

Fabrication and Characterization of Starch-PVA Superabsorbent Polymer for Encapsulation of Clay-NPK Nanocomposites

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Abstract:

This study identified use of chemical fertilizers as one of the courses of pollution due to leaching of the excess chemicals. The study prepared a biodegradable starch-polyvinyl alcohol superabsorbent for coating of a nanofertilizer product. The starch-PVA was prepared from polymerization of equal ratios of corn starch and PVA in methanol solvent. The starch-PVA was characterized on XRD and TGA. It was also tested for water absorption characteristics. The XRD showed presence of semi-crystalline structures in starch-PVA. The physical characterization showed high water retention for starch-PVA with suitable water retention levels for coating materials for clay mineral nanocomposite matrices.

Keywords: biopolymer, coating films, biodegradable.

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I. Introduction

Starch which is extensively found in flour of corn, cassava, wheat, potatoes, rice (Mano *et al.*, 2003) is used in industry as adhesives, thickening materials, stabilizer pasting agents. Starch is available and biodegradable natural polymer that has also extensively been used as an encapsulating matrix. The use of biodegradable polymers for packaging offers an alternative and partial solution to the problem of accumulation of solid waste composed of synthetic inert polymers (Fahmida *et al.*, 2010). On the other hand PVA is frequently used in the preparation of various membranes and hydrogels (Young-Chang *et al.*, 2009). The PVA hydrogels have received increasing attention in biomedical and biochemical applications because of their permeability, biocompatibility and biodegradability (Young-Chang *et al.*, 2009). Starch polymer has been in other cases enhanced by vinyl ethylene or polyvinyl alcohol. For example whereas polycaprolactone-PCL is degraded slowly by micro-organisms, PCLs, montmorillonite and urea mixture have been prepared into CRF pellets (Suppa, 2017) and polyacrylamide hydrogel has been used to bind exfoliated clays like attapulgite.

Fertilizers are organic or inorganic substances that add nutrients to soils when applied (Nguyen, *et al.*, 2015; Zhang *et al.*, 2010). Plants require nitrogen, potassium, calcium and phosphorus as macronutrients and other micronutrients like molybdenum, magnesium, sulphur (Gu *et al.*, 2009) (Cifuentes *et al.*, 2017). Fertilizers are soluble in nature since the nutrients are absorbed either through roots as solutions or through the leaves and stems as liquid foliar feeds. Around 40% of crop yield is attributed to use of fertilizers, but it is noted that over 70 % N, 60 % P and 70 % K are lost to the environment causing soil and water pollution (Amanda *et al.*, 2017). Nanotechnology is increasingly being looked at as the solution, since nanofertilizers are smart and deliver the nutrients on plant need (Trenkel, 1997). There are many ways to make nanofertilizers among them coating the fertilizer with clay minerals, dispersing the fertilizer into the clay matrix, encapsulating the nutrients with a superabsorbent polymers, SAP (Rai *et al.*, 2012). Most of the SAPs researched on are the environmentally friendly composites. Composite materials like starch-PVA are made up of two or more heterogeneous components forming two or more phases (Gulfam *et al.*, 2014). Literature shows that (Corradini *et al.*, 2010) researched on the use of chitosan nanoparticles as coating material while (Khelifa *et al.*, 2018) modified raw

clays in Algeria using poly (o-phenylenediamine) by exfoliating the layers into nanomaterials. In another research it was observed that when xylan is blended into PVA using plasticizers like polyols, the mechanical properties of the biopolymer were improved (Cuan-dian *et al.*, 2014).

SAPs are long chain polymers which are slightly cross-linked with an ability to swell and maintain bulky water and aqueous solutions after being absorbed (Liu & Gao, 2001). These materials can appear in gel form as a result of absorbing huge amounts of water and aqueous solutions (Auda, 2017) and are generally cross linked polymeric chain networks making them overcome their dissolution and support their water diffusion. Some of these SAPs respond to external factors like pH, heat, electric fields and chemical environments making them smart. These smart SAPs are used in pharmacy, biotechnology, agriculture, drug delivery systems among many (Sadeghi & Hossein, 2008).

The degree of the swelling depends on the polarity on the SAP, solvent properties, the particle size and environmental conditions like temperature and pH (Sadeghi, 2012). During swelling the solvent molecules penetrate the network structures causing molecular chains in cross-linked points to expand. Alternatively when in contact with water, hydrogen bonds create cellular structures in the SAP network that can store water. The degree of swelling will also depend on crosslinking process, in which the crosslinks form 3-dimensional network that makes them insoluble in water and opens pockets to trap and store water. Surface crosslinking of SAP particles improves flow and absorption of water against any pressure (Jocksusch *et al.*, 2009) protecting the shapes during swelling process. These crosslinks prevent the SAP from swelling to infinity that causes dissolving. The coiled dry SAP stretches out into a uniform pattern on absorption of water as seen in the diagram on Figure 1.

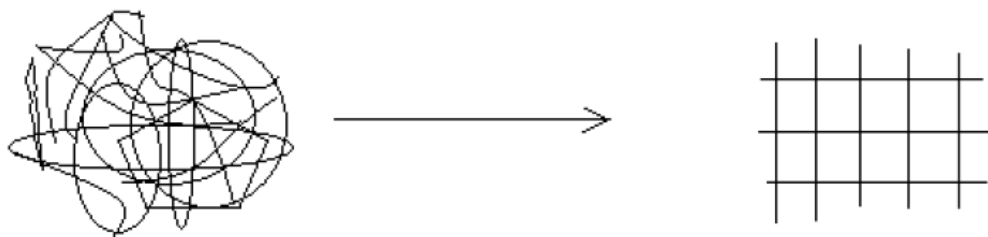


Figure 1: Crosslinking Process

SAPs have hydrophilic groups such as COO^- , OH^- , NH_2^- or NHCO (Ferfera-harrar *et al.*, 2015). This ionic nature enables them absorb large quantities of water through hydrogen bond interactions increasing the molecule disorder in the polymer network which swells them dramatically (Daungtawan *et al.*, 2011). The high water absorption of these materials is attributed to the interconnected super pore structures of diameters that create open channels for capillarity of solutions (Ghazali *et al.*, 2017). In research of (Jamari *et al.*, 2015) carbon synthesized from biomass greatly improved the physical properties of SAPs due to their high cation exchange capacity, CEC and water holding capacity.

II. Material And Methods

Starch-PVA film synthesis

Exactly 10.0 g of corn starch, 200.0 mL of 40 wt % polyvinyl alcohol, PVA and 5.0 mL glycerin were mixed. The mixture was added to 100.0 mL distilled water in a 500 mL glass beaker at room temperature with stirring. The temperature of the suspended mixture was raised to 80 °C by placing it into a hot water bath. Exactly 20.0 mL butanol was added to the mixture to avoid frothing. Exactly 200.0 mL of 20 wt % formaldehyde was added and the mixture mechanically stirred for 3 hours to completely gelatinize the starch. A little water was added continuously to maintain the volume of the mixture. After 3 hours the temperature was raised to 95 °C for 20 minutes. The foam on the mixture was skimmed off while about 100 mL of the starch-PVA solution was poured and leveled into a glass mold. After drying the solution at room temperature the films was removed and dried at 60°C in an oven for 8 hours. The dried starch-PVA films were then removed from the mold and stored into polythene bags. The remaining thick starch-PVA jelly was covered and stored for coating of SRFs.

Water absorbency of starch-PVA

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 with starch-PVA were removed after intervals of I hour and weighed. This was repeated until there was no change in mass. The water absorbency was calculated from equation 3b below (Ghazali *et al.*, 2017).

$W_A = \dots$ equation 3b, 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. The water uptake of the starch-PVA films was also investigated using a similar method in (Fahmida *et al.*, 2010).

Field burial test

Fifteen 10.0 g, fifteen 4.0 g and ten 1.0 g dry spheres of SRF2 prepared elsewhere were dropped into 200.0 mL of starch-PVA jelly in a 1000 mL glass beaker and slowly stirred at 40 °C for 8 hours until the jelly solidified on the SRF2. The SRF2 coated with starch-PVA was labeled CRF3. The CRF3 was left in the beaker for 3 days for it to solidify into thick jelly. The products were dried in an oven at 40 °C for 2 days. The SRFs, CRFs, NPK was put into plastic tins and used to study release and uptake of nutrients by a maize crop. Picture 1 shows the greenhouse optimization for 14 weeks.

Picture 1 planting tins loaded with soil and nutrients



Characterization of SAPs

The SAP were characterized on XRD and TGA.

III. Results and Discussion

Characterization of corn starch

The SAP polymer molecules are held together by both Van der Waals forces and strong hydrogen bonds into a quasi-crystalline form due to the corn starch granules.

Figure 2 Diffractograph of corn starch

Figure 2 has wide peaks at two theta 14.6°, 18.3° and 23.4° just like in the research of (Aytung, 2014). This implies that this covalently bonded compound has semi-crystalline nature in solid state. However it is not possible to establish existence of the basal and prism planes as normally recorded in the seven crystal types of; cubic, monoclinic, orthorhombic, tetragonal, trigonal and hexagonal. A crystal structure is characterized by unit cell, containing atoms in a specific spatial arrangement and a formula. Corn starch is not crystalline compound as seen from Figure 4.2 but exists as granules in solid state. This is probably why the XRD displays only three broad peaks at two theta 14.6°, 18.3° and 23.4°. The bigger peak at two theta 18.3° represent the granular formations in the 75 % amylopectin composites which was also observed by (Sarko *et al.*, 1976). The peak at 23.4° could be due to packing together of the amylopectin molecules in the composites as it compares with one of (Perez & Vergelati, 1987) at a similar angle. The shoulder on the 18.3° peak at two theta 14.6° could represent amylose molecules packed together. The three peaks were also reported in (Marta *et al.*, 2019) though at slightly shifted positions due to the thermal treatments on their starch.

- **XRD analysis**

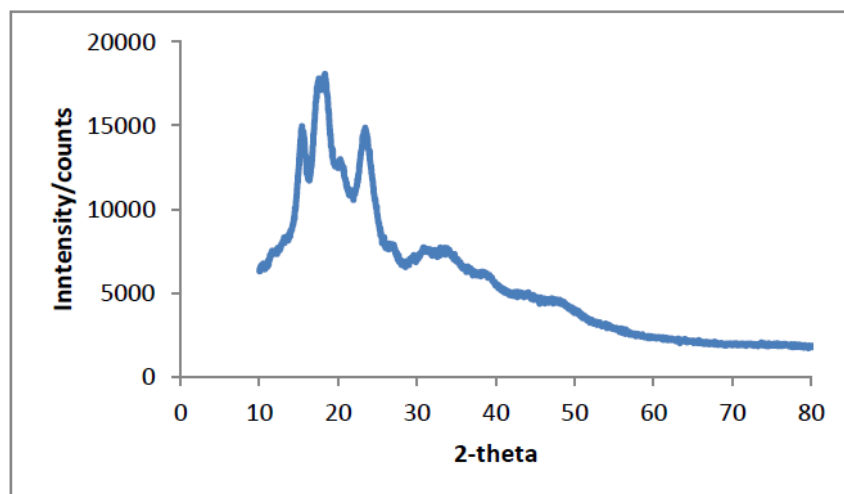


Figure 2: Shows the XRD peaks for corn starch powder.

- **Thermogravimetric analysis**

Figure 3 shows the loss of mass of corn starch on TGA analysis.

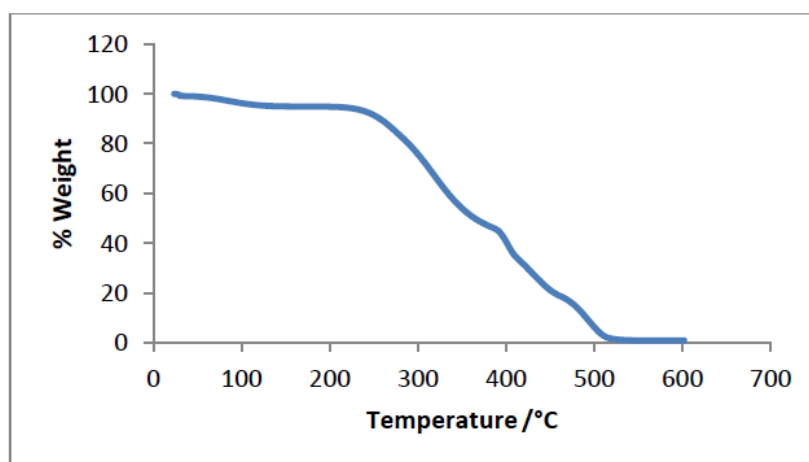


Figure 3: TGA for Corn Starch

This curve can be divided in three major sections as was also observed in the research of (Chagas *et al.*, 2018). The first section has very low percentage loss in mass up to around 250 °C. The next sector runs from 250 °C to around 520 °C before the curve flattens. Corn starch easily forms a gel in water due to inter and intra hydrogen bonding with water at low temperatures of up to 60 °C through a gelation process without loss in mass.

There is water desorption of about 5 % from around 60 °C to 100 °C which can be attributed to loss of all forms of water which compares well with the research of (Mano *et al.*, 2003). There is no loss of mass between 100 °C and 220 °C this can be attributed to retrogradation of both amylose and amylopectin polymer molecules that tend to form suspensions due to extended hydrogen bonds between OH-6 and hemiacetal oxygen as seen also in the research of (Makalalu *et al.*, 2017). This is followed by about 95 % loss in mass from 250 °C up to about 520 °C in a degradation step.

This shoulder structure was also reported by (Mano *et al.*, 2003) which could mean the polymer molecules gelatinize by breaking down at α - 1, 4- hemiacetal oxygen joints up to 400 °C after which the small glucose molecules sublime. Starch gelatinization is a process of breakdown of intermolecular interactions between the molecules of amylose and amylopectin at solid state with heating which retrogrades into a gel over some time rearranging into granules. The formation of tetrahedral oxygen to water molecules with starch molecules generates the gelation of the polymer molecules.

Characterization of PVA

Polyvinyl alcohol is a layered polymer in which the layers are held together by Van Der Waals forces. This study cross-linked the PVA chains by corn starch molecules which introduced hydrogels into the starch-PVA structure.

- *XRD analysis*

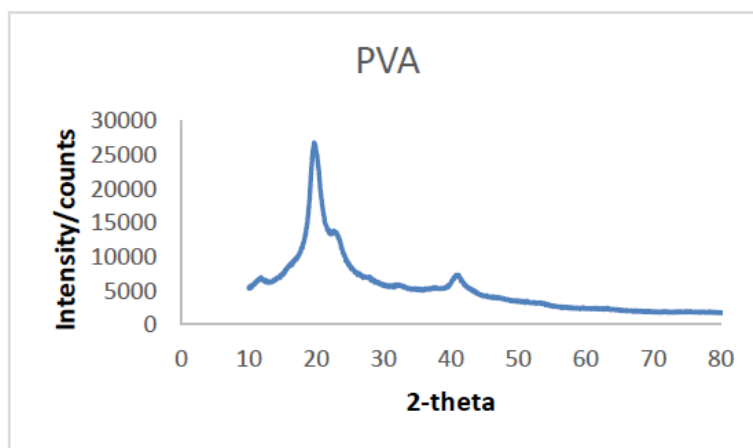


Figure 4: Diffractograph of PVA

Like in the case of corn starch, PVA has a peak at two theta 20° and a small one at around two theta 41° which were also observed by (Kharazmi *et al.*, 2015). The peak at two theta 20° is usually observed in most solid compounds that have repeating pattern, occasionally referred to as semi-crystalline. This is not a crystalline inorganic compound however the peak at 20° as seen on Figure 4.3 provides evidence that the solid nature of this polymer which is made from ethanol and vinyl acetate. PVA has a main peak at two theta 19.8° whose d spacing is 4.4801\AA and is consistent with semi-crystalline structure in (G'eminarda & Bouraya, 2000) research. This peak is identical to the one recorded by (Gulfam *et al.*, 2014), (Kaiwan *et al.*, 2016).

- *Thermogravimetric analysis*

Figure 5 TGA for PVA below shows that there is steady reduction in percentage mass on Figure 5 which is similar to the one of (Chagas *et al.*, 2018). However it is possible to divide this reduction into 4 sections. The one from 26.1°C to 71.3°C , 71.3°C to 262.9°C , 262.9°C to 456.8°C then lastly 456.8°C and beyond. There is a loss in mass of 2 % up to 71.29°C . This loss can be attributed to loss of moisture in the granules. The loss in mass from 71.29°C to 262.97°C of about 2 % represents the decomposition of the polymer followed by removal of the ethanol monomer molecules from the 262.97°C to 456.79°C . The final reduction in mass from 456.79°C and beyond can be attributed to break down of the vinyl acetate polymer which is closely followed by a pyrolysis of the vinyl acetate monomers. This TGA shows that PVA is resistant to heat as in (Fahmida *et al.*, 2010) which is also supported the research of (Kaiwen *et al.*, 2016).

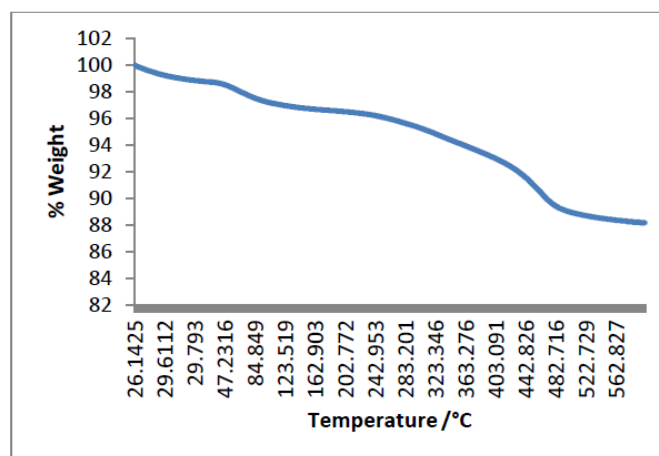


Figure 5: TGA for PVA

Physical characterization of the coating materials

This study developed biodegradable (Trenkel, 2010) SAPs that are geared towards agricultural utility to reinforce the effect of the slow release fertilizer. The following physical tests were performed to test the efficiency of these SAP materials.

1. Water Absorbency of the SAPs

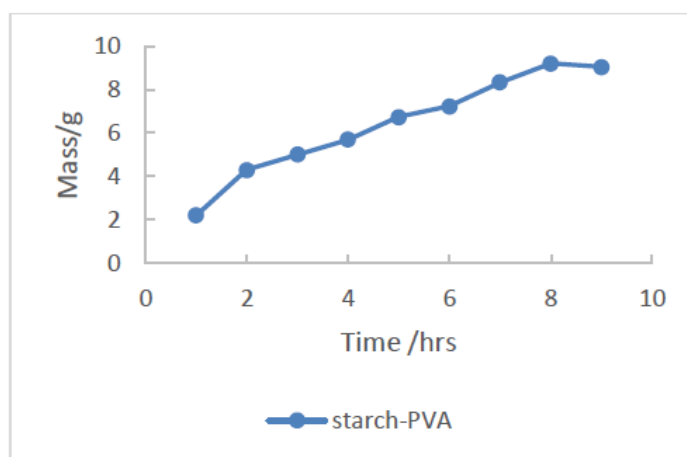
Water absorbency was done to compare the capability of the starch-PVA and starch-GA to hold solutions up to their limits. The results of the study were recorded on Table 1

Table 1: Water Absorbency

TIME	W1±SE	Concentration g/mg x10 ⁻³
H0	2.2±0.000 ^{iA}	2.2
H1	4.3±0.0577 ^{hA}	2.15
H2	5.0±0.000 ^{eA}	1.79
H3	5.7±0.000 ^{fA}	1.63
H4	6.733±0.033 ^{eA}	1.49
H5	7.233±0.033 ^{dA}	1.44
H6	8.333±0.0333 ^{cA}	1.36
H7	9.203±0.0667 ^{aA}	1.31
H8	9.033±0.0333 ^{bA}	1.32

Key: H= time in hours, W1=mass of starch-PVA, Mean values followed by the same capital letter(s) within the same column do not differ significantly from one another while mean values followed by the same small letter(s) within the same row do not differ significantly from one another ($\alpha=0.05$, one-way ANOVA, Posthoc-Tukey-test), while the harmonic mean sample size, n=3.

The concentration of SAP decreases as the amount of water increases. Table 4.1 shows that the 2.2 g strip of starch-PVA absorbed water and increased its maximum mass of up to 9.2 g in 7 hours. There is a reduction at the 8th hour to 9.0 g which could be due to the saturated PVA beginning to dissolve into jelly. It takes 7.0 g water for PVA to reach its maximum equilibrium point. The starch-PVA has more open space between the polymer chain and hydrogen bonds of the OH crosslinks than the raw materials which gives it steady swelling of the starch-PVA from start to 7th hour. Figure 6 shows the absorbency of water for the SAP.



Key: H= time in hours.

Figure 6: Water Absorbency

The curve on Figure 6 on water absorbency of the SAP increased and reached a maximum after which a decrease in mass was recorded. Crosslinking in starch-PVA trapped more water in addition to the water attached to the composite through hydrogen bonds but with reduced overall absorbency rate due to increased time to saturate. This is also observed in the research of (Ghazali *et al.*, 2017). The water weight added to the SAP can be equated to the number of pores that trap the water. These pores increase the water uptake to the

coated fertilizers before slow diffusion into the plant on need takes place (Mohamad *et al.*, 2013) reducing the leaching of the nutrients. This finding was also reported in the research of (Ghazali *et al.*, 2009) on properties of Controlled-Release-Water Retention Fertilizer Coated with Carbonaceous-g-poly (acrylic acid-co- acrylamide) superabsorbent polymer.

Water absorbency into the CRFs involve the water penetration into the coating then slow penetration into the fertilizer to dissolve the nutrients and lastly penetration of the nutrients slowly out of the coating (Trinch & KuShaari, 2016). There is a lag time of about 5% of the release time before the nutrient solution is released out the fertilizer compound and a lag time of about a week for CRF in maize crop to start releasing nutrients after the seed has germinated (Trinch & KuShaari, 2016). This reduces loss of nutrients to the soils before development of roots.

Research of (Mikhailenko *et al.*, 2016) showed that there was water molecules in the conglomerates probably attached to the molecule through hydrogen bonds and trapped into the supramolecular structure through intermolecular interactions of the SAP.

The surface crosslinks began to dissolve at some point causing saturation of water absorptivity. Water diffuses into the SAPs until the water pockets fill. The water then begins to desorb through the same SAP film. Mechanism of sorption often involves chemical reaction of the functional groups on the SAPs or mass-transport processes between the liquid phase containing the nutrients across the liquid film surrounding solid roots and the diffusion into the macro and micropores of the SAP and SRF2.

Picture on plate 3 shows some of the products that were reclaimed from the planting tins in picture 1 at the end of study. The row of CRF3 shows that the product in week 1 and week 6 are similar. Both have soil covering the product. This soil is attached to the starch-PVA jelly giving it long time protection up to week 13 which still shows some soil texture on the product.



Figure 7: Plate 4 some of reclaimed products from tins at end of study

The CRF3 formulas for weeks 1, 6, 10 and 13 have soil particles attached on starch-PVA. This confirms that the formula remained intact over the period of study. The SRF2 formula breaks down into smaller pieces from week 5 which increases the surface area for desorption of nutrients. This result was compared with the soil burial tests in (Fahmida *et al.*, 2010) with comparable similarity.

IV. Conclusion

Starch and PVA polymerized into starch-PVA with high ability to store water and solutions since the PVA crosslinks improved hydrogels increasing the capacity to store large quantities of solutions. The starch and PVA materials are resistant to decomposition up to 520°C which would save nutrients in case of a bush fire. The coating showed resistance to corrosion from water in the field optimization over 14 weeks. Some of the recovered nutrients had soil coating confirming the protection.

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Conflict of Interest

The authors declare that there is no conflict of interest.

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