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To cite this article: Sivashangary Selapa *et al* 2023 *J. Phys.: Conf. Ser.* **2523** 012011

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Fabrication of hydrogel controlled-released Phosphorus encapsulated in starch-polyvinyl alcohol film

Sivashangary Selapa¹, Siew Wei Phang^{*1}, Anis Suhaila Shuib¹, Jen Looi Tee²

¹School of Engineering, Taylor's University, Subang Jaya, Malaysia

²School of Engineering and Technology, Sunway University, Malaysia

*Corresponding author: Siewwei.Phang@taylors.edu.my

Abstract. Traditional soluble phosphorous(P) fertilizers can easily leach into water systems causing water eutrophication, a major environmental problem caused by an excess release of nutrients. Controlling the release of P in response to the plant demand could reduce fertilizer's losses and also reduce environmental pollution. This study establishes a concept of controlled release fertilizer, in which a hydrogel fertilizer film is fabricated by incorporating starch, polyvinyl alcohol and ammonium dihydrogen phosphate fertilizer which tend to immobilize the release of phosphate ions and accelerate responsively their release rate in the presence of water. The experiment aims to study the effect of incorporating Starch, and Polyvinyl alcohol (PVA) to Ammonium Dihydrogen Phosphate fertilizer by varying the composition of PVA-Starch-Ammonium Dihydrogen Phosphate and preparing the films through solution casting method. FTIR is being used to investigate the effect of Starch, PVA, and Ammonium Dihydrogen Phosphate composition on the intermolecular bonding of the fabricated film. A total of 10 samples with different material composition is prepared and the intermolecular bonding between this composition is being compared with that of pure starch, pure PVA and pure Ammonium dihydrogen phosphate fertilizer. The FTIR peak will reveal evidence of hydrogen bonding between phosphate molecules and the functional group of polymer molecules as well as showed all the characteristics band of Starch, PVA and Ammonium Dihydrogen Phosphate. The varying formulation of film corresponded to varying intensity of peak and also stretching vibrations.

Keywords: Phosphorous fertilizer, hydrogel, Polyinyl Alcohol film, Starch,

1. Introduction

The world population is expected to rise by one third (2.3 billion) by 2050, needing increased food production to meet the global demand. Agricultural methods, however, confronts numerous challenges due to a lack of sustainable production processes. For example, rapid worldwide population expansion and significant scarcity of plantation land owing to climate change which is a consequence of urbanization, global warming, and disproportionate resource usage, has had a huge influence on food production and environment. To achieve any significant improving in food production, reasonable application of fertilizer nutrients is required [1].

As a result, the usage of commercial fertilizer is widely used around the globe, where they help promote germination rate and growth of plant by supplying more nutrients to the soil, resulting in greater agricultural yields. The annual crop production and annual fertilizer demand are correlated where both



increase concurrently. As such, the annual crop production is predicted to exceed 200 million tons by 2020, requiring approximately 187 million tonnes of fertilizer [2]. In conjunction to that, fertilizers have been pushed to the top of the priority list for innovative sustainable agricultural techniques capable of satisfying global food demand as well as addressing the food availability [3].

In essence a fertilizer is any natural or synthetic element that is introduced into the soil to aid in the release of nutrients necessary for plant growth. Numerous varieties of fertilizers are used depending on the crop's need for growth requirements [4]. Chemical fertilizers are made up of synthetic or artificial ingredients that are generally made up of three macronutrients: (1) Phosphorus, (2) Potassium and (3) Nitrogen. They are, unfortunately more expensive than natural fertilizers because they may contain harmful compounds that cause allergic responses in plants [5]. Due to the obvious potential for environmental impact, chemical fertilizer usage is highly regulated. Depending on the method of application and soil condition, around 50% of applied fertilizers are lost to the environment, leading to water and soil contamination. Excessive or uncontrolled fertilizer usage reduces the water holding capacity of the soil. Excessive usage may have a negative influence on soil fertility and as a result a negative impact on human health [6].

Plants in their early stages are often unable to absorb all the fertilizer that is applied. Because of the greater rate of fertilization, the usage of these fertilizers diminishes the nutrient utilization efficiency or often known as NUE, resulting in economic deficits [1]. Matching fertilizer supply at this stage and conserving nutrient availability are two major elements that determine the effectiveness of nutrient delivery and enhanced nutrient usage efficiency while limiting environmental pollution. As such, controlled release fertilizers (CRFs) are an effective way to increase nutrient efficiency while lowering environmental concerns can help to decrease environmental concerns while also improving nutrient efficiency. This method is frequently employed with fertilizers whose release rate, pattern and duration are well characterized [4].

CRF is a fertilizer granule that is incorporated into carrier molecules to increase nitrogen release efficiency while reducing environmental, environmental and health risks. Fertilizers encapsulated in either organic or inorganic materials provide nutrients to plants at specific rates and for specific times. CRF provides nutrients for a longer period than traditional fast-release fertilizers [7]. By regulating the flow of nutrients, it improves the availability of nutrients and reduces their environmental impact [4]. In addition, CRFs are often coated with polymers to allow controlled release. Polymers are either natural or synthetic, and nutrients are released at a controlled rate. Encapsulated fertilizers are poorly soluble inorganic salts or biodegradable organic compounds, easily decomposed water-soluble substances, and bacterially bio-enriched, poorly soluble chemicals that have been used in the past. It is a common type of CRF that has been introduced [8, 9]. The type of CRFs that was examined in this study is the those whose release behavior is dependent on its physical barrier. These can be characterized as hydrophilic polymer-encapsulated films or as a matrix wherein the soluble fertilizer component is distributed in a consistent manner to improve fertilizer efficiency. Hydrophilic materials, such as starch, chitosan, alginate, polyvinyl alcohol that tend to form gels which is commonly known as hydrogel are utilized to build the film matrices [10].

Nowadays, only a few natural polymers are being utilized to make CRF films, with starch being the most investigated natural polymer. Starch is a polysaccharide composed of several monosaccharides or sugar (glucose) molecules that are bonded together by 1,4- and/or 1,6-glycosidic bonds. It is also known to a biopolymer that comes from a range of renewable sources, biodegradable and is reasonably inexpensive, making it a good choice for environmentally friendly applications [11]. The availability of hydroxyl makes starch derivatization possible in a variety of ways. Starch and its derivative is regarded a potential material for use as an encapsulating material in CRFs due to ease with which they can be modified, their environmental friendliness, and their cost [12].

However, because of its low solubility, poor mechanical properties, and instability at high temperatures and pH, using starch in its natural condition as an effective encapsulating material for non-food applications is generally limited which encourages the development of modified starch polymers [6]. Starch blends with polymers like polyurethane [13] and polysulfone [14] has been reported earlier

to improve its mechanical properties, but the challenge was to achieve adequate biodegradability of the encapsulated fertilizer film in the soil while minimizing the ratio of synthetic polymers to natural biopolymers.

As such the addition of polyvinyl alcohol to the starch matrix is being considered here in this research. The addition of this component, according to various research is expected to increase the mechanical properties and mix compatibility. PVA is semi crystalline, totally biodegradable as well a non-toxic polymer used in major industries like paper treatment and drug delivery [15]. Also, there have been extensive research carried out in utilizing starch and PVA mix film to encapsulate the control - release fertilizer due to its improved biodegradability, mechanical strength, fertilizer release efficiency and hydrophilicity of film which further validated its effectiveness in blending it with starch [16,17].

Phosphorus fertilizers is known to be one of the demanding plant nutrient because phosphorus is often the most deficient phytonutrient [18]. This is not due to the low total amount of phosphorus in the soil, but to the presence of phosphorus in the soil with a chemical composition that is not available to plants. Water-soluble phosphorus-based fertilizers such as diammonium phosphate, urea, and monoammonium phosphate explode nutrients that do not meet the nutrient needs of plants. Due to the low efficiency of phosphorus fertilizer, only about 10% to 20% of this phosphorus is absorbed by plants. Therefore, currently available phosphorus fertilizers need to be further developed to improve bioavailability in soil. In this regard, sustained release phosphorus fertilizers may increase the effectiveness of phosphorus fertilizers while minimizing their environmental impact [19] Phosphorus fertilizers are highly water soluble and chemically compatible, so they can be used alone or in combination with nitrogen or potassium fertilizers. However, the effectiveness of plant uptake of liquid fertilizers after foliar application is limited and further studies on sustained release hydrogel-based phosphorus fertilizers are needed [20]

Up to date, there is little to no study reported on the controlled released phosphorus fertilizer with the starch-polyvinyl alcohol formulations. There are other phosphorous based CRF's being studied previously however either they are made of expensive sheet material, they are not environmentally friendly, or their phosphorus release efficiency does not meet the needs of plants. This limits the use of controlled release hydrogel-based phosphorus fertilizers in agriculture.

Taking all these factors into account, this study provides further insight into the effects of polyvinyl alcohol (PVA) integration with starch and phosphorus fertilizers on the chemical bonding of the produced hydrogel fertilizer film. In this study we propose using several formulations based on starch and polyvinyl alcohol to encapsulate Ammonium Dihydrogen Phosphate (DAP) fertilizer by altering their composition. The formulations that were being studied can be employed as a new hydrophilic phosphorous fertilizer film that encourages effective phosphorus release relative to the plant demand. The functional group analysis performed will further clarify if there is any interaction among the chemical bonds in the composite film.

2. Material and Method

2.1. Materials

In this research, Ammonium Dihydrogen Phosphate and Polyvinyl Alcohol (99% Hydrolyzed) was purchased from R&M Chemicals. All the reagents were of analytical grade and were used as received without any further treatments. The starch that is used in the film preparation is tapioca starch (Brand Kapal ABC) and is obtained from the local supermarket.

2.2. Sample preparation

The tapioca starch/PVA/Ammonium dihydrogen phosphate was prepared by the solution casting method. 50 phr (10 g) of starch were dissolved in 400ml of distilled water. In the same solution 50 phr (10 g) PVA and 10 phr (2 g) Ammonium Dihydrogen Phosphate was added [21]. The solution was stirred using a mechanical stirrer (CAT.R50D) at 400 rpm in a 97°C-water bath for 2 hours until a homogenized mixture is formed. The mixture was let to cool for 10 minutes. Upon cooling, 36ml were

withdrawn from the solution and casted on a petri dish. The casted solution was dried at 40°C for 48 hours and the dried film were removed from the petri plate. The overall process was repeated with different composition of starch, PVA, and Ammonium Dihydrogen Phosphate as shown in Table 1. As can be seen from the Table 1, the formulation of the film is designed such a way where the composition of starch increases as the composition of the PVA decreases. The set point of the starch composition is 90 phr which decreases linearly by 10 phr as the composition of PVA increases. Higher composition of starch in the film is preferred compared to PVA because increasing starch content enhances the biodegradation rate and water absorption capacity of the film based on study reported by Han, et al [16] and Versino, et al [22] As such the experiments were designed based on these studies with some modifications with the Ammonium Dihydrogen Phosphate fertilizer content in the formulations in which the film with 10 phr Ammonium Dihydrogen Phosphate content is compared with films without any Ammonium Dihydrogen Phosphate content. The pure Starch-Polyvinyl Alcohol formulations without the addition of Ammonium Dihydrogen Phosphate is fabricated as control sample in this study.

Table 1. Composition of PVA, Starch and Ammonium Dihydrogen Phosphate

	Composite Code	Starch, S (phr)^a	Polyvinyl Alcohol. PVA (phr)^a	Ammonium Dihydrogen Phosphate MAP (phr)^a
Batch 1	CRF-1	50	50	0
	CRF-2	60	40	0
	CRF-3	70	30	0
	CRF-4	80	20	0
	CRF-5	90	10	0
Batch 2	CRF-6	50	50	10
	CRF-7	60	40	10
	CRF-8	70	30	10
	CRF-9	80	20	10
	CRF-10	90	10	10

^a phr is part per hundred resins based on the 20g of the total weightage of PVA-Starch blends

2.3. Fourier Transform Infrared (FTIR) Analysis

The functional groups of PVA, starch, and ammonium dihydrogen phosphate present in the composite sample were identified and FTIR (PerkinElmer, Spectrum 100) is used to clearly analyze the bond between the polymer matrix and the particles. The scan area was set to 450-4000 cm⁻¹. This is achieved with a resolution of 4 cm⁻¹ in 16 overlap scans.

3. Results and Discussion

Figure 1 represents the FTIR spectra of Starch-PVA blends with varying content of starch and PVA. The spectra of Starch-PVA were analyzed and compared with the spectra of the Starch-PVA-Diammonium Phosphate blend as shown in Figure 2. Based on Table 2 the absorption peaks from 3200-3500 cm⁻¹ corresponds to the stretching vibration of OH-groups [23]. It can be observed from Figure 1 that the highest stretching peak could be observed in the Starch –PVA blend that contains the highest amount of Starch. Based on the experimental data reported by other research, the wavelength of OH groups for pure tapioca starch were found to form a peak at 3477 cm⁻¹ and pure PVA were found to form a peak at 3608 cm⁻¹. After blending 50 phr starch with 50 phr PVA the spectrum peak is found to significantly shifting to a lower wavelength (3292 cm⁻¹). PVA appears to reduce the quantity of O-H bonds in pure starch, indicating that the free OH groups in the starch are forming hydrogen bonds with

the OH groups with the pure PVA. The detected amount of (O-H) stretching decreases as the amount of hydrogen bonding between Starch and PVA increases [24]. As a result of these findings, it can be deduced that chemical binding was induced between starch and PVA. On the other hand, the bands around 1244 and 1082 cm^{-1} corresponds to the stretching vibration of C-O in the C-O-H groups whereas the peak around 1013 cm^{-1} are attributed to the C-O stretching vibration caused by the C-O-C groups of the amylose and amylopectin unit in starch. As shown in Figure 1 the band around 1422 cm^{-1} which signifies the C-H stretch corresponds to the PVA spectrum and on contrary to that the absorption bands appearing at 1422, 1373 and 847 is attributed by starch solely and this is an excellent reference peak for monitoring starch content in the film. The control sample peaks were as expected and in line with the previous findings by other research [25].

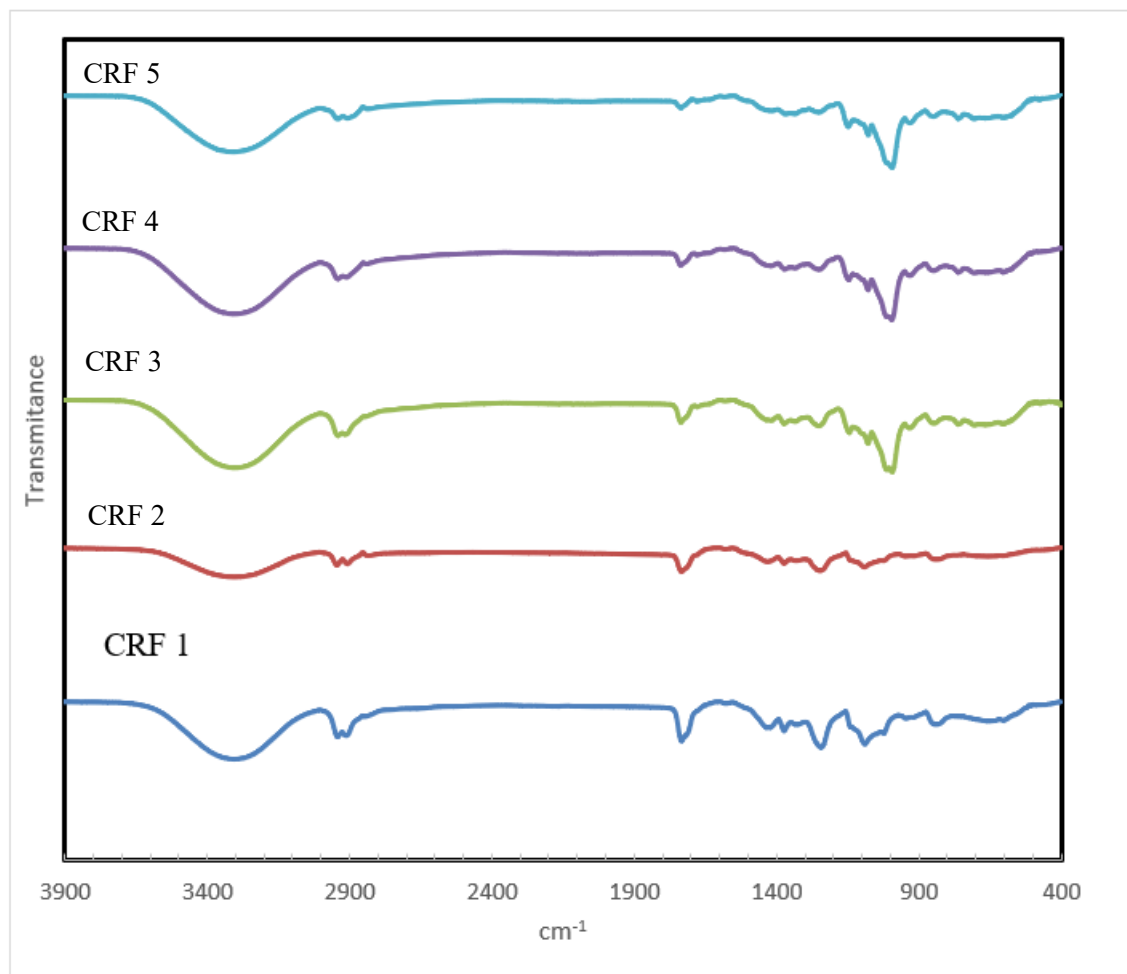
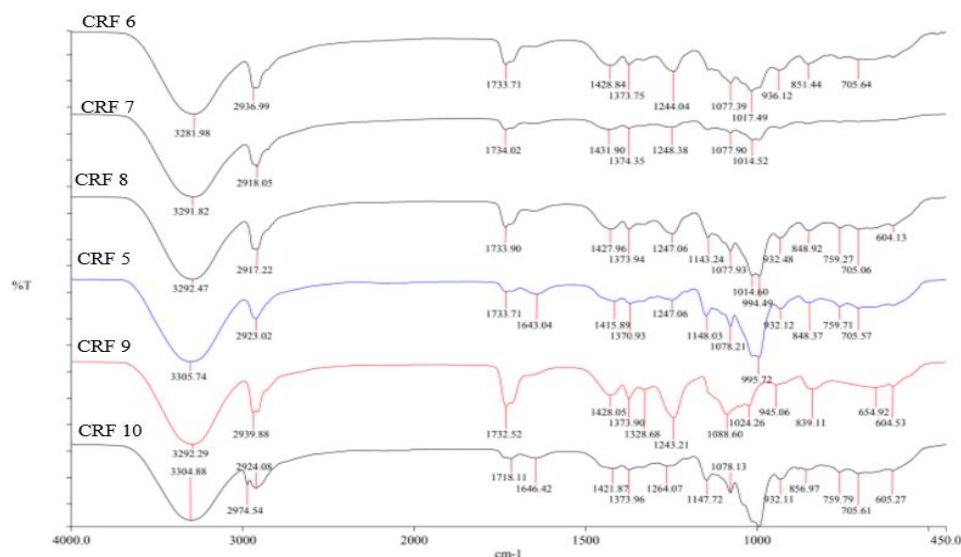


Figure 1 FTIR spectra of Starch/PVA Blends

Table 2. Pure tapioca starch and pure polyvinyl alcohol biplastic reference materials FTIR assignment [23]

Assignment	Tapioca starch	Polyvinyl alcohol
O-H stretching	3477 cm ⁻¹ (broad)	3608 cm ⁻¹ (broad)
C-H stretching of CH ₂	2924 cm ⁻¹	-
Combination of O-H stretching	2150 and 2088 cm ⁻¹	2162 cm ⁻¹
C=O stretching of PVA residue	-	1732 and 1616 cm ⁻¹
O-H bending	1635 cm ⁻¹	-
C-H wagging of CH ₂	-	1328 cm ⁻¹
C-O stretching	1008 cm ⁻¹	1136 cm ⁻¹

Figure 2 represents the FTIR spectra of one control sample (CRF 5) and the Starch-PVA-MAP Blend samples. The spectra are arranged from CRF 6, CRF 7, CRF 8, CRF 5, CRF 9 and CRF 10. Based on the Figure it can be observed that the bands at 3305 cm⁻¹ was assigned to the stretching vibration of –OH groups. Upon adding the ammonium dihydrogen phosphate, the peak shifted to a lower wavelength compared to the one without ammonium dihydrogen phosphate. The bending and stretching vibration at 906 to 1100 cm⁻¹ is found to be contributed by the (PO₄³⁻). The spectrum intensity at 995 cm⁻¹ increases with the addition of ammonium dihydrogen phosphate which is contributed by the group off phosphate PO₄³⁻. The NH₄⁺ exhibits its characteristic bending modes at 1428 cm⁻¹ [26]. The IR analysis of all the tested formulations (CRF 6, CRF 7, CRF 8, CRF 9 and CRF 10) indicates that all the spectra have similar peaks with a gradual application in the intensity of the band located at 3300 cm⁻¹ and at 1015 cm⁻¹ which corresponds to the vibration of C-C and O-H bonds respectively and this is mainly due to the increase in the starch content in the composite film [27]. Characteristic peaks from phosphate, PVA and starch are present in all samples so it can be deduced that the chemical structured of PVA, starch and ammonium dihydrogen phosphate were retained in the composite film.

**Figure 2** FTIR spectra of Starch-PVA & Starch-PVA-MAP Blends

4. Conclusion

Essentially, the objective of this study was to produce a bio-composite fertilizer film that encapsulates the active ingredient (ammonium dihydrogen phosphate) in the hydrogel matrix of starch and polyvinyl alcohol. An important part of the study also focused on the binding of PVA starch diammonium phosphate while maintaining its chemical properties. Therefore, the first step of the study was to prepare the fertilizer composite film with different contents of starch, polyvinyl alcohol and ammonium diammonium phosphate homogeneously mixed with distilled water to form the film by solution casting method. The prepared composite film was then characterized by FTIR to study the intermolecular bonding between starch-polyvinyl alcohol-ammonium dihydrogen phosphate. Various functional groups present in the composite films were identified in the study and the FTIR peaks show evidence of hydrogen bonding between phosphate molecules and the functional group of the polymer molecules, indicating successful bond formation between the active ingredient and the polymer.

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