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Modification of PCC with agar and its application in papermaking

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Abstract. Modification of filler with polysaccharides such as starch, cellulose and their derivatives by preflocculation is an effective means to overcome the main drawback of mechanical strength decline resulting from filler addition. Agar is a mucilaginous polysaccharide extracted from red algae and was used to modify precipitated calcium carbonate (PCC) for papermaking in our studies. Results showed that when 0.03% cationic polyacrylamide (CPAM) was used as retention aid, tensile index of handsheets using agar (3%, based on PCC) modified PCC as filler was 29.5% higher than native PCC, whereas filler retention did not change obviously. Optical microscope observation and laser diffraction particle size analysis confirmed that PCC was flocculated and coated by agar after modification. Characterizations of mechanical strength and filler retention of handsheets at different filler content indicated the handsheets can be filled with about 10% more agar modified PCC but to maintain the same strength level.

1. Introduction

Mineral fillers such as calcium carbonate, talc or kaolin (china clay) play an important role in papermaking industry because of their extensive sources and cheapness. Filler loading facilitates to reduce the amount of relatively expensive cellulose fibers needed or impart the paper products functions designed. However, the addition of filler in cellulose fibers also leads to some side effects. Decrease of paper strength and inefficient filler retention are the main problems that researchers concern. Considerable works has been done on improving the fillers to conquer the disadvantages (Shen et al. 2009; Huang et al. 2013; Chen et al. 2014; Huang et al. 2014; Huang et al. 2015). Strength of paper origins mainly from hydrogen bonding of hydroxyl groups on cellulose fibers and thus modification of filler by compounds with plenty of hydroxyl groups should be an effective way. Polysaccharides such as starch, cellulose, guar gum and their derivatives were previously used to modify the fillers (Yan et al. 2005; Gamelas et al. 2014; Xie et al. 2016). In these studies, the modified filler show improved impact on strength properties and filler retention compared with the unmodified filler.

Agar is a natural carbohydrate (polysaccharide) obtained mainly from some families of red algae (Rhodophyta), mainly Gracilariaceae and Gelidiaceae (Armisen R 1987). Except for agar, another major composition of the algae i.e. endofiber has been attempted for using as additional source of papermaking cellulose fiber (Seo et al. 2010; Pei et al. 2013). With regard to agar, its main component is agarose built up from alternative 3-linked- β -D-galactose and 4-linked-3, 6-anhydro- α -L-galactose



units. Some of hydroxyl groups of agarose is substituted by carboxyl, sulfate groups etc. and form another minor component of agar, namely agaroectin (Sousa et al. 2013). The gel-forming ability of agar is applied in many fields, especially in food, medical and biological industries and its properties have been researched in detail (Arnott et al. 1974; Sousa et al. 2013). Application prospects of agar in papermaking industry have also been illustrated. Bio-based gelatine and agar were added by spraying sequentially to yield high extensibility paper suitable for producing 3D-packaging material (Vishtal et al. 2015). Furthermore, oxidatively depolymerized agar can be used as surface sizing materials in papermaking and improve strength and printability as much as starch, demonstrating its great potential to be used as inexpensive and high quality surface size in future (Youn 2008).

As for filler modification, for all we know, the use of agar or its derivatives has not been reported in the literature. Agar is almost insoluble in cold water but can be gelatinized with hot water. This trait gives us a hint to use to modify filler. Filler selected in our studies was PCC because of its broad applications in papermaking (Morsy et al.). The size attribute of the modified products was characterized. Also, the relationship between agar/filler dosage and resulting handsheets properties was investigated.

2. Experimental

2.1. Material

Agar was purchased from Fujian Fuli Agar Co., Ltd. (China). PCC was purchased from Guilin Wuhuan Industry Development Co., Ltd. (China). CPAM was obtained from BASF Corporation. Fully bleached pinewood kraft pulp used in handsheets preparation was made in Canada and beaten to 38 to 40 °SR using a Valley beater at 2% consistency. The beaten pulp was thickened to about 13% consistency for use.

2.2. Preparation of modified PCC

Agar was gelatinized with certain amount of water in evaporating dish on heating. 10 g of PCC was added into the paste with stirring continuously to disperse the PCC homogeneously. Then the mixture was oven dried and ground to pass through a 38 μ m sized sieve for use.

2.3. Preparation of handsheets and measurement of properties

0.03 wt% CPAM (based on the total mass of oven-dry pulp fiber and filler) as a retention aid was added to suspension of pulp fibers and fillers (modified or native PCC). The handsheets were formed by ZQJ2-200 handsheets former which with a target 80 g/m² grammage. The handsheets were pressed at 4 MPa for 1 min by ZQYC-200 handsheets and were dried at 80 °C for 10 min by DB-3 temperature control electric heating plate. We condition the handsheets at 23 °C and 50% RH for more than 24 h. Measuring the mechanical properties (tensile, bursting and tearing indices) of the handsheets according to the Chinese National Standards (GB/T 12914-2008, GB/T 454-2002 and GB/T 455-2002). The filler content was analyzed by ashing the paper in a muffle oven conforming to GB/T 463-1989.

2.4. Instrumental analyses

Microscope observation was performed by Olympus CX21 optical microscope.

The size characteristics of the particles were determined with a Mastersizer 2000 laser diffraction particle size analyzer from Malvern Instruments. Before particle size measurement aqueous suspension of the particles was treated with ultrasound for 5 min at 80 W (50 kHz).

3. Results and discussion

3.1. Characteristics of modified PCC

Optical microscope observation and particle size distribution determination were performed to characterize the particle size change after modification.

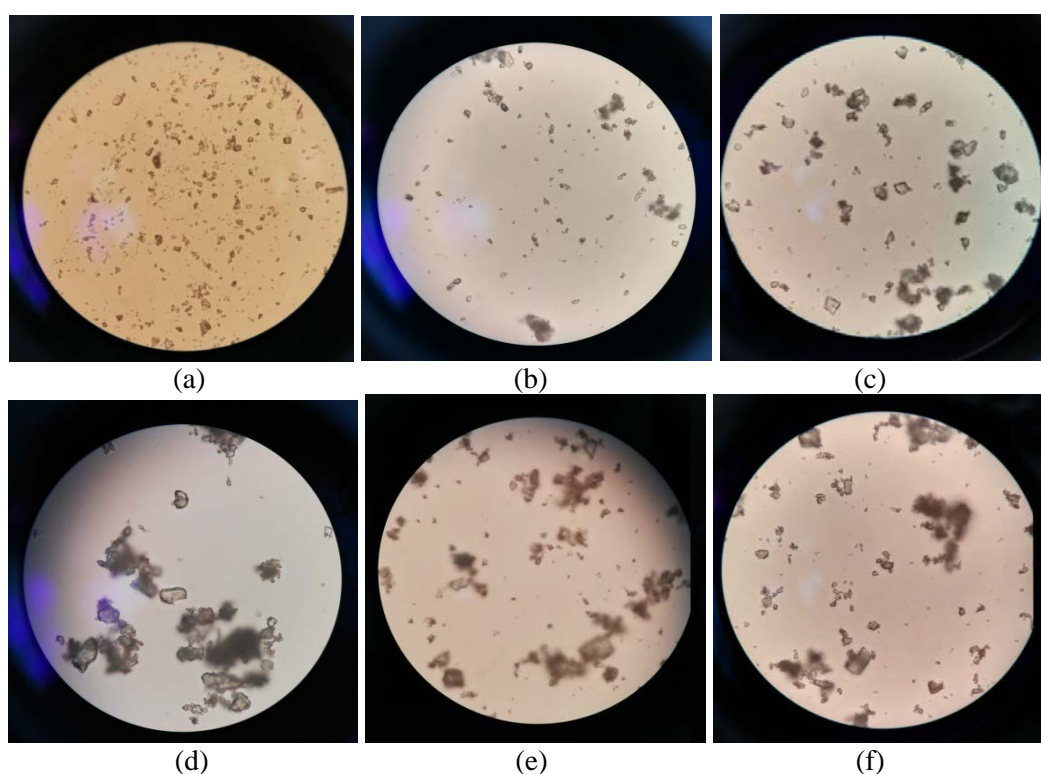


Figure 1. Images of particles at 40 \times magnification taken by a digital camera modified with different dosages of agar (w% based on PCC): 0% (a), 1% (b), 2% (c); 3% (d), 4(e), and 5% (f).

Figure 1 Images of particles at 40 \times magnification taken by a digital camera modified with different dosages of agar (w% based on PCC): 0% (a), 1% (b), 2% (c); 3% (d), 4(e), and 5% (f).

The images of native and agar modified PCC obtained by optical microscope are shown in figure 1. As presented in figure 1a, the native PCC was single, almost transparent irregular crystallite. After modification PCC aggregated to form flocs with agar. Figure 1b to 1f show with increasing agar dosage, more PCC flocculated with agar and gradually the flocs became larger and seemed opaque. At agar dosage 1% (Figure 1b), only a small number of PCC particles aggregated with agar. At agar dosage 3% (Figure 1d), the flocs apparently became larger and the size tended to be unchanged even more agar was used (figure 1e and 1f). Besides the flocs formed by PCC and agar, single PCC coated by agar (core-shell structure) and original PCC was believed also to exist in the powders. All these images indicated that PCC was successfully modified by agar.

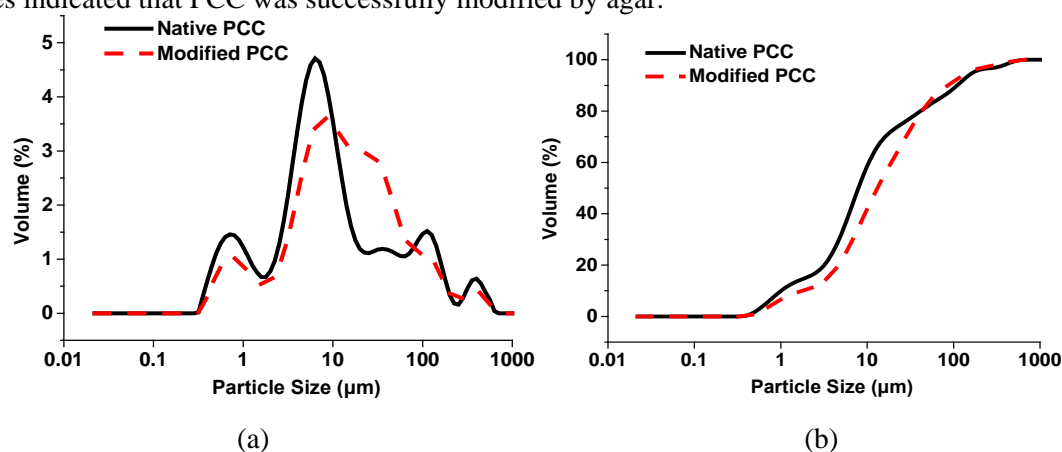


Figure 2. Particle size distribution for PCC and PCC modified by agar at the dosage of 3%: (a) relative distribution, (b) cumulative distribution.

Since optical microscope observation showed that PCC flocs formed after modification with agar, the size distribution of the particles should also display difference, which was confirmed by the results obtained from laser diffraction particle size analyzer. As shown in figure 2a, compared with native PCC, the main peak of particle size distribution curve apparently shifted towards the larger particle size for PCC modified by 3% agar and the d50 value of native PCC increased from 7.0 μm to 11.7 μm after modification (figure 2b).

3.2. Characteristics of handsheets filled with agar

Table 1. Strength properties and filler retention of handsheets prepared at different agar addition dosages (w%, based on PCC).

Agar dosage (%)	Tensile index (Nm/g)	Bursting index (kPa·m ² /g)	Tearing index (mN·m ² /g)	Filler retention (%)
0	31.95±1.11	2.35±0.1	16.61±0.82	70.12±2.9
2	31.85±1.31	2.36±0.1	16.57±0.78	69.21±2.94
4	32.13±1.4	2.37±0.08	16.68±0.66	70.89±3.48
6	32.33±1.16	2.39±0.1	16.64±0.6	69.76±3.37

Preparation of modified PCC involved grinding of the PCC/agar hybrid. It is difficult to separate agar which hadn't bonded to PCC with the modified PCC yield we wanted. It is essential to assess if the agar powder had an effect on properties of handsheets we made. Hence agar was ground with mortar to pass through a 38 μm sized sieve for papermaking. At the dosage of 0%, 2%, 4% and 6% (based on the PCC), the prepared agar was used as additive to make handsheets with a native PCC addition level of 20%. Apart from separate addition of agar and PCC, other operations for preparation of handsheets and determination of their properties were performed as previous described. Results in table 1 demonstrate both strength properties and PCC retention were almost the same with agar as additive (2%, 4%, 6%) or without (0%). Carbonhydrate polymers like starch, guar gum, chitosan are widely used as paper dry strength additives because of their plenty of hydroxyl groups to enhance the hydrogen bonding between cellulose fibers (Ashori et al. 2012; Ghasemian et al. 2012). Accordingly addition of agar should enhance mechanical properties of handsheets, however, results in this research were not anticipated. Reasons are that agar was added as solid particles and they were not dissolved in the handsheets preparing processes, so the particles acted like cellulose fiber and properties of handsheets didn't change in terms of strength and filler retention. It can also be inferred from this study that the agar modified PCC should be endurable in the papermaking processes.

3.3. Characteristics of handsheets filled with agar modified PCC

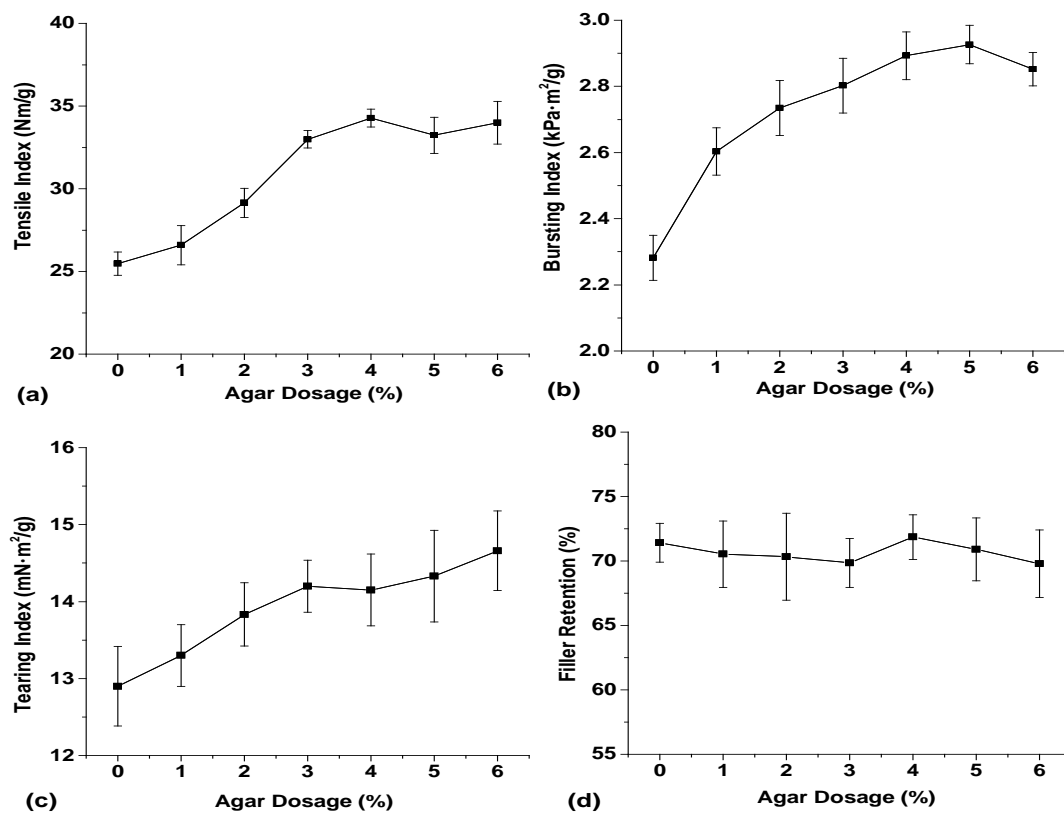


Figure 3. Effect of agar dosage on mechanical strength and filler retention of handsheets prepared with 20% agar modified PCC as filler.

Results above showed separate addition of agar particles had no obvious effect on investigated properties of PCC filled handsheets. The following studies explored if the agar modified PCC would take effect. PCC was modified by agar at different dosage and applied in papermaking at the net PCC addition level of 20%. Factors impacting paper strength are mainly properties of fibers (fibers length and strength) as well as fiber-to-fiber interaction. Hydrogen bonds and friction forces between fibers are the dominating of them (Przybysz et al. 2016). Addition of PCC filler mostly leads to the decrease of hydrogen bonding between fibers. When agar was used to modify PCC, PCC was aggregated together to form flocs with agar and the surface of the PCC was coated by agar. The more agar was used, the more PCC was coated or flocculated, which has been proved in figure 1. As a polysaccharide, abundant hydroxyl groups of agar and cellulose fibers can form hydrogen bonding to offset the decrease of strength properties caused by the presence of PCC. Therefore, the mechanical properties (i.e., tensile, bursting, and tearing indices) of handsheets were increased with increasing agar dosage, which can be concluded from figure 3. Moreover, particle size analysis results in figure 2 show size of agar modified PCC increased and the change of particle size caused by PCC preflocculation may also account for the increase of strength (Chauhan and Bhardwaj). Consist with results in figure 1, at the agar dosage of about 3%, the PCC can be flocculated or the surface area of PCC can be coated seemed to reached the limit, so even more agar was used to modify PCC, paper strength didn't increase. At agar dosage 3%, tensile, bursting and tearing index was respectively 32.99 Nm/g, 2.80 kPa·g/m², 14.20 mN·m²/g, increased by 29.5%, 22.8% and 13.2% compared to handsheets with native PCC (agar dosage 0%). Retention of filler depends mainly on colloid adsorption and mechanical interception (Cho et al. 2009; Gesenhues 2011). CPAM is an efficient polymer flocculant for filler retention (Antunes et al. 2008). 70% or so seemed to be the highest filler retention value CPAM can achieved in our handsheets forming process whether or not the PCC was modified by agar, as shown in figure 3d.

3.4. Effect of agar modified PCC content on properties of handsheets

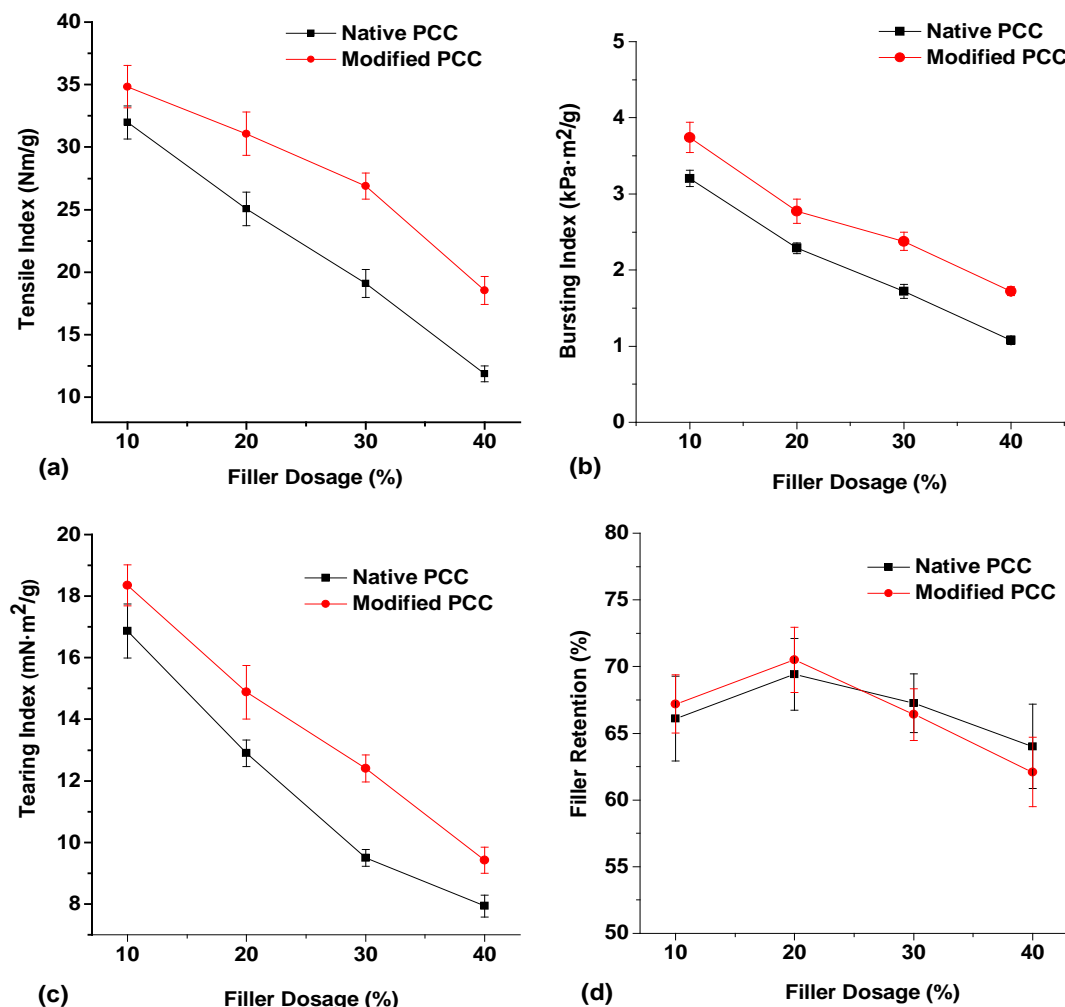


Figure 4. Effect of filler dosage on mechanical strength and filler retention of handsheets prepared with 3% agar modified PCC as filler.

The effect of filler content on paper strength is shown in figure 4a, 4b and 4c. As expected, strength of handsheets using agar modified PCC as filler is higher than using native PCC, especially at higher filler content. Similar results have been also attained by previous researchers (Yan et al. 2005; Xie et al. 2016), who use guar gum and starch to modify the filler respectively. So, analogous to those terrestrial plant polysaccharides, agar can also be used to modify PCC for application as filler in papermaking. Compared to native PCC, agar modified PCC can be filled about 10% higher and maintain the same strength level. As discussed in previous section about effect of CPAM in filler retention, figure 4d shows filler retention change slightly in different filler application situations. It can be inferred the agar modified PCC could be used to manufacture high filler content paper products.

4. Conclusion

As a polysaccharide from marine plant red algae, agar was used to modify PCC for the first time by an easy and simple way. The modified product was used to prepare handsheets as filler. From this research work the following conclusions can be drawn:

- (1) PCC was preflocculated by agar and particle size of d₅₀ became larger through modification.
- (2) Paper strength could be improved using agar modified PCC as filler compared with native PCC and the improvement was resulted from flocculation/coating of PCC by agar.

(3) Filler retention of handsheets using agar modified PCC or native PCC showed no difference at different agar or filler dosages when CPAM was used as retention aid.

(4) The agar modified PCC was endurable in the papermaking process and could be used to manufacture paper products with high filler content.

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References

- [1] Antunes, E., Garcia, F. A. P., Ferreira, P. and Rasteiro, M. G. (2008). "Flocculation of PCC filler in papermaking: Influence of the particle characteristics," *Chemical Engineering Research and Design* 86(10), 1155-1160. [doi]: <http://dx.doi.org/10.1016/j.cherd.2008.04.004>
- [2] Armisen R, G. F. (1987) Production, properties and uses of agar. Paper presented at the Production and Utilization of Products from Commercial Seaweeds, Fisheries Technical Paper 288, McHugh DJ (ed.)
- [3] Arnott, S., Fulmer, A., Scott, W. E., Dea, I. C. M., Moorhouse, R. and Rees, D. A. (1974). "The agarose double helix and its function in agarose gel structure," *Journal of Molecular Biology* 90(2), 269-284. [doi]: [http://dx.doi.org/10.1016/0022-2836\(74\)90372-6](http://dx.doi.org/10.1016/0022-2836(74)90372-6)
- [4] Ashori, A., Marashi, M., Ghasemian, A. and Afra, E. (2012). "Utilization of sugarcane molasses as a dry-strength additive for old corrugated container recycled paper," *Composites Part B: Engineering* 45(1), 1595-1600. [doi]: [10.1016/j.compositesb.2012.09.030](http://dx.doi.org/10.1016/j.compositesb.2012.09.030)
- [5] Chauhan, V. S. and Bhardwaj, N. K. "Efficacy of carbohydrate polymers in filler preflocculation for use in papermaking," *Arabian Journal of Chemistry*, [doi]: <http://dx.doi.org/10.1016/j.arabjc.2015.08.002>
- [6] Chen, Z., Li, C., Song, Z. and Qian, X. (2014). "Modification of Precipitated Calcium Carbonate Filler for Papermaking with Adsorption of Cationically Derivatized Chitosan and Carboxymethyl Chitosan," *BioResources*; Vol 9, No 4 (2014)
- [7] Cho, B.-U., Garnier, G., van de Ven, T. G. M. and Perrier, M. (2009). "A deposition efficiency model for fiber–filler flocculation by microparticle retention system," *Journal of Industrial and Engineering Chemistry* 15(2), 217-223. [doi]: <http://dx.doi.org/10.1016/j.jiec.2008.09.020>
- [8] Gamelas, J. A. F., Lourenço, A. F., Xavier, M. and Ferreira, P. J. (2014). "Modification of precipitated calcium carbonate with cellulose esters and use as filler in papermaking," *Chemical Engineering Research and Design* 92(11), 2425-2430. [doi]: <http://dx.doi.org/10.1016/j.cherd.2014.02.003>
- [9] Gesenhues, U. (2011). "The mechanism of polyelectrolyte-assisted retention of TiO₂ filler particles during paper formation," *Advances in Colloid and Interface Science* 162(1–2), 1-21. [doi]: <http://dx.doi.org/10.1016/j.cis.2010.08.005>
- [10] Ghasemian, A., Ghaffari, M. and Ashori, A. (2012). "Strength-enhancing effect of cationic starch on mixed recycled and virgin pulps," *Carbohydrate Polymers* 87(2), 1269-1274. [doi]: [10.1016/j.carbpol.2011.09.010](http://dx.doi.org/10.1016/j.carbpol.2011.09.010)
- [11] Huang, X., Qian, X., Li, J., Lou, S. and Shen, J. (2015). "Starch/rosin complexes for improving the interaction of mineral filler particles with cellulosic fibers," *Carbohydrate Polymers* 117, 78-82. [doi]: <http://dx.doi.org/10.1016/j.carbpol.2014.09.047>
- [12] Huang, X., Shen, J. and Qian, X. (2013). "Filler modification for papermaking with starch/oleic acid complexes with the aid of calcium ions," *Carbohydrate Polymers* 98(1), 931-935. [doi]: <http://dx.doi.org/10.1016/j.carbpol.2013.07.024>
- [13] Huang, X., Sun, Z., Qian, X., Li, J. and Shen, J. (2014). "Starch/Sodium Oleate/Calcium Chloride Modified Filler for Papermaking: Impact of Filler Modification Process Conditions and Retention Systems As Evaluated by Filler Bondability Factor in Combination with Other Parameters," *Industrial & Engineering Chemistry Research* 53(15), 6426-6432. [doi]: [10.1021/ie500770r](http://dx.doi.org/10.1021/ie500770r)

- [14] Morsy, F. A., El-Sheikh, S. M. and Barhoum, A. "Nano-silica and SiO₂/CaCO₃ nanocomposite prepared from semi-burned rice straw ash as modified papermaking fillers," *Arabian Journal of Chemistry*, [doi]: <http://dx.doi.org/10.1016/j.arabjc.2014.11.032>
- [15] Pei, J., Lin, A., Zhang, F., Zhu, D., Li, J. and Wang, G. (2013). "Using agar extraction waste of *Gracilaria lemaneiformis* in the papermaking industry," *Journal of Applied Phycology* 25(4), 1135-1141. [doi]: 10.1007/s10811-012-9929-7
- [16] Przybysz, P., Dubowik, M., Kucner, M. A., Przybysz, K. and Przybysz Buzala, K. (2016). "Contribution of Hydrogen Bonds to Paper Strength Properties," *PLoS ONE* 11(5), e0155809. [doi]: 10.1371/journal.pone.0155809
- [17] Seo, Y.-B., Lee, Y.-W., Lee, C.-H. and You, H.-C. (2010). "Red algae and their use in papermaking," *Bioresource Technology* 101(7), 2549-2553. [doi]: <http://dx.doi.org/10.1016/j.biortech.2009.11.088>
- [18] Shen, J., Song, Z., Qian, X. and Liu, W. (2009). "MODIFICATION OF PAPERMAKING GRADE FILLERS: A BRIEF REVIEW," *BioResources* 4(3), 1190-1209.
- [19] Sousa, A. M. M., Borges, J., Silva, A. F. and Gonçalves, M. P. (2013). "Influence of the extraction process on the rheological and structural properties of agars," *Carbohydrate Polymers* 96(1), 163-171. [doi]: <http://dx.doi.org/10.1016/j.carbpol.2013.03.070>
- [20] Vishtal, A., Khakalo, A., Rojas, O. and Retulainen, E. (2015). "Improving the extensibility of paper: Sequential spray addition of gelatine and agar," *NORDIC PULP AND PAPER RESEARCH JOURNAL* 30(3), 452-460.
- [21] Xie, W., Song, Z., Liu, Z. and Qian, X. (2016). "Surface modification of PCC with guar gum using organic titanium ionic crosslinking agent and its application as papermaking filler," *Carbohydrate Polymers* 150, 114-120. [doi]: <http://dx.doi.org/10.1016/j.carbpol.2016.05.010>
- [22] Yan, Z., Liu, Q., Deng, Y. and Ragauskas, A. (2005). "Improvement of paper strength with starch modified clay," *Journal of Applied Polymer Science* 97(1), 44-50. [doi]: 10.1002/app.21727
- [23] Youn, S. K. S., Y.B.; (2008). "Use of Agar as Surface Sizing Materials in Papermaking," *Journal of Korea Technical Association of The Pulp and Paper Industry* 40(3)