

Properties and Characterization of Starch as a Natural Binder: A Brief Overview

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Abstract

This paper was reviewed about the properties and characterization of starch as a natural binders. Starch is one of the most abundant organic compounds and applied as a binder. The efficiency of binder are affected by the characteristic and properties of starch. The characteristics of starch are determined by the biological origin. Starch is composed of D-glucose in polysaccharides and it was isolated from leaves, stems, tubers, seeds, and roots of higher plants where it serves as an energy reserve. This review concentrates the several types of characterization which are structural properties, morphology properties, viscosity and functional group of starch. The X-ray diffraction result shows that the relative crystallinity decreased for modified starch compared with native starch while scanning electron microscope shows the modified starch slightly has rough surface compared with native starch. Nowadays, the concern on eco-environmental issues is increasing and this review has shown that starch is eco-environmental friendly binder that can be used in various application.

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1. Introduction

Starch is one of the most abundant organic compounds and applied as a binder in a pharmaceutical industry. It is adjustable polymer, low cost, diluent, granulating agent and biodegradable. It is also act as a starting material for chemicals such as ethanol, cyclodextrin and glucose (Yadav and Garg, 2013). Starch is a main raw material in glue and adhesive industries due to abundantly available and low cost (Yu et al., 2009). There are many uses of starch such as a filler material and bonding agent for making tablets. On the other hand, starch is an important raw material for powder in the cosmetics industries. In detergent soap manufacture, starch is used to get better recovery and to improve the shelf life of detergents while in the rubber and foam industries, starch is employed for getting better foaming and color (Tokunari, 2004). It is also widely used as a precious ingredient in the food industry due to its unique thermal, structural and functional properties (Dura and Rosell, 2016).

The efficiency of binder are affected by the characteristic and properties of starch. Starch binder has good ductility, good adhesion properties, self-curing properties and non-hygroscopicity. Hygroscopicity means that the binder have ability to absorb the water, non-hygroscopicity means that the binder can prevent from the swelling because it is can't absorb the water. There are two methods that can improve the structure and binding property of starch as a natural binder which are modified by physical or chemical methods.

2. Properties of Natural Binder

Starch one of the most plentiful polysaccharides in nature (Adak and Banerjee, 2016). Polysaccharides are an important class of biological polymers. It is joined by glycosidic bonds and universally found in almost all living organisms (Sinha and Kumria, 2001; Karaki et al., 2016). The biological function of polysaccharides is usually either structural or storage-related such as starch is a storage in plants (Klemm et al., 2005).

Figure 1 shows the molecular structure of starch component. Starch is composed of D-glucose in polysaccharides. It was isolated from leaves, stems, tubers, seeds, and roots of higher plants where it serves as an energy reserve. Starch cease to exist as a primary carbohydrate storage product in all plant which contain green pigment called as chlorophyll (Kenneth et al., 2014). Starch is a carbohydrate polymer consisting of anhydroglucose units linked by α -D-(1, 4) glucosidic bonds (Manek et al., 2012). In addition, it consists of two inherently incompatible molecules which is amylose and amylopectin. Amylose is a linear polymer while amylopectin is a branched chain polymer (Manek et al., 2012; Masri et al., 2013).

In plants, starch occurs as granules that are characteristic in size, shape, and morphology. These characteristics are determined by the biological origin (Ahmad et al., 1998; Manek et al., 2012; Tokunari, 2004). The characteristic and properties of starch affect the efficiency of binder. There are many disadvantages of

native starches which can limit its application and industrial used (Waliszewski et al., 2003). To improve the structure and binding property of starch as a main binder, starch can be modified by physical or chemical methods (Oluwole and Avwerosuoghene, 2015).

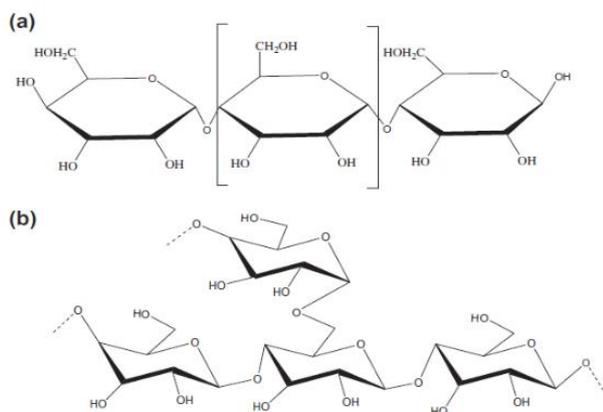


Figure 1: Molecular structure of the starch components (a) amylose and (b) amylopectin (Masri et al., 2013)

Functional properties of starches available on the commercial market. It is usually obtained from corn, cassava, potato, banana or other cereals which are often through the physical modification and chemical modifications to fulfil needs of industries (Waliszewski et al., 2003). Starch has been dominated to enhance its applicability by modification process (Adak and Banerjee, 2016). Modification of starch by chemical methods generally involves esterification, etherification and oxidation of the available hydroxyl groups on the α -D-glucopyranosyl units that make up the starch polymers. Chemical modification will improve the stability and film forming properties to partially degraded starches that will be used in paper surface sizing, textile warp sizing and adhesives (Chiu and Solarek, 2009).

Starch esters with higher degree of substitution have various limitations and only can be used in non-food application (Biswas et al., 2008). Based on previous study, stated that chemical modification can improve starch water binding because the hydrophilic groups were incorporated (Waliszewski et al., 2003). Chemical modification has been developed to overcome the weakness of native starch such as water repellence, failure of granules to swell and develop viscosity in cold water and uncontrolled viscosity after cooking (Aggarwal and Dollimore, 1998). The effective method to improve the functionality of starch is chemical modification which can adjust physicochemical properties by bringing in new functional groups in starches (Sukhija et al., 2016).

Physical modification process can be considered as a natural material that is safe to the environment. The most common physical modifications are heat-moisture treatment, retrogradation, pregelatinization and annealing treatment (Pinto et al., 2015). Compared with chemical and

physical modifications, enzymatic modification of starch has advantages to act as replacement of synthetic chemicals, lowering energy consumption levels and fewer byproducts due to the increasing interest for clean labeled modified starches. Enzymatic treatment can obtain the porous starches without changing their thermal characteristics but shows different pasting behavior which depends on the pHs of the enzymatic treatment. (Dura and Rosell, 2016).

3. Starch Binder

The characteristic and properties of starch affect the efficiency of binder. Starch binder has good ductility, good adhesion properties, self-curing properties and hygroscopicity resistance. Hygroscopicity resistance means that the binder does not have the ability to absorb water, so it can prevent swelling. To improve the structure and binding property of starch as a main binder, starch can be modified by physical or chemical methods.

The useful materials of starch were obtained by enhancing the native properties because of the high water sensitivity of starch. Since starch made from renewable resources, starch has a much lower undesirable impact on the environment. Starch are sources of phosphate bond polymeric materials that can generally provide a lower modulus of elasticity (Oluwole and Avwerosuoghene, 2015).

There are several variations in the properties of starch. These variations are from different botanical sources which are related to the differences in their amylose and amylopectin contents. The amylose and amylopectin content will affect the properties of starch such as gelatinization, paste viscosity, gel stability, and solubility (Builder et al., 2013).

4. Characterization of Starch Binder

This subchapter covers about the characterization of starch as a binder. There are four types of characterization covered in this subchapter which are structural properties, morphology properties, viscosity preparation of starch and functional groups of starch. According to Adak and Banerjee (2016), the starch undergoes a modification process showing better hydrophobicity and thermoplasticity with equivalent structural changes portrayed by FTIR, XRD and SEM.

4.1 Structural of Starch

Structural properties of starch is characterized by using X-Ray Diffraction (XRD). According to Klein et al., (2014) the XRD patterns for native cassava starch are similar with modified cassava starch. The diffraction pattern for native and modified cassava starch shows in Figure 2 shows that small peaks at 5.6, 11.25, 19 and 30° while main peaks at 15, 17, 17.8 and 23°. The relative crystallinity decreased for modified cassava starch.

The starches showed differences in the peak intensity values and relative crystallinity. The XRD and relative crystallinity of the native and modified starch verified by the intensity of the main peak. The starch modified with low concentration of active chlorine had the lowest peak intensity. The higher concentrations of active chlorine used will increase peak intensities. Higher concentrations of active chlorine will produce greater peak intensity (Vanier et al., 2012).

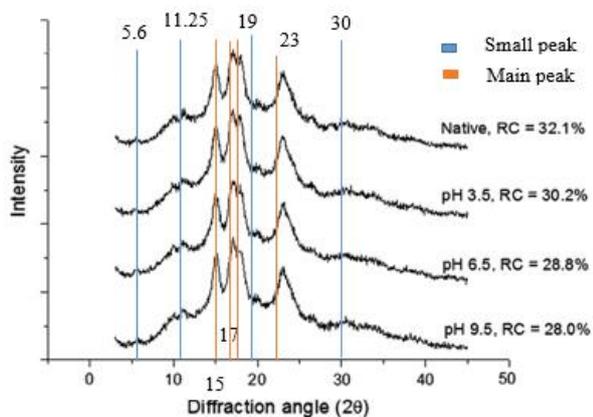


Figure 2: The diffraction pattern of native and modified starch (Klein et al., 2014)

The differences of starch crystallinity are caused by four factors which are crystal size, the number of crystalline region affected by crystalline content and length of chain, the orientation of double helices within the crystalline area and the extent of interaction between the double helices. Based on Gao et al., (2012), the modified starch only had dispersive broad peak and no crystalline peaks showed. This is because the crystalline region of native starch was completely damaged during modification process. The loss of crystallinity will weakened the intermolecular and intramolecular hydrogen bonds of starch.

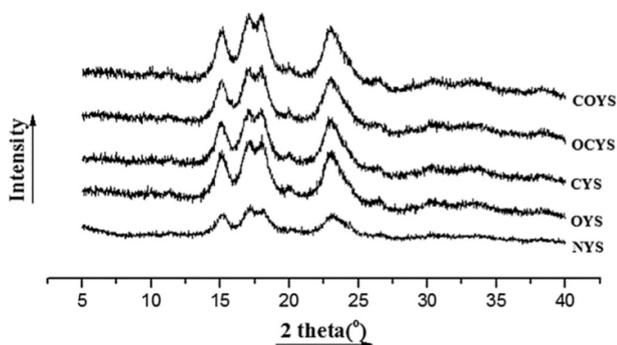


Figure 3: XRD pattern of native (NYS), modified (OYS, CYS, OCYS and COYS) starches (Sukhija et al., 2016)

Figure 3 shows the XRD pattern for native and modified starches based on Sukhija et al., (2016). The native starch showed peaks at 15.1, 23.2° and doublet at 17, 18.1° representing a typical type-A starch pattern. The XRD pattern for modified starches were also similar to that of native starch. The intensities of the peaks for modified

starches are higher than native starch which is in sharper peaks (Sukhija et al., 2016).

4.2. Morphology of starch

The surface morphology of starch is characterized by using scanning electron microscopy (SEM). Based on previous study, SEM of native starch granules is shown in Figure 4(a) has round shape with truncated end on one side and the surface of native starch granules are smooth with no evidence on any fissures or pores. The modified starch slightly has rough surface is shown in Figure 4(b) (Sangseethong et al., 2010; Klein et al., 2014).

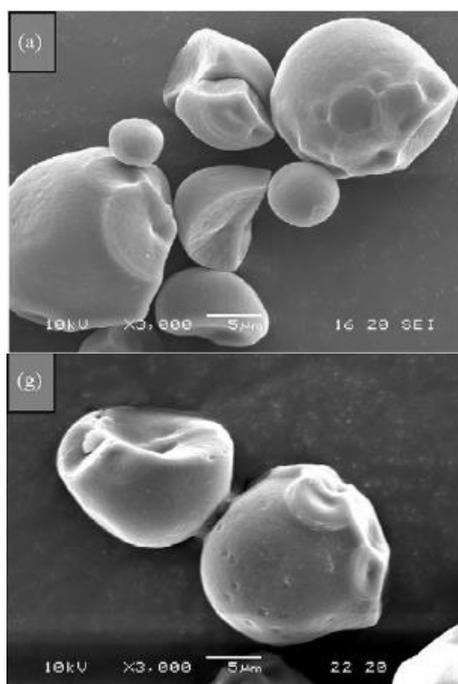


Figure 4: Morphology of (a) native starch and (b) modified starch (Sangseethong et al., 2010)

According to Dacanal et al., (2016), for native starch at 1500x magnification, cassava starch particles present a hemispheric shape. The shape of particles can affect the cohesiveness and fluid dynamics behavior. Aviara et al., (2014) had stated that the morphology for starch granules are mostly spherical in shape with a few having indentations similar to an egg that has been cut at various positions. The details of this explanation was approved by Figure 5. The surface morphology for hybrid binder are rough surface which is similar with Figure 4(b).

4.3 Viscosity of Starch

Studying the rheological properties of fluids or gels are important because the operation design depends on the way the product flows through a pipe, stirring in a mixer and packaging into containers. The viscosity of fluid is its resistance to flow (Hussain and Nasr, 2010). The knowledge of viscosity can help to characterize polymers and to determine indirectly molecular mass (Osemeahon and Dimas, 2014).

At low concentration of cassava starch, the viscosity of binder decreased and will increased with increasing of cassava starch concentration. The higher the concentration of starch, the higher viscosity observed (Osemeahon et al., 2013). Lower viscosity are produced because of incompletely degraded network. It would not be resistant to shear and also could not maintain the integrity of the starch granules (Chan et al., 2012). The result for the viscosity of hybrid binder are the higher concentration of cassava starch, the higher viscosity of hybrid binder.

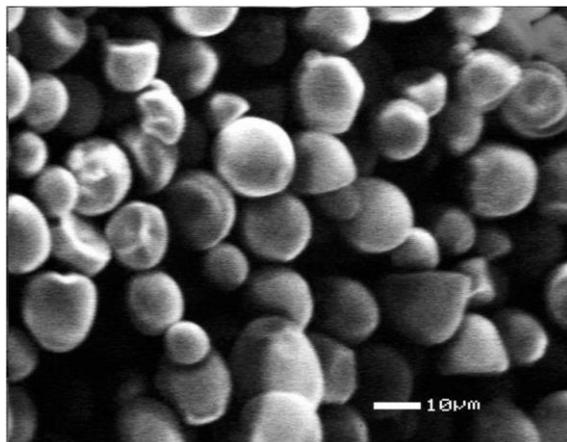


Figure 5: SEM of cassava starch (Aviara et al., 2014)

4.4. Functional Group of Starch

FTIR is a machine used to identify and investigate the presence of functional groups in molecule. In addition, it is also can obtain the structural and bond information (Kaniappan and Latha, 2011). For this study, FTIR will be used to determine the functional group, structural and bonding information of cassava starch

Figure 6 shows that the FTIR spectral pattern for native starch and modified starch. Klein et al., (2014) shows that the spectral patterns of native starch sample and modified starch sample were similar. Many researcher assign and match the band absorbance in starch with the vibrational modes of the chemical bonds. Moreover, starch exhibited over 10 peaks in the regions of 4000–500 cm^{-1} . Crystalline phase existed in the native starch was indicated by the higher value. The modification process of starch will alter the chain packing and will generate more amorphous structures in starch.

Ma et al., (2006) had stated that the low peak are resulted from the strong hydrogen bonds that drag the relative groups to a lower vibration frequency while high peak due to weak interaction of hydrogen bonding. The less hydrogen bonding in modified starch were studied in previous research. Figure 7 shows the example of FTIR spectra of native and modified starches according to Sukhija et al., (2016) results. The band at 1644 cm^{-1} represents the intramolecular hydrogen bond and a sharper peak for native starch (Sukhija et al., 2016).

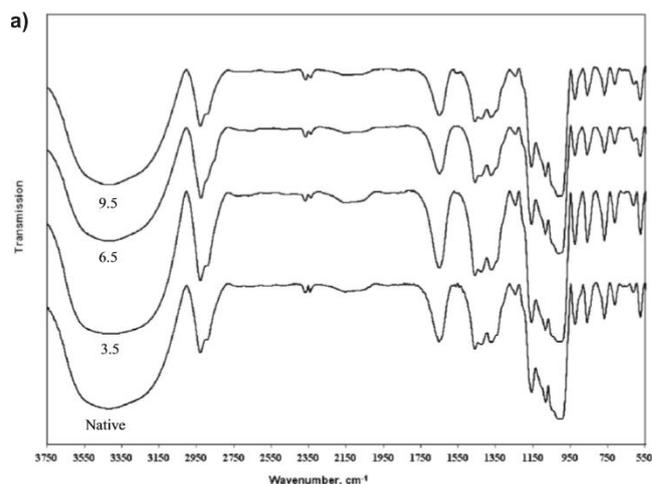


Figure 6: FTIR spectral pattern for native starch and modified starch (Klein et al., 2014)

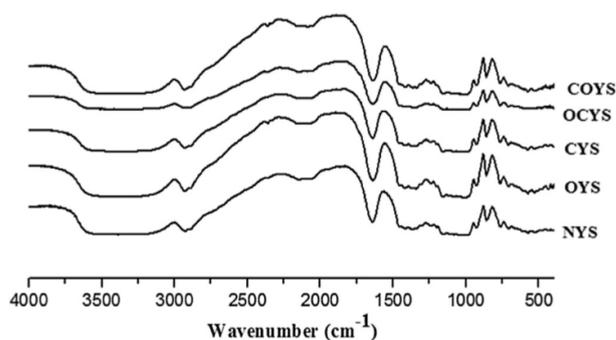


Figure 7: FTIR spectra of native (NYS) and modified (OYS, CYS, OCYS, COYS) starches (Sukhija et al., 2016)

5. Conclusion

This paper introduces the review about the properties and characterization of starch as a natural binder. A broad study has been produced to give the reader a comprehensive discussion about the starch which is used as natural binder. The paper discussed about the structural properties, morphology properties, viscosity preparation of starch and functional group of starch. Therefore, this review has shown that properties of starch have several variations. The review shows that the modification of starch has higher viscosity compared with native starch. The starch undergoes modification process exhibit better hydrophobicity and thermoplasticity based on FTIR, XRD and SEM. Increasing the production and processing of starches can lead to better income in agro technology industries also can creates the job opportunity. This is also can increased competitiveness with synthetic polymer.

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References

- Adak, S., & Banerjee, R. (2016). A green approach for starch modification: esterification by lipase and novel imidazolium surfactant. *Carbohydrate Polymers*, 150, 359-368.
- Aggarwal, P., & Dollimore, D. (1998). The effect of chemical modification on starch studied using thermal analysis. *Thermochimica Acta*, 324, 1-8.
- Ahmad, F., Williams, P. A., Doublier, J., Durand, S., & Buleon, A. (1998). Physico-chemical characterization of sago starch. *Carbohydrate Polymers*, 38, 361-370.
- Aviara, N. A., Onuoha, L. N., Falola, O. E., & Igbeka, J. C. (2014). Energy and exergy analyses of native cassava starch drying in a tray dryer. *Energy*, 73, 809-817.
- Biswas, A., Shogren, R. L., Selling, G., Salch, J., Willet, J. L., & Buchanan, C. M. (2008). Rapid and environmentally friendly preparation of starch esters. *Carbohydrate polymers*, 74, 137-141.
- Builders, P. F., Mbah, C. C., Adama, K. K., & Audu, M. M. (2013). Effect of pH on the physicochemical and binder properties of tigernut starch. *Starch Journal* 281-293.
- Chan, H. T., Fazilah, A., Bhat, R., Leh, C. P., & Karim, A. A. (2012). Effect of deproteinization on degree of oxidation of ozonated starch. *Food Hydrocolloids*, 26, 339-343.
- Chiu, C. W., & Solarek, D. (2009). Modification of starches. *Food Sciences and technology*, 3, 629-655.
- Dacanal, G. C., Feltre, G., Thomazi, M. G., & Menegalli, F. C. (2016). Effects of pulsating air flow in fluid bed agglomeration of starch particles. *Journal of Food Engineering*, 181, 67-83.
- Dura, A., & Rosell, C. M. (2016). Physico-chemical properties of corn starch modified with cyclodextrin glycosyltransferase. *International Journal of Biological Macromolecules*, 87, 466-472.
- Gao, J., Luo, Z. G., & Luo, F. X. (2012). Ionic liquids as solvents for dissolution of corn starch and homogeneous synthesis of fatty-acid starch esters without catalysts. *Carbohydrate Polymers*, 89, 1215-1221.
- Hussain, A. L., & Nasr, H. E. (2010). The role of carboxylic acid on the characterization and evaluation seed emulsion of styrene/butyl acrylate copolymer lattices as paint. *Nature science*, 8(8), 94-103.
- Kaniappan, K., & Latha, S. (2011). Certain investigations on the formulation and characterization of polystyrene/ poly (methylmethacrylate) blends. *Int J. Chem. Res.*, 3(2), 708-717.
- Karaki, N., Aljawish, A., Humeau, C., Muniglia, L., and Jasniewski, J. (2016). Enzymatic modification of polysaccharides mechanisms, properties, and potential applications: A review. *Enzyme and Microbial Technology*, 90, 1-18.
- Kenneth, K. A., Michael, O. A., Anthony, A. O., & Sunday, T. (2014). Isolation and physicochemical characterization of tigernut (*Cyperus esculentus*) starch as potential industrial biomaterial. *International Journal of materials Science and Applications*, 3, 37-41.
- Klein, B., Vanier, N. L., Moomand, K., Pinto, V. Z., Colussi, R., Zavareze, E. D. R., & Dias, A. R. G. (2014). Ozone oxidation of cassava starch in aqueous solution at different pH. *Food Chemistry*, 155, 167-173.
- Klemm, D., Heublein, B., Fink, H. P., Bohn, A. (2005). Cellulose: Fascinating biopolymer and sustainable raw material. *Angewandte Chemie International Edition*, 44, 3358-3393.
- Ma, X., Yu, J., & Zhao, A. (2006). Properties of biodegradable poly (propylene carbonate)/starch composites with succinic anhydride. *Composites Science and Technology*, 66, 2360-2366.
- Manek, R. V., Builder, P. F., Kolling, W. M., Emeje, M., & Kunle, O. O. (2012). Physicochemical and binder properties of starch obtained from *Cyperus esculentus*. *PharmSciTech*, 13, 379-388.
- Masri, M. N., Nazeri, M. F. M., Chai Y. N., & Mohamad, A. A. (2013). Tapioca binder for porous zinc anodes electrode in zinc-air batteries. *Journal of King Saud University – Engineering Sciences*, 27, 217-224.
- Oluwole, O. I., & Avverosuoghene, O. M. (2015). Effects of cassava starch and natural rubber as binders on the flexural and water absorption properties of recycled paper pulp based composites. *International Journal of Engineering and Technology Innovation*, 5, 255-263.
- Osemeahon, S. A., & Dimas, B. J., (2014). Development of urea formaldehyde and polystyrene waste as copolymer binder for emulsion paint formulation. *Journal of Toxicology and Environmental Health Sciences*, 6(3), 75-88.
- Osemeahon, S. A., Maitera, O. N., Hotton, A. J., & Dimas, B. J. (2013). Influence of starch addition on properties of urea formaldehyde/starch copolymer blends for application as a binder in the coating industry. *Journal of environmental chemistry and ecotoxicology*, 5(7), 181-189.
- Pinto, V. Z., Vanier, N. L., Deon, V. G., Moomand, K., Halal, S. L. M. E., Zavareze, E. D. R., Lim, L. T., & Dias, A. R. G. (2015). Effect of single and dual physical modifications on pinhoa starch. *Food Chemistry*, 187, 98-105.
- Sangseethong, K., Termvejsayanon, N., & Sriroth, K. (2010). Characterization of physicochemical properties of hypochlorite- and peroxide-oxidized cassava starches. *Carbohydrate Polymers*, 82, 446-453.
- Sinha, V. R., & Kumria, R. (2001). Polysaccharides in colon-specific drug delivery. *Int. J. Pharm*, 224, 19-38.
- Sukhija, S., Singh, S., & Riar, S. C. (2016). Effect of oxidation, cross-linking and dual modification on physicochemical, crystallinity, morphological, pasting and thermal characteristics of elephant foot yam (*amorphophallus paeoniifolius*) starch. *Food Hydrocolloids*, 55, 56-64.
- Tonukari, N. J. (2004). Cassava and the future of starch. *Electronic Journal of Biotechnology*, 7, 5-8.
- Vanier, N. L., Zavareze, E. D. R., Pinto, V. Z., Klein, B., Botelho, F. T., Dias, A. R. G., & Elias, M. C. (2012). Physicochemical, crystallinity, pasting and morphological properties of bean starch oxidised by different concentrations of sodium hypochlorite. *Food Chemistry*, 131, 1255-1262.
- Waliszewski, K. N., Aparicio, M. A., Bello, L.A., & Monray, J. A. (2003). Changes of banana starch by chemical and physical modification. *Carbohydrate Polymers*, 52, 237-242.
- Yadav, R., & Garg, G. (2013). A review on Indian sago starch and its pharmaceutical applications. *International Journal of Pharmaceutical and Life Sciences*, 2(3), 99-106.
- Yu, W., He, H., Cheng, N., Gan, B., & Li, X. (2009). Preparation and experiments for a novel kind of foundry core binder made from modified potato starch. *Materials and Design*, 30, 210-213.