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Preparation of Starch-Gum Acacia to into Multifunctional Superabsorbent Polymers.

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Abstract:
Chemical fertilizers are extensively used to improve crop yield, however they are identified with pollution effects due to leaching of the excess chemicals. This study prepared starch-gum arabic, superabsorbent for coating of nanofertilizer products. The Starch-GA was characterized on XRD and TGA. It was also tested for water absorption characteristics. The XRD showed presence of semi-crystalline structures in the amorphous starch-GA. TGA showed that the formed product was stable to heat up to 500°C. The physical characterization showed high water retention for starch-GA.
Keywords: *Sap, Gum Arabic, Biodegradable, Absorbency*

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I. Introduction

Starch is found in flour of maize, cassava, wheat, potatoes, rice (Mano *et al.*, 2003) and is used as adhesives, thickening materials, stabilizers, pasting agents among many uses. Starch is readily available and biodegradable natural polymer that has extensively been used as a coating matrix. The starch polymer has been in other cases enhanced by vinyl ethylene or polyvinyl alcohol. For instance polycaprolactone-PCL which is degraded slowly by micro-organisms, has been mixed with montmorillonite and urea to produce Coated slow Release Fertilizer pellets (Suppa, 2017). Likewise polyacrylamide hydrogel has been used to bind exfoliated clays like attapulgite as acoating.

A hydrogel is a network of polymer chains that are hydrophilic, sometimes found as colloidal gel in which water is the dispersion medium. Such polymer molecules in solution have random chains but can adopt an ordered conformation on addition of a crosslinking agent like glycerol. Hydrogels, like linear sulfated polysaccharide kappa carrageenan has been evaluated and found to possess sufficient fertilizer coating properties (Cifuentes *et al.*, 2017). Ghazali *et al.*, (2017) noted that the main factor that affects growth of plants and their quality include the amount of water and fertilizer that can be absorbed by the plant. They used superabsorbent polymer-SAP on Controlled Release and Water Retention fertilizers (CRWR) to improve on nutrient absorption.

There are two important processes in SAPs, the swelling process, which occurs when the SAPs interact with nature whose degree of swelling depends on the polarity of the SAP, pH among other physical properties (Sadeghi, 2012). Solvent molecules penetrate the network structures causing molecular chains in cross-linked points to expand. The other important process is crosslinking in which the crosslinks form 3-D network that makes them insoluble in water and opens pockets to trap and store water as seen in figure 1

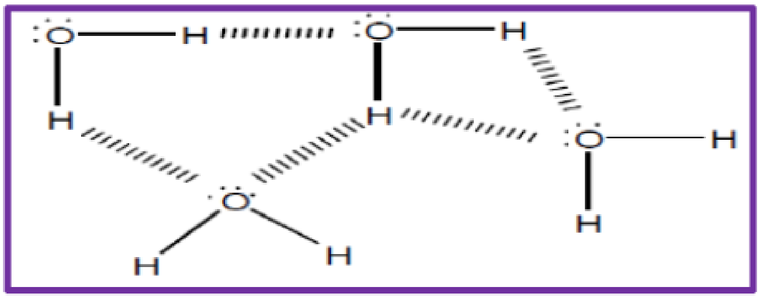

Figure 1: Hydrogen bonds in water (Auda, 2017)

Surface crosslinking of SAP particles improves flow and absorption of water against any pressure (Jocksusch *et al.*, 2009) protecting the shapes during swelling process.

Corn starch is a polysaccharide of large polymeric carbohydrate molecules comprising glucose molecule monomers joined in α-1.4 linkages, the unbranched being amylose while the branched one is amylopectin. Corn starch contains 25 % amylose and 75 % amylopectin (Rahul *et al.*, 2017); (Masakuni *et al.*, 2014). The polymer molecules are held together by both Van der Waals forces and strong hydrogen bonds into a quasicrystalline form due to the corn starch granules.

The other component in formation of starch-GA is gum Arabic. There are very many species of gum acacia extracted from acacia trees. Gum Senegal and gum seyal are the most used species for extraction of gum Arabic an exudate tree gum (Jamaludin *et al.*, 2017) for commercial uses. GA is obtained in the stems and branches of these trees as seen on picture 1.

Figure 3: Photograph of gum acacia (Musa *et al.*, 2018)

Gum arabic is a natural branched multifunctional hydrocolloid, an arabino-galactan-protein complex that contains Ca, Mg and K. Hydrolysis of GA produces arabinogalactan polysaccharides, arabinogalactan protein and glycoproteins.

II. Material And Methods

- **Starch-acacia synthesis**

Exactly 50.0 g of gum acacia was mixed with 20.0 g corn starch in a 250 mL glass beaker. Accurately measured 100.0 mL methanol solvent was added into the mixture. The mixture was manually stirred with temperature being raised at 2 °C per minute until it reached 60 °C. About 10.0 mL glycerine was added and the mixture continually stirred until it formed a gel. Part of the jelly was dried into an oven at 60°C. The dried starch-GA was cut into pieces of 2.0g for characterization.

- **Physical properties of starch-GA**
- **Water absorbency**

Three pieces of starch-GA films each weighing 2.0 g were cut and each of them put into dry clean tea bag. They were lowered into a 250 mL glass beaker containing 100.0 mL tap water. The three tea bags were removed after intervals of I hour and weighed. This was repeated until there was no change in mass. The water absorbency determined by gravimetric method as in research of (Cun-dian *et al.*, 2014) was calculated from equation 3b below (Ghazali *et al.*, 2017).

$W_A = \frac{M_1 - M_0}{M_0}$ ……………………………………………equation 1, where M_1 is mass of the S-GA at time t and M_0 initial mass of the starch-Gum acacia which was 2g.

Characterization of SAPs
The SAP were characterized on XRD and TGA.

III. Results and Discussion

Characterization of corn starch
Figure 4 below shows the XRD spectra for corn starch.

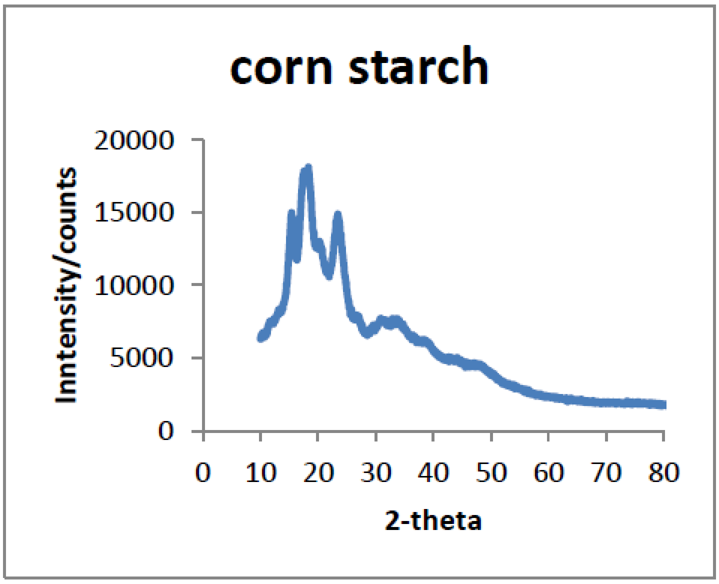

Figure 4: Diffractograph of Corn Starch

Corn starch is a semi crystalline compound and exists as granules in solid state with three broad peaks at two theta 14.6°, 18.3° and 23.4°. These peaks show that some of the molecules in the composite pack either as amylose or amylopectin. The biggest peak at two theta 18.3° represent the granular (Sarko *et al.*, 1976) formations in the 75% amylopectin composites. The peak at two theta 23.4° could be due to packing together of the amylopectin molecules (Perez and Vergelati, 1987) in the composites. The shoulder on the two theta 18.3° peak could represent amylose molecules packed together. The three peaks above were also reported in (Marta *et al.*, 2019 though at shifted positions due to the thermal treatments on their starch.
Figure 4 below shows the TGA analysis of corn starch.

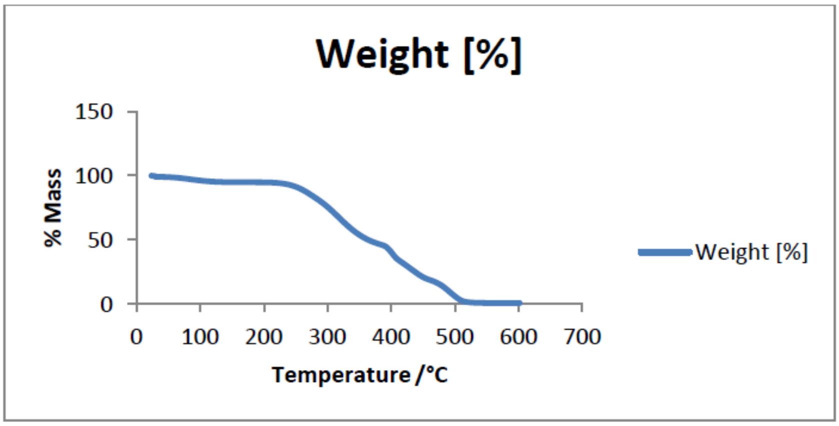

Figure 5: TGA for Corn starch

Corn starch easily forms a gel in water due to hydrogen bonding with the water at low temperatures of up to 60 °C, through gelation process without loss in mass. The loss of mass of about 5 % from around 60 °C to 100 °C can be attributed to loss of moisture and adsorbed water as was also noted in the research of (Mano *et al.*, 2003). There is no loss of mass between 100 °C and 220 °C which can be attributed to the retrogradation of both amylose and amylopectin polymer molecules that tend to form suspensions/granules due to extended hydrogen bonds between OH-6 and hemiacetal O. However there is a very big loss in mass between 250° C to 510° C which due decomposition of the amylopectin and amylose polymer chains

- **Characterization of gum Arabic**

XRD of the gum Arabic was performed and the diffractograph is given on Figure 5.

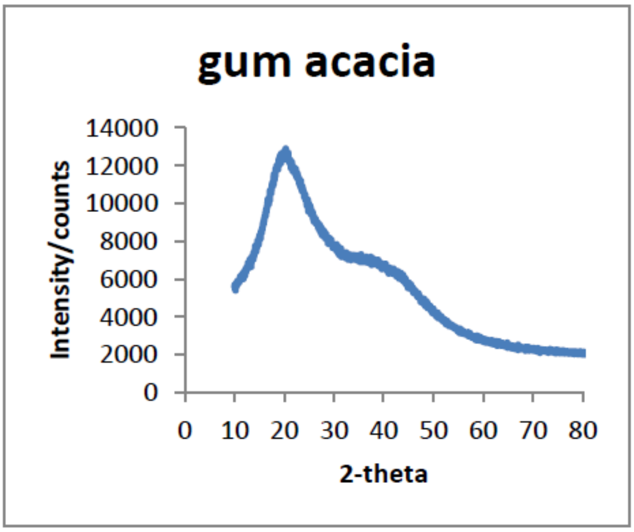

Figure 6: Diffractogram for the gum acacia

The diffractograph has a broad single peak hence not easily defined on the two theta. This means it is not possible to place this molecule into a unit cell. This compound is not crystalline by any percentage. There is a two theta peak at 19.9° due to the solid nature and presence of the calcium, magnesium and potassium as also noted by (Nafie *et al.*, 2012). The XRD shows that GA is an amorphous solid and it compares closely with that of (Gulfam *et al.*, 2014) with a two theta at 19.895° with a d spacing of 4.4375Å.

Thermogravimetric analysis of gum Arabic was performed to establish its level of resistance to temperature increase in case of outbreak of fires in fields where the coated formulas are used.

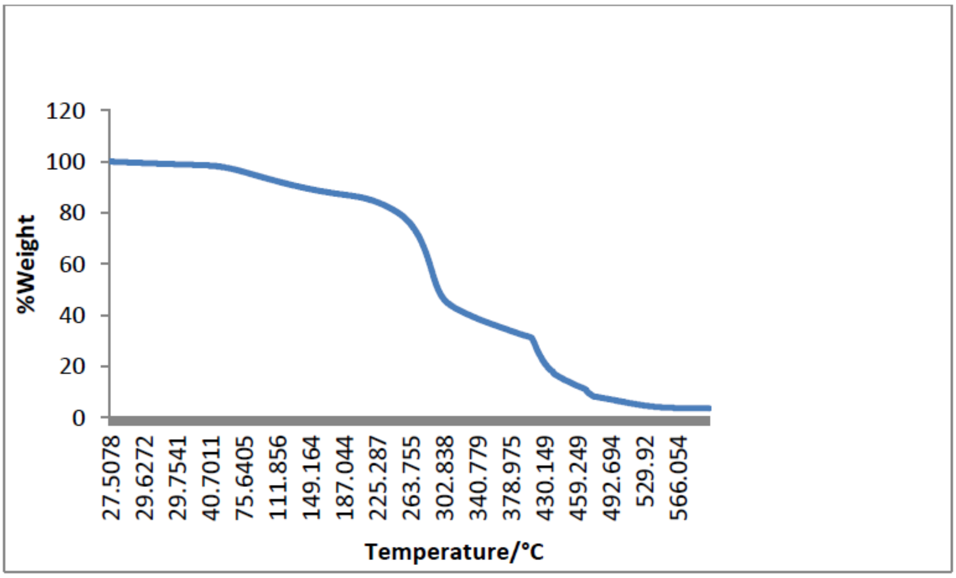

Figure 7: TGA for Acacia

Figure 7 can be divided into six sections; 27.51 °C to 68.2 °C, 68.2 °C to 242.94 °C, 242.94 °C to 324.52 °C, 324.52 °C to 408.67 °C, 408.67 °C to 485.66 °C, 485.66 °C and beyond. The TGA of the coating materials tells of the level of decomposition these products will have in the environment. For example should a fire raze through the farm after planting would the flame temperature break down the coat on a fertilizer coated by this film? This curve on Figure 7 is similar to the one reported by (Jamaludin *et al.*, 2017). There is no significant loss in mass up to 34.9 °C. The small loss in mass between 34 °C to 68.2 °C can be attributed to evaporation of moisture from the crystalline compound in a water desorption step also reported by (Mothe & Rao, 2000) and (Jamaludin *et al.*, 2017). There is however a significant loss of mass of about 19 % from 68 °C to 242.94 °C which could be due to the decomposition of the complex product into the polysaccharide and the protein residues and the degradation from 242.94 °C to 324.52 °C of about 40 % could be due to the decomposition of the polysaccharide molecules into glucose and the decomposition of the aminoacids in the proteins. The loss in mass of around 30 % between 324.52 °C to 408.67 °C could be due to sublimation of the individual sugar monomers and 408.67 °C to 485.66 °C represent decomposition of protein molecules reaching a mass residue of about 5% a similar trend to in (Cozi *et al* ., 2009) research. Temperature of 485.66 °C and beyond represents sublimation of the residues.

Water absorbency of SAPs

The graph on figure 8 shows the water Absorbency for the SAP. The absorbency of the SAP increased and reached a maximum after which a decrease in mass was observed. Starch-GA saturates at 4 hours with a maximum absorbency of 2.4g H_2O per 2g sample. Crosslinking in Starch-GA trapped water in addition to the water attached to the composite through hydrogen bonds though with reduced absorbency rate due to increased time to saturate. This is also noted in the research of Ghazali *et al.*, 2017 on properties of controlled-Release-Water Retention Fertilizer Coated with Carbonaceous-g-poly(acrylic acid-co- acrylamide) superabsorbent polymer. The weight added to the SAP in water represents the pores that trap the water. These pores increase the water uptake to the coated fertilizers before slow diffusion into the plant takes place (Mohamad *et al.*, 2013) reducing the leaching of the nutrients.

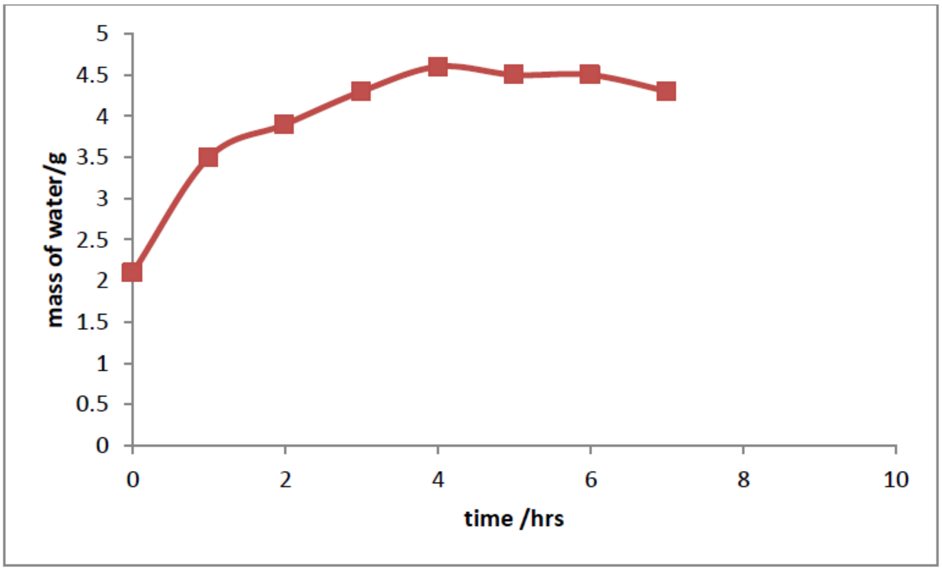

Figure 8: Water absorbency for Starch-GA

IV. Conclusion

The starch-GA was successfully prepared as SAP. This product showed stability at normal outside temperatures of up to 50°C. The SAP has a swelling property that enables it to absorb water into its cross links that can later be diffused with nutrients into plants on need achieving a Slow Release Fertilizer status.

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Conflict of Interest

The authors declare that there is no conflict of interest

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