

12-1-2018

Section: Chemistry

MODIFIED STARCH AS ADDITIVES TO IMPROVE TISSUE PAPER PROPERTIES

Mohamed Ghazy

Chemistry Department, Faculty of Science, Al –Azhar University, Nasr City, Cairo, Egypt

Waleed El-Zawawy

National Research Center, Cellulose, and Paper Department, 33 El-Bohuth St. former El-Tahrir St., Dokki, Giza, Egypt

M. Owda

Chemistry Department, Faculty of Science, Al –Azhar University, Nasr City, Cairo, Egypt

Abd-Allah Elmeshtawy

Chemistry Department, Faculty of Science, Al –Azhar University, Nasr City, Cairo, Egypt

Follow this and additional works at: <https://absb.researchcommons.org/journal>

 Part of the [Life Sciences Commons](#)

How to Cite This Article

Ghazy, Mohamed; El-Zawawy, Waleed; Owda, M.; and Elmeshtawy, Abd-Allah (2018) "MODIFIED STARCH AS ADDITIVES TO IMPROVE TISSUE PAPER PROPERTIES," *Al-Azhar Bulletin of Science*: Vol. 29: Iss. 2, Article 17.

DOI: <https://doi.org/10.21608/absb.2018.33769>

This Original Article is brought to you for free and open access by Al-Azhar Bulletin of Science. It has been accepted for inclusion in Al-Azhar Bulletin of Science by an authorized editor of Al-Azhar Bulletin of Science. For more information, please contact kh_Mekheimer@azhar.edu.eg.

MODIFIED STARCH AS ADDITIVES TO IMPROVE TISSUE PAPER PROPERTIES

Mohamed B.Ghazy¹, Waleed K. El-Zawawy^{2*}, M. E. Owda¹, Abd-Allah M. A. Elmeshtawy

1-Chemistry Department, Faculty of Science, Al –Azhar University, Nasr City, Cairo, Egypt.

*2-National Research Center, Cellulose, and Paper Department, 33 El-Bohuth St. former El-Tahrir St., Dokki, Giza, Egypt (*e-mail: wkwzawawy@yahoo.com).*

ABSTRACT

Our research tries to share solutions of the problems that faced who are working in the papermaking industries, especially the retention of the filler, fine fibers, drainage and machine run ability, besides paper strength, softness, smoothness and the increase in the absorption properties of the tissue paper. Starch, which is the most widely used as strengthening agent in papermaking, was modified in the current work with urea, caustic soda and were added to the pulp paste in ratios of 5 to 20 ml. On the other hand, the starch-caustic soda was further modified with trimethylamine hydrochloride in the presence of epichlorohydrin (ECH) as a cross-linker and was also added in the same above ratios to the pulp paste. Another modification was made to the starch which was polymerized with acrylic acid to give hydrogel which was added to the pulp paste in a tiny amount, i.e. 0.001g, and in the same manner, the bleached bagasse pulp was polymerized and added to the pulp paste. The results showed an improvement of the strength, softness, smoothness, stiffness, absorption and zeta potential compared to the blank, enabling them to be promising for making tissue paper or absorbing paper. The research also approaches the environmental address since the bagasse considered as a renewable and sustainable resource coming from agricultural residue (sugarcane) which lead to the decrease in both their environmental impact and economic cost.

Keywords: Starch, bagasse, acrylic acid, modification, hydrogel, papermaking.

1- INTRODUCTION

Pulp and paper production are mainly based on wood, whether soft or hard especially on the countries with forests or non-woody plant (e.g., agricultural residues) in the countries which are lack in forests like Egypt. Agricultural residues can be the main source of cellulose, which is the basic principal component of industrial products such as pulp and paper, pharmaceutical, cosmetics, tissue paper, toilet, paper and food industries [1].

This work was concerned with tissue paper since there are wide ranges to use; such as toilet paper, kitchen towels, facial tissues, napkins. These products exhibit the typical characteristics properties of the tissue papers such as softness, high absorption capacity, and structural strengths. Tissue papers sometimes used in contact with food by end users. The tissue papers for kitchen towels and napkins have multifunctional products, where the main uses are hygiene, cleaning and absorption purposes, but they are not specifically intended to contact with food for a long time. For the manufacturing of the tissue papers, kitchen towels and napkins, there are many restrictions

on some types of dry strengths, such as polyacrylamide and acrylonitrile, and some dyes like anionic and cationic direct dyes. For improving their properties, filler (kaolin, clay or talc), additives (natural or synthetic), polymers, et, can be used. Starch is the widely dry strength agent in the papermaking [2], where the most common method for using starch as a wet end strength additive in the papermaking is the additions of cooked starch to the pulp furnish under a controlled charge condition. When mixed with fiber and filler [3], the starch adsorbs on the surface of both filler and fiber as soft gel layer between fiber-fiber joints which increased tensile index and stiffness of the paper. Ibrahim *et al.* [4] modified talc with starch (cooked talc –starch) which improved the mechanical properties by 61.9%. Zegui *et al.* [5] reported that the retention of neutral starch in a pulp furnish is less than 40%. Thus, starches are often modified as cationic charged or amphoteric starches to increase starch retention and this is because pulp furnishes are negatively charged [6]. Lim *et. al.* [7] found that cationic starch increased Scott bond, tensile strength, and burst index. Starch modification process usually increases

the cost of starch. Although the cationic starches show improvement of the adsorption on fibers and fillers, achieving a high retention of starch on fibers, it still poses a problem in the papermaking process, if the retention of starch cannot be well controlled, unretained starch will accumulate in the white-water and create pitch, slime, and stickiness problems. Alternatively, if the starch can be strongly coated to the filler surface, it is expected that the filler-fiber bonding can be significantly improved, and strong paper sheets can be obtained. The effectiveness of cationic starch as a pre-flocculating agent enabled the production of highly filled mechanical pulp grades of paper [8-11]. Zegui *et al.* [5] developed a new clay filler modification method at very low cost, which can increase the filler loading in the paper while maintaining sheet strength. As we know polyvinyl alcohol and starch are the best drying strengthen agent using extensively in the papermaking especially when converted to cationic through which they can act with the negative sites of the fibers besides hydroxyl groups enhancing formation of the hydrogen bonding between them. Fatehi *et al.* [12] found that cationic-modified polyvinyl alcohol could be a promising dry strength additive for unbleached soda air AQ straw pulps, where it increased the mechanical strength of the paper and its impact on the stiffness of the fibers was more considerable. Hanxue *et al.* [13] found that oxidation with semi-dry process, resulted in significant changes in the degree of crystallinity of starch and texture properties, so physicochemical properties of starches (corn, wheat, and oat) were altered. Hak Lee and his workers [14] made a comparison between cationic starch and oxidized starch when used as a sizing agent and they found that adsorption ratio of cationic starch was twice larger than that of oxidized starch and both the fines retention and the strength were increased so as stiffness was improved when cationic starch was used in the film transfer size press.

Since starch is the most widely used strength agent in paper due to its low price, high performance returned to its containing of high numbers of hydroxyl groups which

capable of forming hydrogen bonding with the cellulosic fibers to improve retention of fines fibers, fillers, and internal sizing agents, so it was modified to be used as additives in paper pulp to increase paper strength, and to improve the running of the papermaking machine, where it is aimed to be added at the wet end of the paper machine process.

2. EXPERIMENTAL

2.1. Insoluble Starch modification with urea

For first modification, where insoluble starch was mixed with 4% of its weight urea with three times of its weight water in a flask fitted with a mechanical stirrer. The stirring was continued for 3.5 hours at 95°C. After the desired reaction time had elapsed, the mixture was added as 25ml, 17ml, and 7ml, respectively, to the pulp of the paper sheet.

2.2. Insoluble Starch modification with caustic soda

In the second modification, insoluble starch (3.4 g) was mixed with 75 ml of 10% NaOH in a flask fitted with a mechanical stirrer. The stirring was continued until the insoluble starch was dissolved then the mixture was added as 20ml, 10 ml, and 5 ml, respectively, to the pulp of the paper sheet.

2.3. Insoluble Starch - Caustic Soda modification with Trimethylamine (TMA)-HCl in the presence of ECH as a crosslinker.

For the third modification, 36% trimethylamine hydrochloride (TMA-HCl) (9g in 25 ml distilled water) was added drop by drop to the starch-caustic soda in fitted flask with mechanical stirrer, followed by the addition of 10 ml Epichlorohydrin (ECH) (drop by drop) with continuous stirring at room temperature for 4 hours (till miscibility). Then, it was used as an additive modified starch in 20 ml, 10 ml, and 5ml.

2.4. Insoluble Starch-caustic soda modification with acrylic acid using ECH as a crosslinker

In the fourth modification, insoluble starch - caustic soda was initiated with 1% potassium persulfate in fitted flask, for 30 minutes at 30-

60°C with magnetic stirring, then the solution was grafted with acrylic acid in liquor ratio 1:10, under nitrogen stream, followed by addition of 10 ml ECH as across linker with raising the temperature up to 80°C for 2 hours, where the gelation was finished then washed with 75% ethanol and left to dry, grind to powder and was added as 0.001% of the paper pulp weight.

2.5. Bagasse pulp modification with acrylic acid using ECH as a crosslinker

In the fifth modification, bagasse pulp (1g) was activated with 20 ml of 10% NaOH (w/v) at 40°C for 4 hours then initiated with 1% potassium persulfate for 30 minutes at 30°C under continues stirring. The grafting step was carried out with acrylic acid in liquor ratio 1:10, under nitrogen, then 10 ml of ECH was added as a crosslinker. The temperature was raised up to 80°C and after 2 hours the hydrogel was formed then washed with 75% ethanol and left to dry before grinding to powder. The hydrogel was added as 0.01 % of the paper pulp weight.

2.6. Sheet making and loading

The paper sheets were prepared using an SCA-model sheet former (1), where 12g of bagasse pulp was suspended in 600 ml water after that, divided into 6 samples each of them has 2% consistency (w/v), where the first division was used for preparation of pure sheet (blank) and the second division was used for preparation of paper sheets that were loaded with modified starch-urea in different volumes (25ml, 17ml and 7ml), respectively. While in the third division the paper sheets were loaded with modified starch-caustic soda in different volumes (20ml, 10ml, and 5ml). The fourth division was used for the preparation of sheets that were loaded with modified starch-caustic soda with TMA-HCl in the presence of ECH in different volumes (20ml, 10ml and 5ml), respectively, while the fifth division was used for preparation of paper sheet that was loaded with 0.01g (dry powder) of modified starch with acrylic acid in the presence of ECH as a crosslinker. For the sixth division, the paper sheet was loaded with 0.01g (dry powder) of

the modified bagasse pulp (cellulose) with acrylic acid using ECH as a crosslinker.

2.7. Testing

After conditioning the hand sheets at 20°C and 65% relative humidity for 72 hours, they were weighed and divided into suitable sizes for the mechanical tests (tensile strength) and softness according to TAPPI T4940 om-88 and T414 om 88 [2], respectively, using HANDL METER TENSILE UNIVERSAL TESTING MACHINE. Also, the tensile strength was used, where the maximum strength was obtained by dividing maximum load at the time of fracture by the cross-sectional area (width X thickness) of the specimen.

2.8. Physical Properties

2.8.1. The absorption rates

The absorption rate was determined gravimetrically by immersing a weighed dry sample (w_d) in distilled water at room temperature for 24 hours then filtered through a sieve, where excess water was removed by hanging the sieve till no water was dropped. The swollen sample was weighed (w_w) and the amount of absorption water was calculated from the following equation

$$Q_{H_2O} = \frac{w_w - w_d}{w_d} \times 100$$

2.8.2. FT-IR structure

FT-IR spectra of bleached bagasse pulp, grafted bagasse pulp (hydrogel) and the paper sheets results from the addition of bagasse grafted acrylic acid, starch, and starch grafted with acrylic acid were measured after mixing with KBr and pressed in pellets using JASCO FT-IR 6100 instrument in the range of 4000 – 400 cm^{-1} .

2.8.3. Morphological structure

SEM was carried out using JEOL JXA-840A electron microprobe analyzer (JOEL USA Inc, Peabody, MA) on aluminum stubs and coated with a thin layer of palladium-gold alloy to illustrate the morphological structure for samples.

2.8.4. Charge Demand

Zeta Potential analysis was carried out for all the samples using PCD04 devise to measure the demand charge.

3. RESULTS AND DISCUSSION

Sugarcane bagasse, which kindly provided from Quena Pulp and Paper Company, is the raw material in this study. The pulp was bleached to gain high purity to the pulp and all the analysis were carried out and the results were collected in Table 1.

The results indicate that the bleached bagasse pulp has 79.75% of the holocellulose, i.e. α -cellulose and hemicelluloses, and 5.3% of lignin with high ash content that reached 13.82%. On the other hand, the SEM for the bleached bagasse pulp was noticed in Figure (1), where the fiber can be seen.

Table 1; Analysis of the bleached bagasse.

α -cellulose	Hemicellulose	Lignin	Ash
62.12	17.63	5.3	13.82

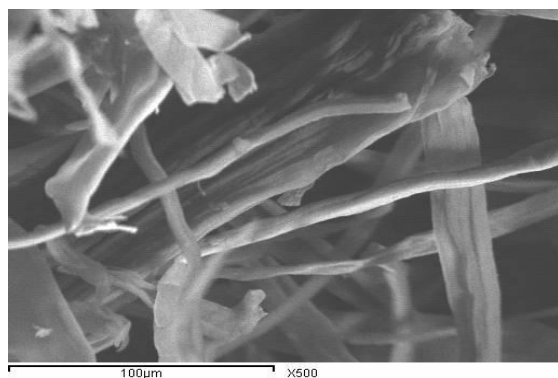


Figure (1): SEM of bagasse

The FT-IR of bleached bagasse pulp was carried out to identify the characteristic groups. Figure 2a shows the specific bands for cellulose at 3300-3413 cm^{-1} which related to O-H groups and C-H stretched at 2912 cm^{-1} [15]. The bands between 800 cm^{-1} and 1628 cm^{-1} are specific for cellulose structure. Also, bands at 1431, 1372, 1322, 1162, 1033, 896 cm^{-1} are typical of pure cellulose. Generally, bands at 897 cm^{-1} and 1165 cm^{-1} are assigned as C-O-C stretching at the β -(1-4) glucosidic linkage and band at 1337 cm^{-1} is assigned as the C-O-H bending at C-2 or C-3 while the band at 1431 cm^{-1} assigned to the absorbance of C-O-H bending in plane at C-6 which arise by changing the environment at C-6 [16].

On the other hand, the FT-IR for the starch, Figure 2b, show O-H stretching produces a broadband that occurs in the range 3600-3500 cm^{-1} . The C-H stretching bands occur in 2850 cm^{-1} . The bands in the 1700-1500 cm^{-1} region are due to C=C and C=O stretching. Carbonyl stretching is one of the easiest absorptions to recognize in an infrared spectrum. It is usually the most intense band in the spectrum and depending on the type of C=O bond, occurs in the 1830-1650 cm^{-1} region [17].

3.1. Bagasse pulp and starch modification with acrylic acid using ECH as a crosslinker

As mentioned previously, bagasse pulp was modified with acrylic acid to prepare hydrogel (grafted bagasse) and the sample was analyzed.

3.1.1. FT-IR for grafted bagasse

FT-IR spectra for the grafted bagasse, as shown in the Figure 3a, indicated an absorption band at 3459 cm^{-1} , 2924 cm^{-1} , 2340 cm^{-1} which are characterized for the -OH group of cellulose, C-H stretching and acrylic acid [18-20], while 1728 cm^{-1} is characterized for the C=O of the carboxylic group of acrylic acid (-COO) [21], and the C=C absorption band was shifted to small band at 1555 cm^{-1} which means that vinyl group transferred to C-C free radical. On the other hand, the absorption band at 1455 cm^{-1} and 1271 cm^{-1} are characterized to -CH& -OH and the absorption band at 1163 cm^{-1} is characterized to -CH of bending vibration [19, 22].

Moreover, the FT-IR spectra for the grafted starch, as shown in the Figure 3b, indicated an absorption band at 3462 cm^{-1} which is characteristic for the -OH group of starch and acrylic acid. The bands at 2924 cm^{-1} and 2857 cm^{-1} represent the C-H stretching, while that at 1730 cm^{-1} is characterized for the C=O of the carboxylic group of acrylic acid (-COO) [23], and the C=C absorption band was shifted to small band at 1549 cm^{-1} which means that vinyl group transferred to C-C free radical. On the other hand, the absorption band at 1407 cm^{-1} and 1159 cm^{-1} are characterized to -CH & -OH and the absorption band at 1010 cm^{-1} is characterized to C-O band [22].

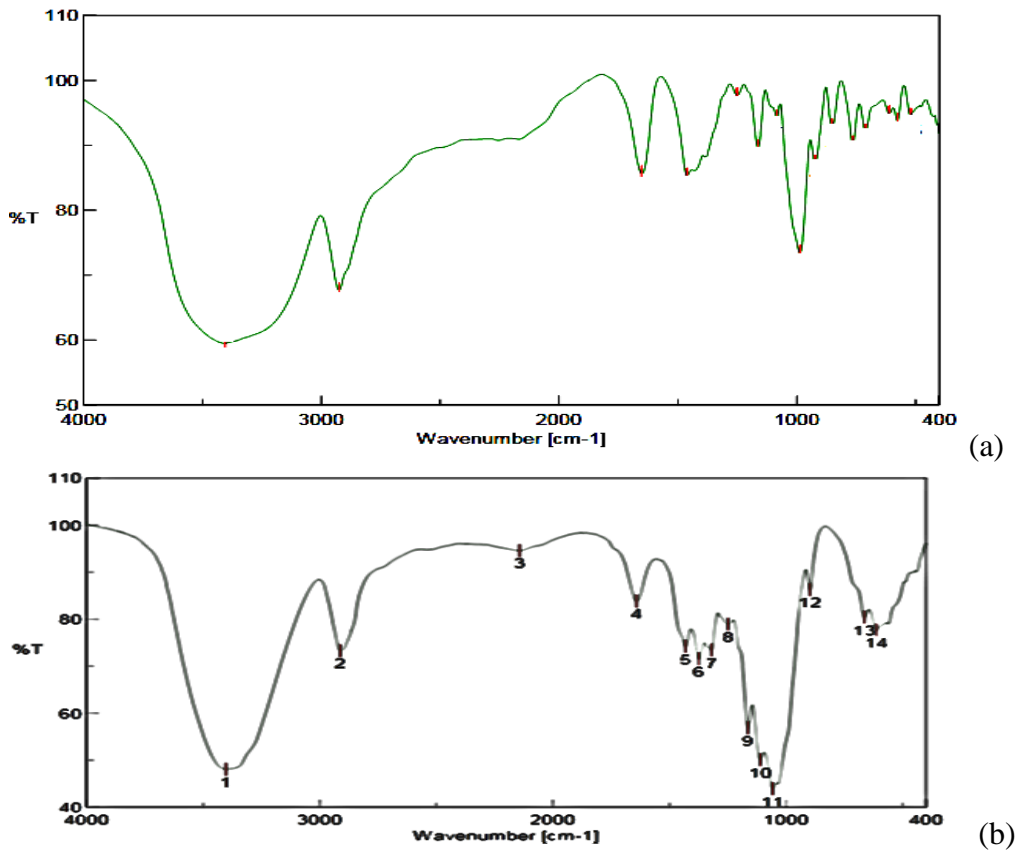


Figure (2): FT-IR spectra of (a) bleached bagasse pulp and (b) starch

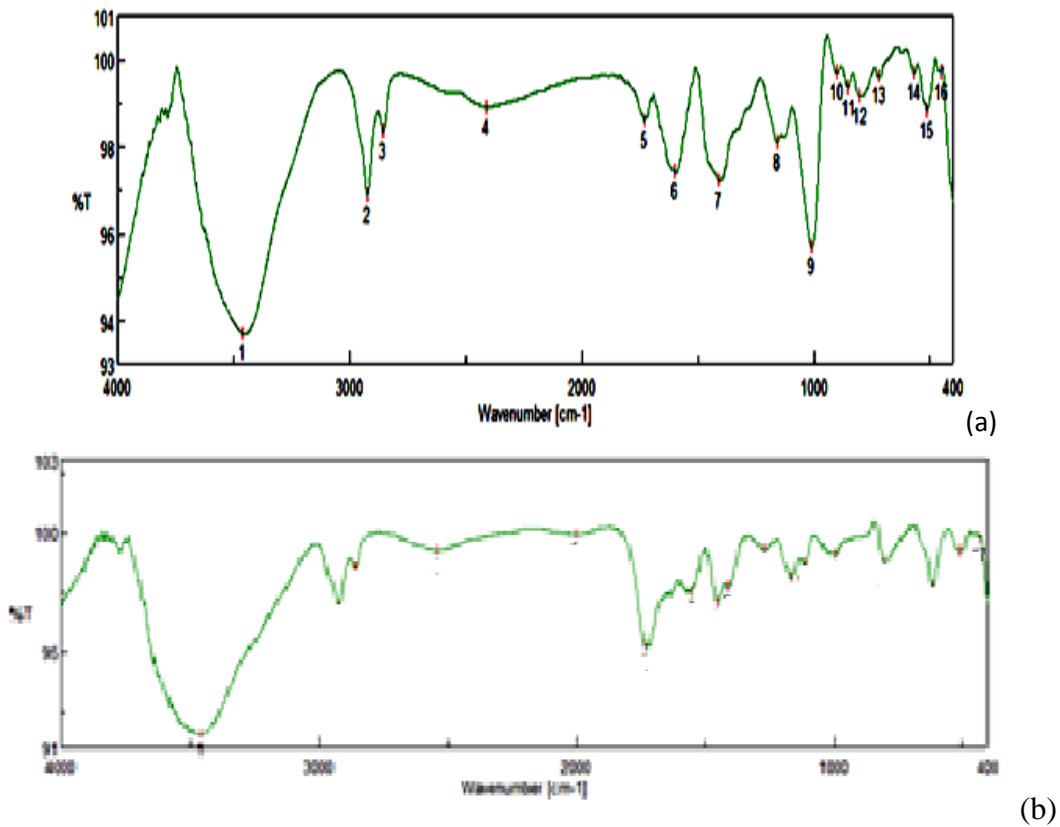


Figure 3: FT-IR for (a) grafted bagasse pulp (hydrogel from bagasse) and (b) grafted starch (starch-hydrogel).

3.1.2. Mechanism of the reaction

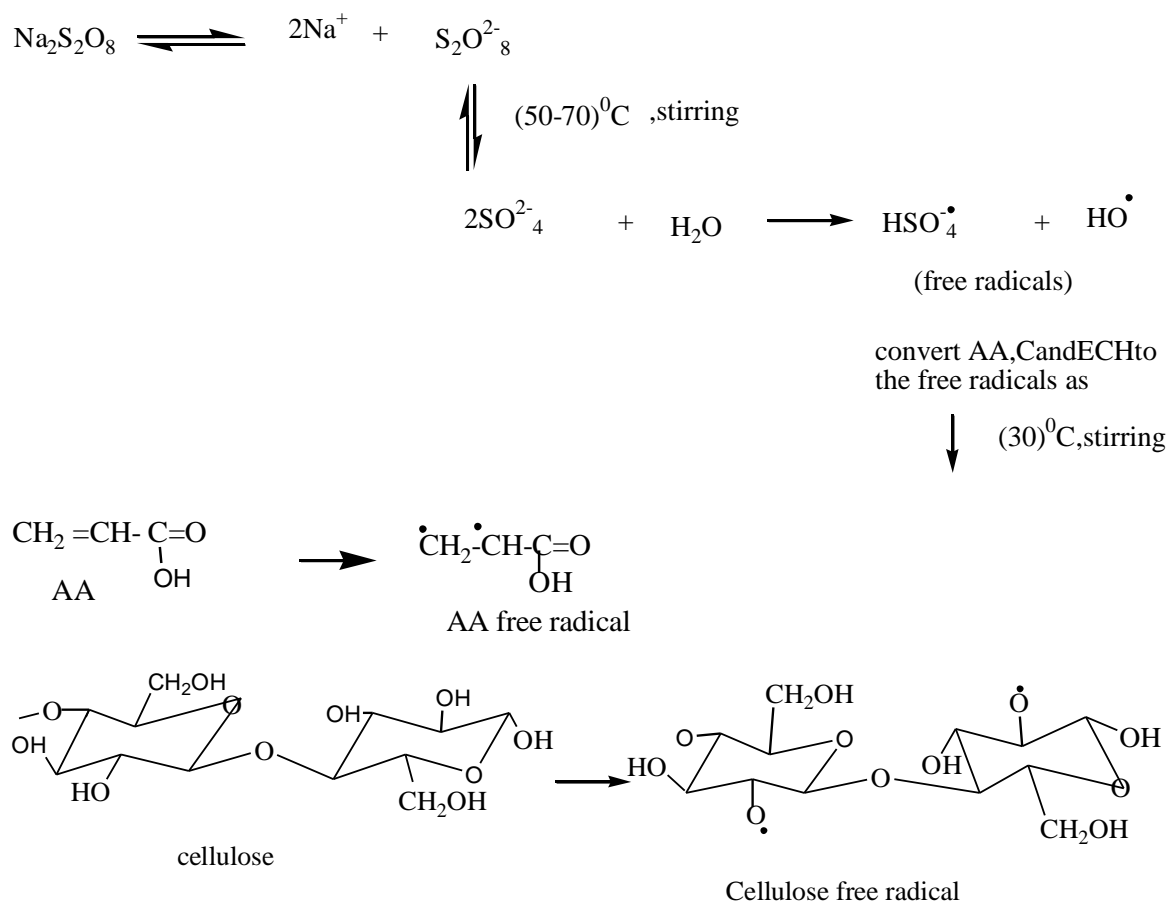
The polymerization process was carried out through three steps;

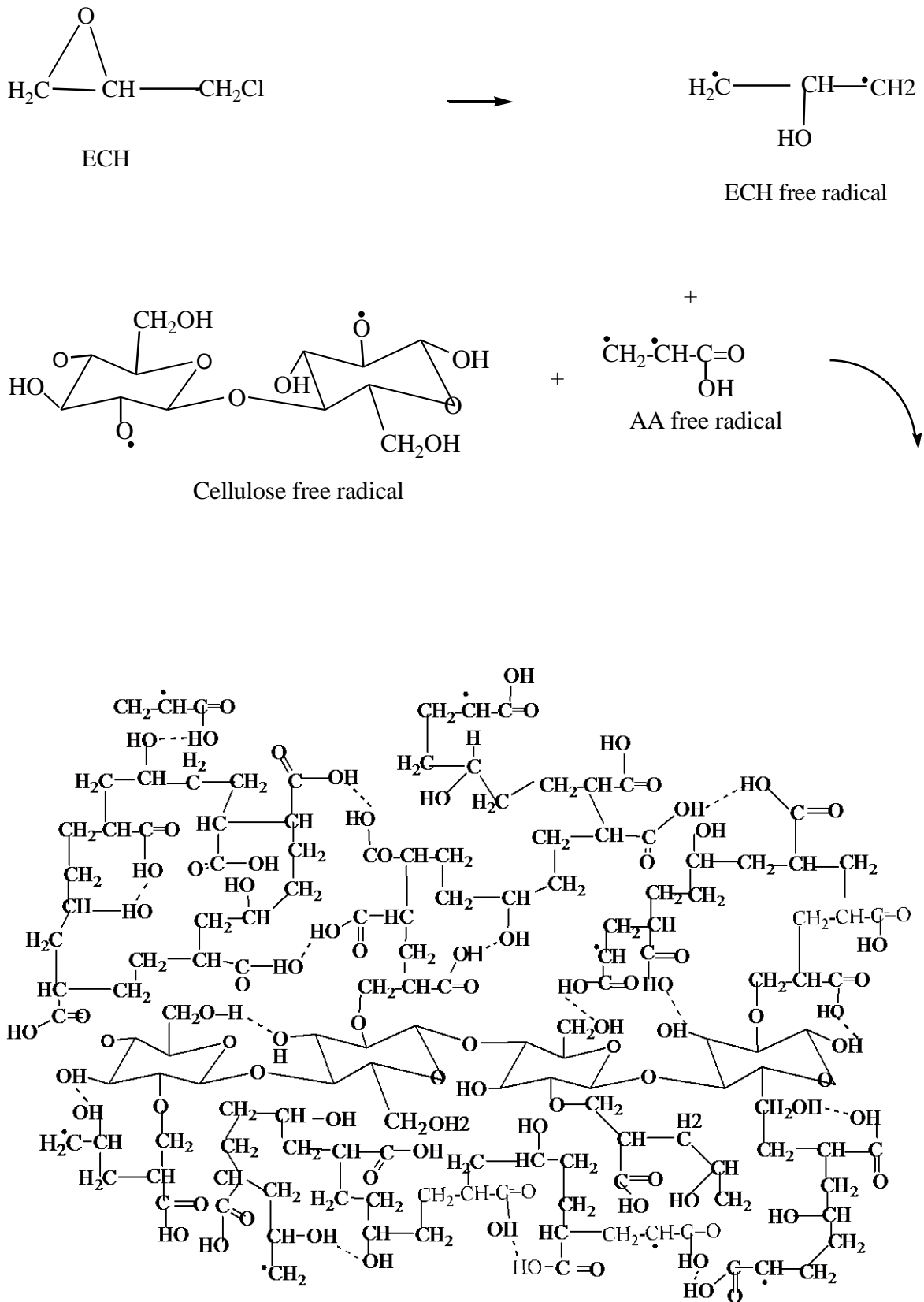
- i) Activation; where the pulp was activated with sodium hydroxide for 4 hours at 80°C, to swell the fibers. This step was followed by
- ii) Initiation step; in which potassium persulfate creates the free radicals $\text{SO}_4^{\cdot-}$ and HO^{\cdot} which creates active sites onto both the cellulose fiber backbone and the acrylic acid (AA) molecule by converting the vinyl group to $\cdot\text{CH}-\dot{\text{C}}\text{H}$ and the OH of cellulose to $\cdot\text{O}$, so as the cross-linker ECH where CH_2-OCH converts to $\cdot\text{CH}_2-\dot{\text{C}}\text{HOH}$.
- iii) Propagation and polymerization; in this step AA-free radical and cellulose free radical or starch free radical were cross-linked through MBA forming the hydrogels. Schemes (1 and 2) show the

mechanism of the formation of the hydrogel for both the bagasse (cellulose) and the starch, where it shows that the cellulose free radicals form hydrogel through the covalent and the hydrogen bonds while that with the starch are mainly hydrogen bonds. This makes the cellulose hydrogel takes time to swell than the starch hydrogel.

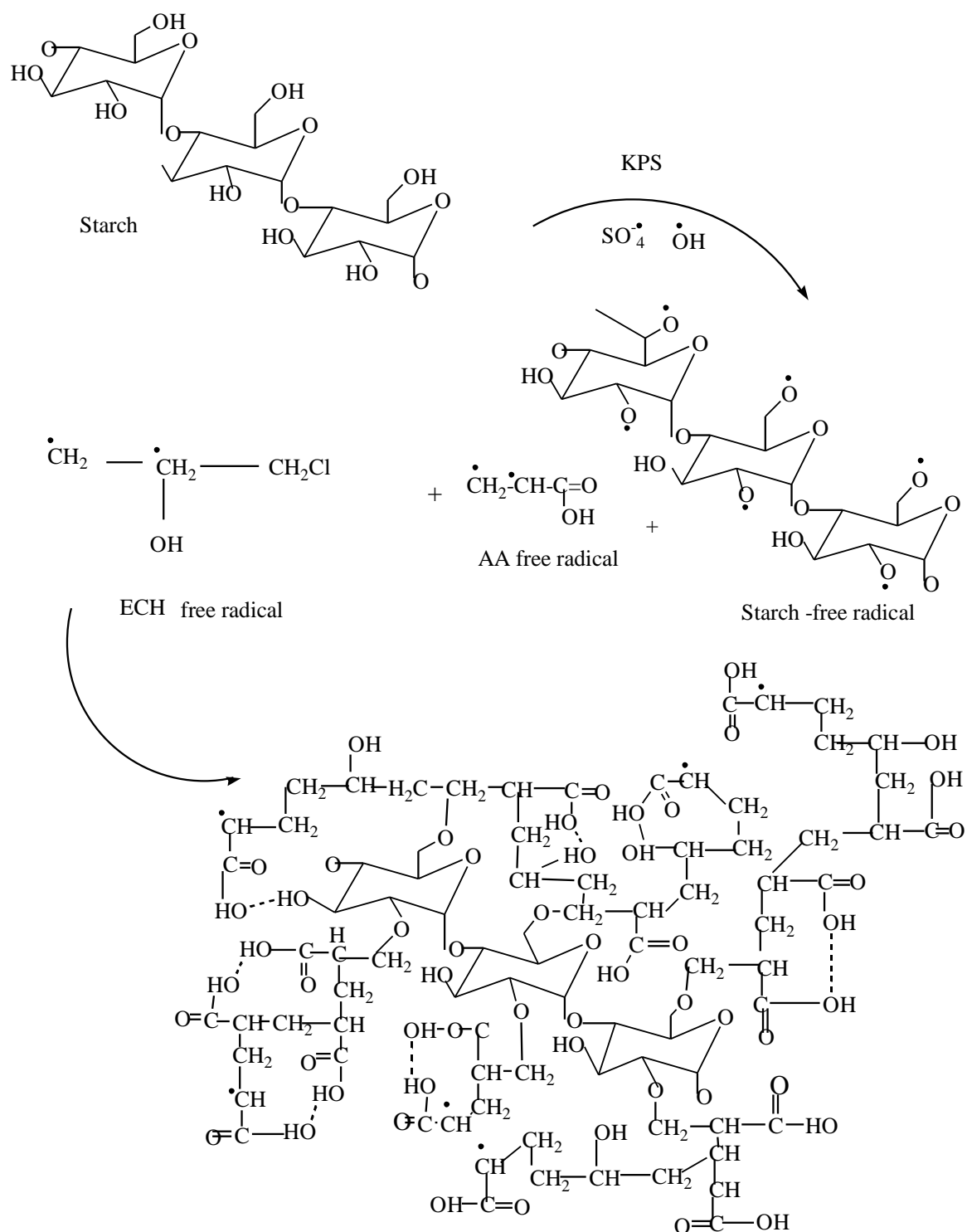
3.2. The appearance of the hydrogel.

Figure 4 indicated that the prepared hydrogel from both starch and bagasse pulp are in powder shape in their dry state. This appearance changed after absorption where they appear as a translucent mass in the swelling state. After drying, they shrank again due to losing the absorbed water and this makes them more important for biodegradable materials for wide applications.





Scheme1: Mechanism of the bagasse (cellulose) hydrogel preparation



Scheme 2: Mechanism of starch-acrylic acid hydrogel



Starch hydrogel in the dry state



bagasse hydrogel in the dry state



Starch hydrogel after swelling



bagasse hydrogel after swelling



Starch hydrogel after drying



bagasse hydrogel after drying

Figure 4. The appearance of both starch and bagasse hydrogel in their different states

3.4. Morphological Structure

Figure (5) shows the SEM for swollen starch-hydrogel. The Figure clears an exhibited macropores architecture. It can be seen that there is an increase in the pore size that causes more open structure and makes it loosely which interpreted by the occurrence of electrostatic repulsion which causes enlargement of the space in the networks of the hydrogel in the swelling state. As the pore size is very large so, a numerous water molecules can easily diffuse into the hydrogel to form the large pores leading to the higher swelling ratio.

3.5. The rate of water - absorption

The rate of water absorption was calculated, and it was noticed that 1g of the bagasse-hydrogel absorbs 155g of water within 2minutes, where 1g of the starch-hydrogel absorbs 44.25g of water within 5 minutes.

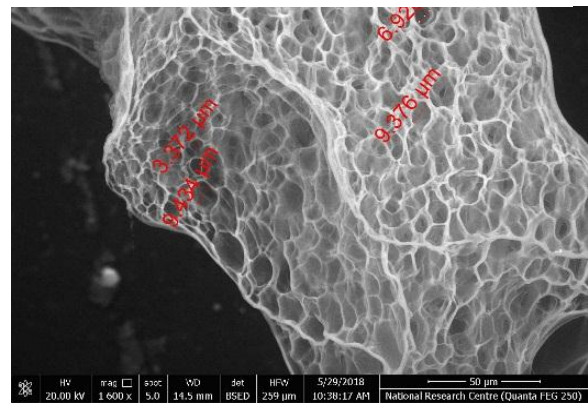


Figure 5: SEM of starch-hydrogel

As mentioned before, the bagasse pulp past was divided into six divisions. The 1st one of them was used as a pure pulp for preparation of the blank sheets, while each one of the other three divisions (2nd, 3rd, and 4th) were loaded with one type of modified starch in different concentrations, while the 5th and the 6th were loaded with modified starch-hydrogel and bagasse-hydrogel in one concentration (0.001g/

8g pulp). The dry strength, softness and stiffness, absorption, zeta potential and demand charge were analyzed, and all the results were collected in Table (2).

The improvement in the paper strength using different starch's modifications that collected in Table (2) show that the dry strength was generally increased more than the blank, but the best was given with third modification, since starch alone is used as filler to improve the dry strength where it has abundant hydroxyl groups that are capable of forming hydrogen bonds with cellulose fiber to improve the strength of the paper. In the pulping process, more than 60% of the resulting pulp carries a negative charge, so the treatment of the starch with sodium hydroxide makes it positive and helps in the formation of starch-fiber bond that makes the strength of the paper higher than that without modification. Besides that, as mentioned by Ragheb *et.al.* [6]. Alkali treatment reveals that treatment of starch with sodium hydroxide is accompanied by some physicochemical changes in the structure of starch. Also, Hanxue Hou *et.al.* [13] mentioned that oxidation of starch resulted in significant changes in the degree of crystallinity and the changes increased with the increase of carboxyl content of starch and treatment with alkali gives a high dispersed starch paste which inhibits paste retrogradation and makes it easy to be a homogenized liquid. In the second case, where starch was modified with urea, it produced starch-urea complex which acquires very high affinity to water, thereby causing swelling and gelatinization of starch that can improve the strength of the paper. While in the fourth treatment, the starch became cationic starch (quaternary ammonium ion) that enables it to form starch-fiber bond to improve the strength of the paper, but the improvement with soda is more than this modification, which returns to the quaternary ammonium ion which is a large molecule and enters into the starch molecule forming macromolecule of cationic starch and cellulosic fiber, and since the bonding strength is dependent on the fiber contact area and the intrinsic strength per unit

area of contact it is considered the reason for decreasing the strength. This is confirmed by the results of the cellulose-acrylic acid hydrogel and starch-acrylic acid hydrogel in the presence of ECH where the strength decreased to 1666 and 1927 N/cm, respectively.

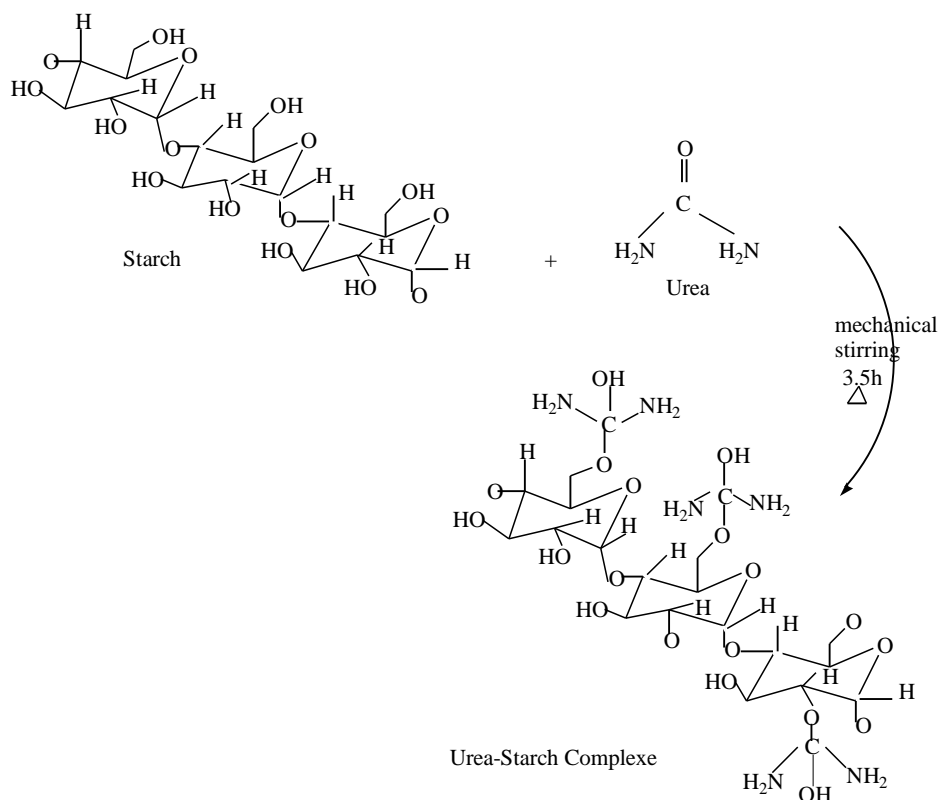
Table 2 also shows that real softness was generally increased and the third modification still has the best results of all, since the real softness increased from 36.5 to 49.9 followed by the fourth one then the second modification, and this was due to the addition of the cationic starch which was added to the pulp as soft gel containing a large amount of water making it easier to adsorb into fiber-fiber joints thus increasing the softness. The Table shows also that the best results for zeta potential was obtained with the fourth modification especially with the higher concentration (20 ml) where it reached to 6.8, followed by the higher concentration (20 ml) of third modification which was improved, since reducing the value of zeta potential close to zero increases retention values of starch, drainage of water and run ability of the machine. Zeta potential with both the fifth and the sixth modifications are low due to the presence of a large number of carboxylic groups (COO^-) related to acrylic acid, and hydroxyl groups (HO^-) of cellulose or starch which forms negative cloud (repulsion force) over the structure causing more negative zeta potential, so the fibers do not approach to each other, and the strength became lower but still more than the blank.

The schemes (1, 2) declared the possibility of the presence of the different modification. Table 2 shows also that, the high addition of any kind of starch modifications gave the best result and decreases with decreasing the amount of the modified starch addition. This means that increasing the addition amount of modified starch increases the formation of the fiber-fiber bond and the distribution of the fibers within the sheet, thus increasing the strength of the paper.

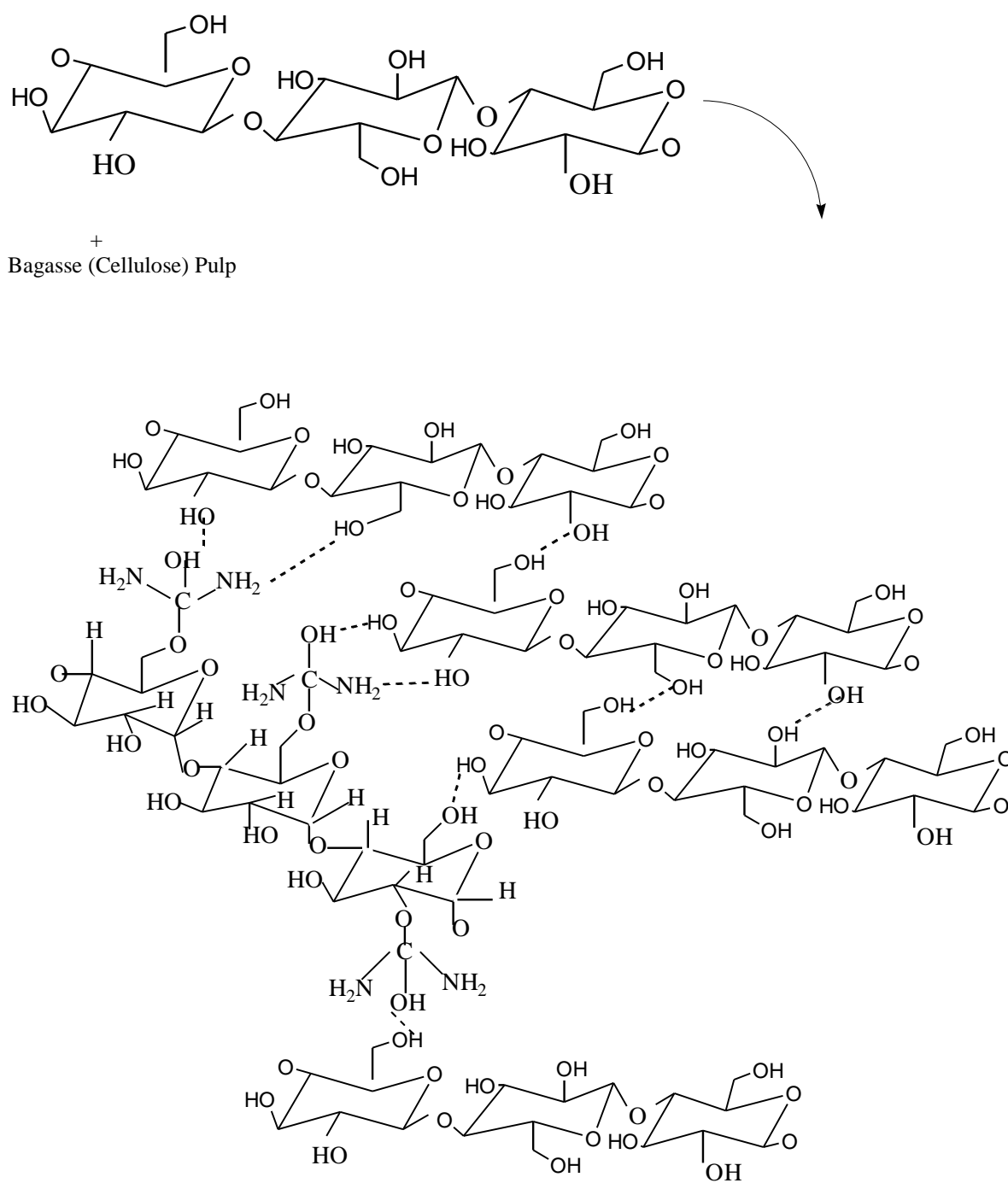
In the third modification, the starch was modified with sodium hydroxide to form oxidized starch as in scheme 5.

Table (2); The effect of the six modification on the tensile, softness, absorption, zeta potential, and demand charge.

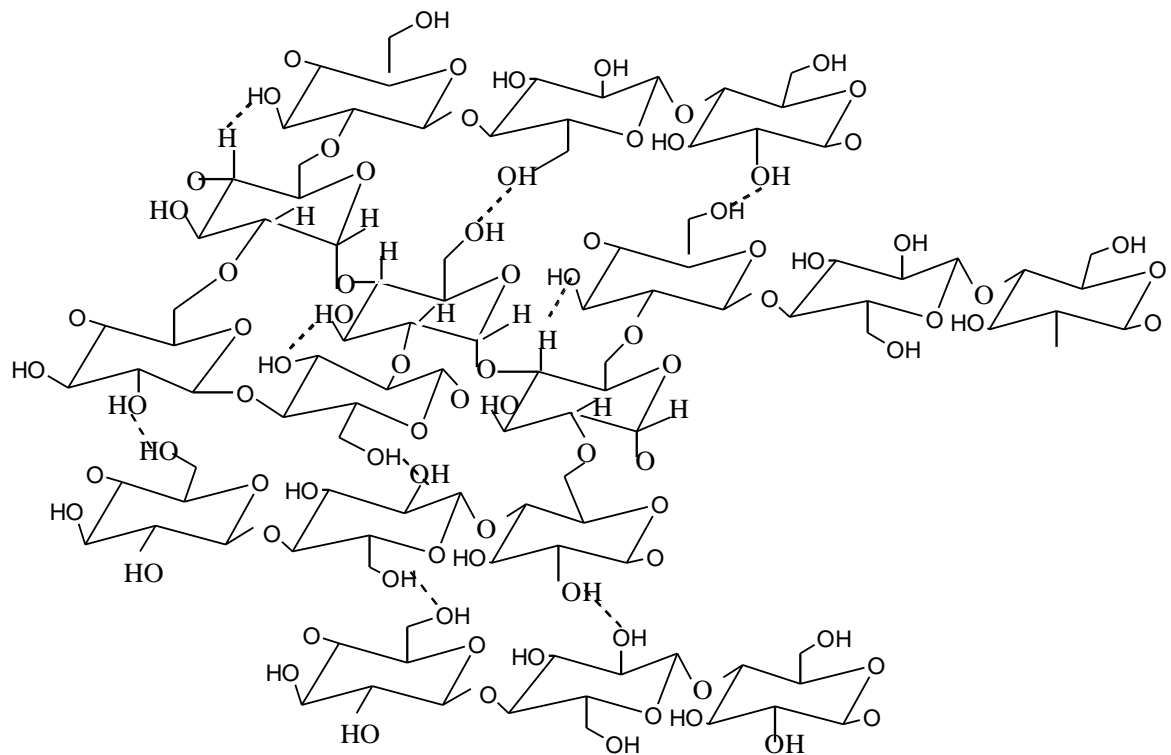
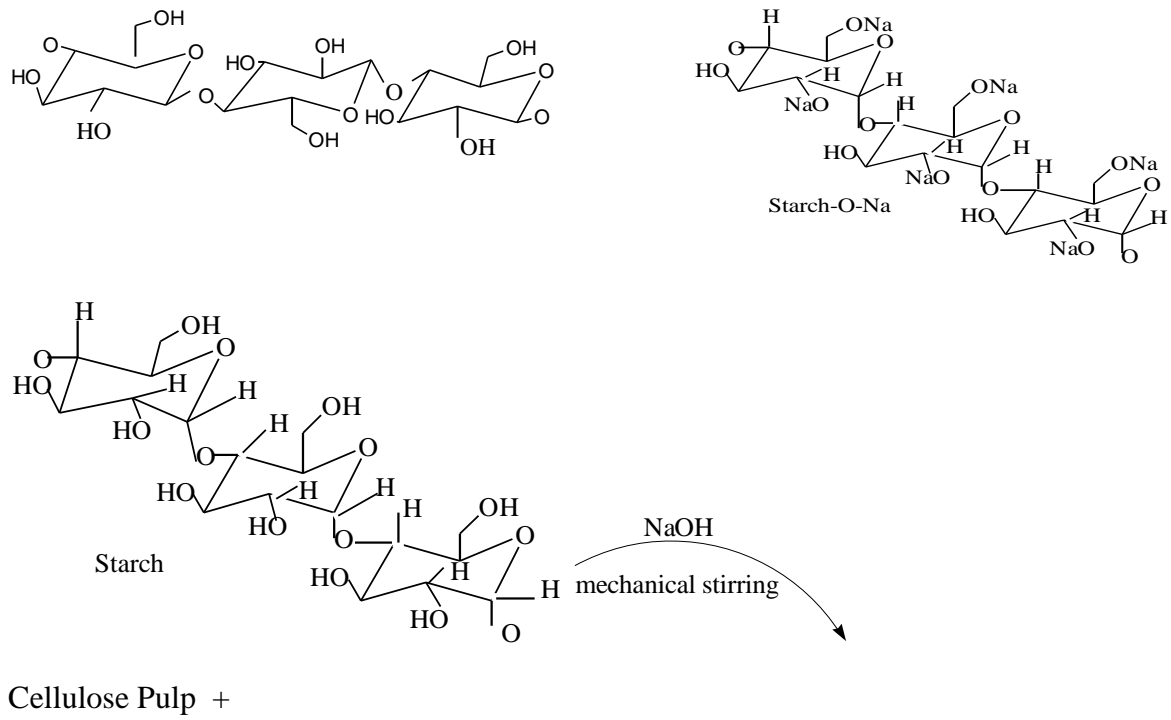
Sample	Tensile strength N/Cm	Softness			Stiffness	Absorption		Zeta Potential	Demand charge
		Hand fell	Real softness	Felt smoothness		Time of abs.	% of abs.		
Blank (1 st)									
	1583	5.6	36.57	167.16	1.02	4.1	4.99	-8.2	-258
Sample (2 nd)									
25ml.	2131	-17.7	41.13	451.7	1.55	3.3	5.8	-7.8	-66
14ml	2068	-9.6	41.18	220.8	0.69	3.0	5.7	-8.7	-74
7ml	1795	15.8	33.21	.103.62	1.4	2.2	5.6	-8.8	-79
Sample (3 rd)									
20ml.	2240	-23.5	49.9	124.19	1.01	6.1	5.21	-6.1	-247
10ml.	1953	-3.6	41.5	90.28	1.13	15	5.12	-7.3	-248
5ml.	1878	4.3	32.23	157.1	1.01	4.1	5.08	-7.9	-251
Sample (4 th)									
20ml.	2176	11.1	35.16	93.14	0.97	9.6	5.3	-6.8	-58
10ml.	2126	10.3	37.04	112.37	1.59	4.2	5.3	-7.8	-66
5ml.	1808	7.5	44.07	150.63	1.16	3.9	5.2	-7.9	-69
Sample (5 th)									
0.001g	1666	4.5	15.5	87	1	0.0	150	-78.8	22
Sample (6 th)									
0.001g	1927	1.1	16.5	92	1.1	0.0	140	-30.9	15



Scheme 3: Urea-Starch complex

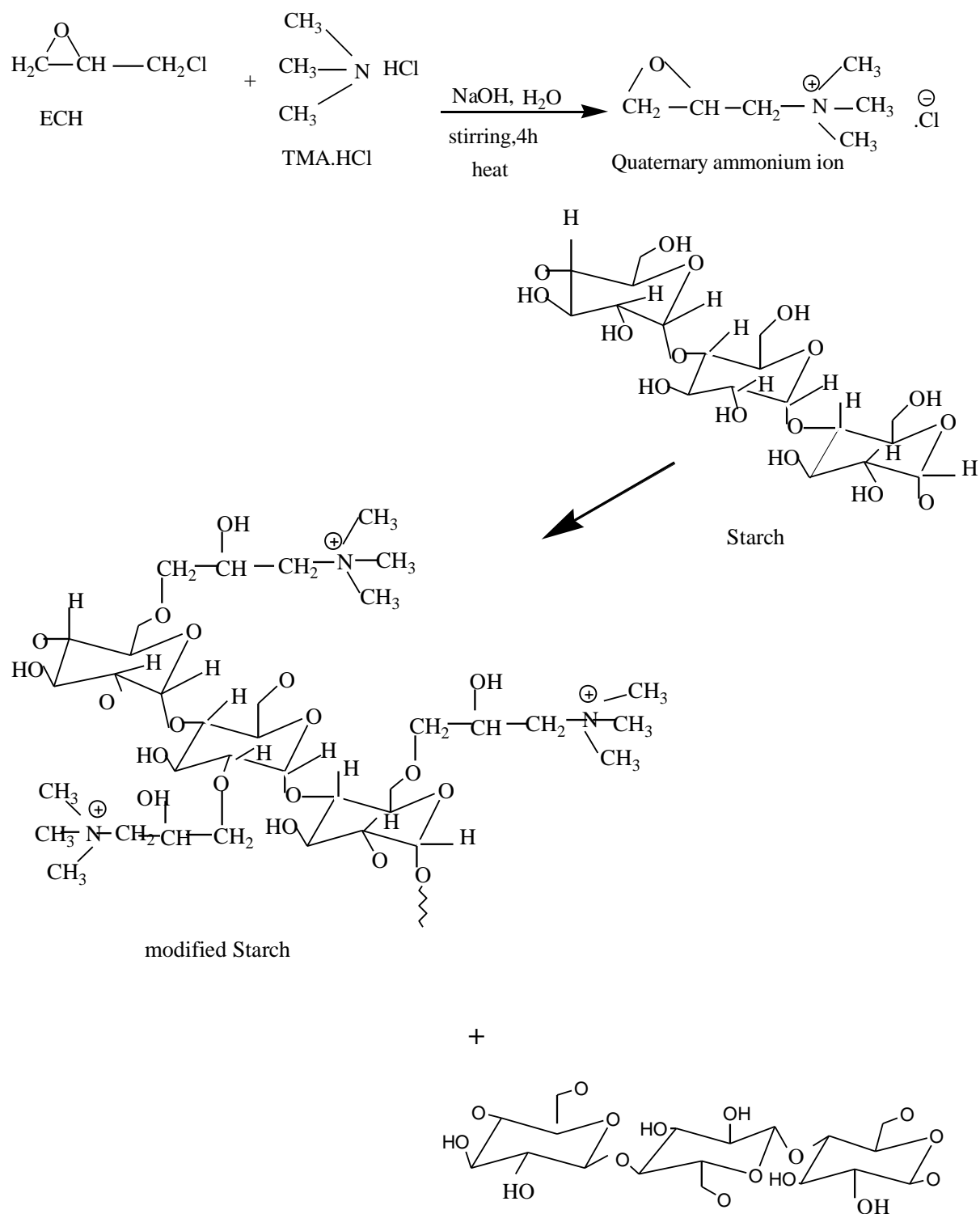


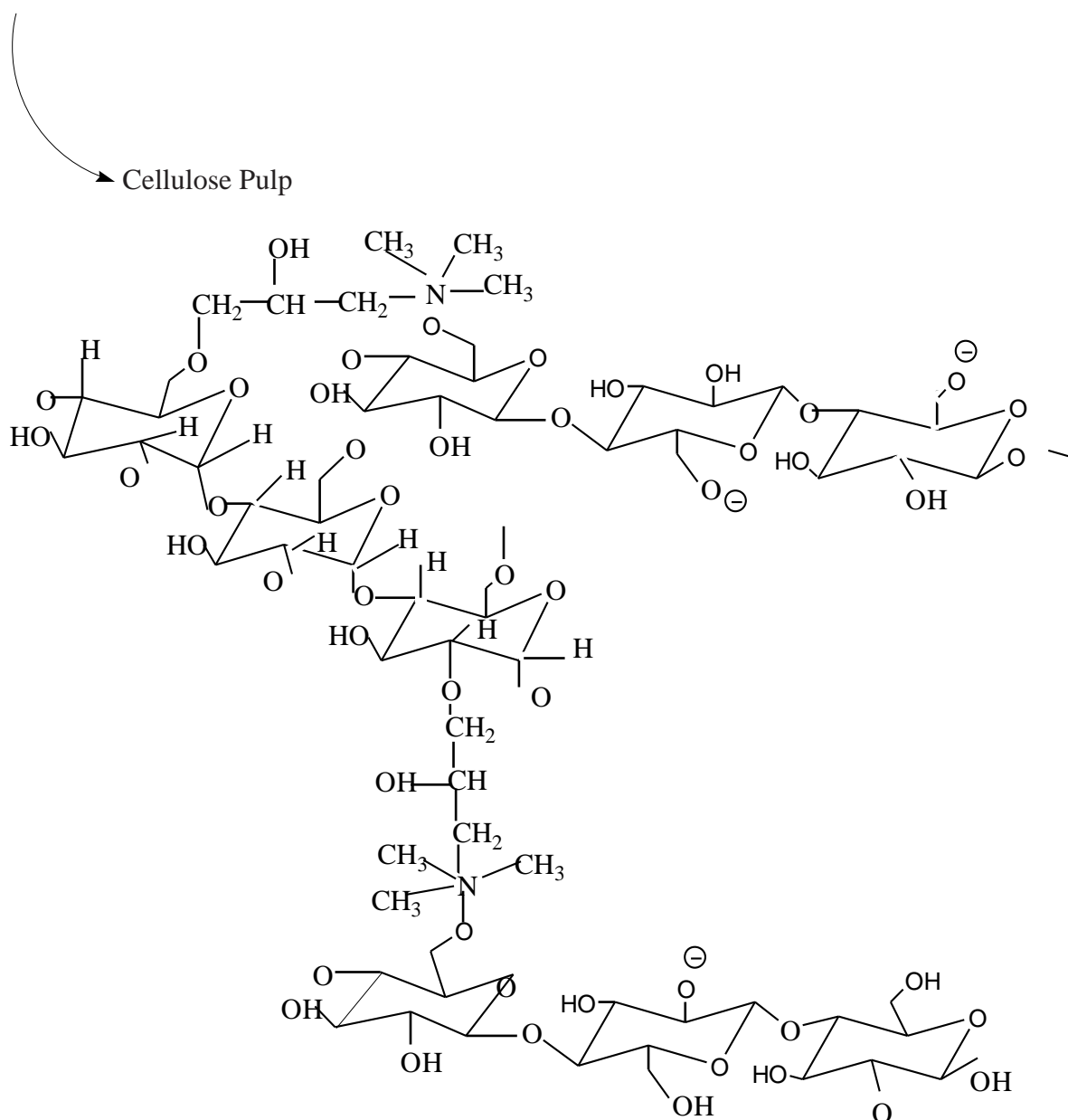
Scheme 4: Addition of starch modified with urea to the pulp



Scheme 5: Mechanism of addition of starch modified with caustic soda to the pulp

The fourth treatment, where starch was modified with caustic soda and ECH and TMA-HCl, is shown in scheme 6.





Scheme 6: Addition of modified starch with TMA-ECH (the fourth treatment) to the pulp

4. CONCLUSION

The results indicate that modifying both starch and bagasse to be used in tissue paper results in improving the mechanical properties as well as the absorption properties. This was due to the formation of large pore size in the fibers that can help in absorbing the water as well as the bond results between the modified starch with the fibers during the papermaking process.

REFERENCES

- 1 Chaker, A., Mutjé, P., Vilar, M. R., & Boufi, S. (2014). Agriculture crop residues as a source for the production of nanofibrillated cellulose with low energy demand. *Cellulose*, 21(6), 4247–4259.
- 2 Jensen, B. M., Winters, J. C., & Hubbe, M. (1986). Cationic potato starches proven effective as wet-end additives. *Pulp Pap*, 60(4), 83.

- 3 Strand, A., Khakalo, A., Kouko, J., Oksanen, A., Ketola, A., Salminen, K., Sundberg, A. (2017). The effect of chemical additives on the strength, stiffness and elongation potential of paper - OPEN ACCESS. *Nordic Pulp and Paper Research Journal*, 32(03), 324–335.
- 4 Ibrahim, M. M., Mobarak, F., El-Din, E. I. S., Ebaid, A. E. H. E., & Youssef, M. A. (2009). Modified Egyptian talc as internal sizing agent for papermaking. *Carbohydrate Polymers*, 75(1), 130–134.
- 5 Yan, Z., Liu, Q., Deng, Y., & Ragauskas, A. (2005). Improvement of paper strength with starch modified clay. *Journal of Applied Polymer Science*, 97, 44–50.
- 6 Ragheb, A. A., Abd, E. T. I., & Tawfik, S. (1995). Gelatinization of starch in alkaline solutions. *Starch - Stärke*, 47(9), 338–345.
- 7 Lim, W. J., Liang, Y. T., & Seib, P. A. (1992). Cationic Oat Starch: Preparation and Effect on Paper Strength. *Cereal Chemistry*, 69(3), 237–239.
- 8 Hubbe, M. A., & Gill, R. A. (2016). Fillers for Papermaking: A Review of their Properties, Usage Practices, and their Mechanistic Role. *BioResources*, 11(1), 2886–2963.
- 9 Shen, J., Song, Z., Qian, X., & Ni, Y. (2011). Carbohydrate-based fillers and pigments for papermaking: A review. *Carbohydrate Polymers*, 85(1), 17–22.
- 10 Osong, S. H., Norgren, S., Pettersson, G., & Engstrand, P. (2012). The use of cationic starch and microfibrillated cellulose to improve strength properties of CTMP-based paperboard.
- 11 Yang, H., Qiu, L., Qian, X., & Shen, J. (2013). Filler modification for papermaking with cationic starch and carboxymethyl cellulose: A comparative study. *BioResources*, 8(4), 5449–5460.
- 12 Fatehi, P., Tutus, A., & Xiao, H. (2009). Cationic-modified PVA as a dry strength additive for rice straw fibers. *Bioresour. Technology*, 100(2), 749–755.
- 13 Hou, H., Dong, H., Liu, G., & Zhang, H. (2007). Preparation and properties of oxidized corn starches by semi-dry process. *Cereal Chemistry*, 84(3), 225–230.
- 14 Lee, H. L., Shin, J. Y., Koh, C. H., Ryu, H., Lee, D. J., & Sohn, C. (2002). Surface sizing with cationic starch: its effect on paper quality and papermaking process. *TAPPI Journal*, 1(1), 34–40.
- 15 Zaman, M., Xiao, H., Chibante, F., & Ni, Y. (2012). Synthesis and characterization of cationically modified nanocrystalline cellulose. *Carbohydrate Polymers*, 89(1), 163–170.
- 16 Ibrahim, M. M., Fahmy, A. Y., Salaheldin, I. E., Fardous, M., Youssef, A. M., Mabrook, R. M., (2015). Synthesis of tosylated and trimethylsilylated methyl cellulose as pH-sensitive carrier matrix. *Life Science Journal* 2015;12(1), 29-37.
- 17 Fang, J. M., Fowler, P. A., Tomkinson, J., & Hill, C. A. S. (2002). The preparation and characterisation of a series of chemically modified potato starches. *Carbohydrate Polymers*, 47(3), 245–252.
- 18 Oh, S. Y., Dong, I. Y., Shin, Y., Hwan, C. K., Hak, Y. K., Yong, S. C., Ji, H. Y. (2005). Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy. *Carbohydrate Research*, 340(15), 2376–2391.
- 19 Schwanninger, M., Rodrigues, J. C., Pereira, H., & Hinterstoisser, B. (2004). Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose. *Vibrational Spectroscopy*, 36(1), 23–40.
- 20 Garg, U. K., Kaur, M. P., Garg, V. K., & Sud, D. (2007). Removal of hexavalent chromium from aqueous solution by agricultural waste biomass. *Journal of Hazardous Materials*, 140(1–2), 60–68.
- 21 Dawy, M., Shabaka, A. A., & Nada, A. M. A. (1998). Molecular structure and dielectric properties of some treated lignins. *Polymer Degradation and Stability*, 62(3), 455–462.
- 22 Zhang, K., Sun, P., Liu, H., Shang, S., Song, J., & Wang, D. (2016). Extraction and comparison of carboxylated cellulose nanocrystals from bleached sugarcane bagasse pulp using two different oxidation methods. *Carbohydrate Polymers*, 138, 237–243.
- 23 Abdel Ghaffar, A. M., Radwan, R. R., & Ali, H. E. (2016). Radiation Synthesis of Poly(Starch/Acrylic acid) pH Sensitive Hydrogel for Rutin Controlled Release. *International Journal of Biological Macromolecules*, 92, 957–964.