared to the control pulp sheet (1.7%) after heating at 600 °C (Figure 9) which is due to starch nanoparticle−DTPA−chitosan crosslinking to the pulp fiber.

Scanning electron microscopy images of OCC recycle pulp samples and SNX/C derivatives-treated OCC recycle pulp samples are shown in Figure 10. The OCC pulp sample control shows a continuous smooth pore structure with plate-like solid pore walls, but the SNX/C derivative-treated OCC pulp sample SEM images reveal a rougher surface with the appearance of smaller irregular fragments on the fiber's surface. It may be that these are aggregations of starch nanoparticles and associated fines/fibrils that increase the bonded area among the OCC pulp fibers to make more compact fiber assemblies.

3.4. Effect of Starch Nanoparticle Derivatives Coating on OCC Pulp Hand Sheet. A summary of the tensile and other properties of 1% starch nanoparticle derivatives-coated OCC pulp samples is shown in Table 2. The OCC pulp hand sheet was immersed into 1% of SN, SN/C, and SNX/C derivative solution separately and then passed through a laboratory sizing press machine. The hand sheets were then dried at room temperature and cured at 105 °C for 1 h. The tensile and burst index of SN-, SN/C-, and SNX/C-treated samples increased 19.4, 62.5, and 120% and 17.2, 61, and 70.1%, respectively, compared to the control sample. This may happen due to (1) bond formation between the hydroxyl group of the pulp fibers and the −COOH, −NH$_2$, and −OH groups of the SNX/C additive and (2) increased density of the SNX/C-treated pulp sheet compared to the control sample.[26] It is also observed from Table 2 that the SNX/C coating-treated sample gloss increased about four times, and tear strength and roughness significantly decreased. The contact angle of starch nanoparticle derivatives, e.g., SN/C- and SNX/C-treated samples, increased significantly, but the starch nanoparticle (SN)-treated sample decreased compared to the control. This may be explained by the fact that the starch nanoparticle is extremely hydrophilic thus showing not surprisingly a very low surface contact angle measurement in the typical contact angle time frame. However, SN/C and SNX/C additives contain chitosan, which is strongly hydrophobic and also produces a sticky gel under acidic pH (wet) that adopts a plastic-like

character under dry conditions. Thus, when a pulp sheet is generated with the additive, under the pressing time, it spreads very evenly over the rough surface, covering it very uniformly to produce a paper surface that is very smooth and also possesses increased gloss (Table 2). Thus, because the additive-treated sheet surface was hydrophobic due to the plastic-like chitosan under the dry conditions, the contact angle increased somewhat. In this study, we did not attempt to provide a systematic analysis of the gelation phenomenon because the study focused on the industrially relevant conditions without their optimization. It is possible that the coverage based on the chitosan gelation could influence its spreading and final paper properties.

It is important to note, additionally, that the starch nanoparticle−DTPA−chitosan may possess strong antimicrobial activity based on preliminary work in this lab (unpublished results) that may protect the OOC pulp sheet from fouling and thus avoid the use of any biocide.

4. CONCLUSIONS

Starch nanoparticles (SNs) were modified with diethylenetriamine pentaacetic acid (X) in the presence of sodium hypophosphite (SHP) to increase their ability to better bond recycled fibers during paper formation. It was found that the carboxyl group content, degree of esterification, and degree of substitution of diethylenetriamine pentaacetic acid with starch nanoparticles significantly increased relative to the unmodified starch nanoparticle. The modified starch nanoparticle (SNX) was later coupled with chitosan (C). Approximately 2% of starch nanoparticles (SNs) and their derivatives such as SNX, SN/C, and SNX/C were blended with OCC recycle pulp separately prior to making a sample. The tensile and burst index increased 27, 30, 44, and 50% and 22, 24, 37, and 49%, respectively, compared to the control samples. It was also significantly higher than what is typically found for commercial dry strength agents and blended OCC pulp. In addition, when the OCC pulp hand sheet was coated with a 1% starch nanoparticle derivative (SNX/C) solution, the tensile and burst index increased 120 and 70%, respectively, while there was also a significant increase in gloss and decrease in roughness and tear index compared to the control sample. The increased strength is an agreement with increased bonding between the starch nanoparticle derivative and pulp fibers.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Jenkins, P. J.; Donald, A. M. *Biol. Macromol.* **1995**, *17*, 315−321.

(2) Isabel, M. T. M.; Paulo, J. T. F.; Margarida, L. F. *Biol. Res.* **2011**, *6*, 4259−4270.

(3) Sheikhi, P.; Talaeipour, M. *World Acad. Sci., Eng. Technol.* **2011**, *57*, 490−494.

(4) Zhao, Y.; Li, J.; Rao, L. Q.; Cheng, W. Furnish pretreatment to improve paper strength and performance in papermaking. Publication No. WO2013078133 A1, Patent Issued on May 30, 2013.

(5) Anon. *Mill Trade J. Recycl. Markets* **1996**, *34*, 3.

(6) Stone, J. E.; Scallan, A. M. *Br. Pap. Board Makers' Assoc.* **1966**, 145.

(7) Klungness, J. H.; Caufield, D.F. *Tappi J.* **1982**, *65*, 94−97.

(8) Gruber, E.; Weigert, J. *Papier* **1998**, *52*, 20−26.

(9) Laivins, J. V.; Scallan, A. M. *Pulp Pap. Sci.* **1996**, *22*, 178.

(10) Mohammad, N.; Nima, S.; Ahmad, S.; Mohammad, J. S. *Basic Appl. Sci. Res.* **2011**, *1*, 2314−2318.

(11) Howard, R. C.; Jowsay, C. *J. Pulp Pap. Sci.* **1989**, *15*, 225.

(12) Corre, D. L; Bras, J.; Dufresne, A. *Biomacromolecules* **2010**, *11*, 1139−1153.

(13) Xiaofei, M.; Ruijuan, J.; Peter, R. C.; Jiugao, Y. *Biomacromolecules* **2008**, *9*, 3314−3320.

(14) Salam, A.; Pawlak, J. J.; Venditti, A. R.; El-tahlaw, K. *Biomacromolecules* **2010**, *11*, 1453−1459.

(15) Salam, A.; Pawlak, J. J.; Venditti, A. R.; El-tahlaw, K. *Carbohydr. Polym.* **2011**, *84*, 1221−1229.

(16) Salam, A.; Pawlak, J. J.; Venditti, A. R.; El-tahlaw, K. *Cellulose* **2011**, *18*, 1033−1041.

(17) Cellulose acetate excellent in physical strength and process for production thereof. US Patent 5990304. US Patent Issued on November, 23, 1999.

(18) Pushpamalar, V.; Langford, J.S.; Ahmad, M.; Lim, Y.Y. *Carbohydr. Polym.* **2004**, *57*, 261−267.

(19) Christian, D.; Roberta, D. S.; Francesca, S.; Alessandro, S.; Giuseppe, V.; Alfonso, M.; Luigi, N. *Appl. Polym. Sci.* **2008**, *110*, 2453−2460.

(20) Diana, A.; Miquel, G.; Roberto, O.; Humberto, V. T.; José, D. S. S.; Keiko, S. *Carbohydr. Polym.* **2009**, *77*, 536−543.

(21) Rui, S.; Zizheng, Z.; Quanyong, L.; Yanming, H.; Liqun, Z.; Dafu, C.; Wei, T. *Carbohydr. Polym.* **2007**, *69*, 748−755.

(22) Liu, X.; Yu, L.; Liu, H.; Chen, L.; Li, L. *Polym. Degrad. Stab.* **2008**, *93*, 260−262.

(23) Bernabé, P.; Peniche, C.; Argüelles-Monal, W. *Polym. Bull.* **2005**, *55*, 367−375.

(24) Mitikka-Eklund, M.; Halttunen, M.; Melander, M.; Ruuttune, K.; Vuorinen, T. *Yokohama* **1999**, *6*, 432−439.

(25) Fors, C. Licentiate Thesis, Royal Institute of Technology, Department of Pulp and Paper Chemistry and Technology. Stockholm, Sweden, 2000; p 78.

(26) Koran, Z. *Tappi J.* **1993**, *77*, 167−170.

(27) Mucha, M.; Miskiewicz, D. *J. Appl. Polym. Sci.* **2000**, *77*, 3210.

(28) Duker, E.; Lindstrom, T.; STFI-Packforsk, A. B.; Sweden, S. *Nord. Pulp Pap. Res. J.* **2008**, *23*, 57−64.