

# Synthesis of the Swelling Polymers based on Cellulose Grafted with Acrylic Monomers and Survey on Mustard Greens

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**Abstract** – Acrylic acid (AA) were grafted polymerized onto cellulose. Acrylic groups were introduced onto cellulose backbone by a homogeneous synthesis. This reaction was carried out in aqueous solution using ammonium per sulfate (APS) as an initiator and Methylene Bis Acrylamide (MBA) as a crosslink agent. Infrared spectroscopy (FT-IR) was carryout to confirm the chemical structure of swelling polymer. Moreover, morphology of samples was examined by scanning electron microscopy (SEM). The element composition of polymer was determined by energy dispersive analysis of X-rays (EDX). Their equilibrium swelling degree was evaluated in various conditions by tea-bag method. The results showed that the maximum swelling of polymer is about 250 grams per gram in distilled water. Initial experiment on mustard green, this material has the ability to moisturize and provide nutrients for plants, as demonstrated by the rate of germination, plant height, and leaf area in the CT2, CT3 with additional 3% and 5% swelling polymers were both higher than CT1 – the control formula. The leaf area in CT1, CT2, CT3 arranged in turn were 115,37cm<sup>2</sup>, 180,69cm<sup>2</sup>, 187,51cm<sup>2</sup> respectively. This swelling polymers can be used as a moisturizer and keep water for trees.

**Keywords** – Cellulose, Swelling, Polymer, Crosslink, Acrylic Acid, Mustard Greens.

## I. INTRODUCTION

Cellulose is an organic compound with the formula (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>, a polysaccharide consisting of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units. Cellulose is the structural component of the primary cell wall of green plants. Cellulose is the most common organic compound on Earth. About 33% of all plant matter is cellulose, the cellulose content of cotton is 90% and that of wood is 40–50% [1, 2].

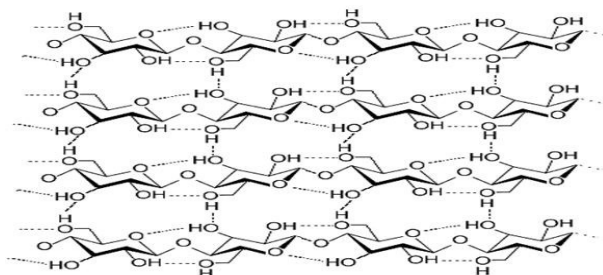


Fig. 1. The structure of cellulose

For industrial use, cellulose is mainly obtained from wood pulp and cotton. It is mainly used to produce paperboard and paper; to a smaller extent it is converted into a wide variety of derivative products such as

cellophane and rayon. Converting cellulose from energy crops into biofuels such as cellulosic ethanol is under investigation as an alternative fuel source. Cellulose has no taste, is odourless, is hydrophilic with the contact angle of 20–30°, is insoluble in water and most organic solvents, is chiral and is biodegradable. It can be broken down chemically into its glucose units by treating it with concentrated acids at high temperature [2].

Cellulose is one of the inexpensive, biodegradable, renewable and the most abundant organic raw material and it has been widely studied during the past decades. Cellulose lacks some properties that synthetic polymers have in some applications although it has many useful properties. Modification of cellulose by graft copolymerization provides a significant route to alter the physical and chemical properties of cellulose materials. Cellulose has been graft polymerized using various techniques. Most of them are based on a grafting-from process, where radical is formed along polymer backbone either by various chemical initiators or by irradiation, and then, the free radical polymerization of vinyl monomers occurs [3, 4, 5, 6]. In these methods, chain scission can occur and cellulose backbone is not kept intact to form the flexible circuits and then to form swelling polymer. Super absorbents are widely used in many products such as in disposable diapers, feminine napkins, soil for agriculture and horticulture, gel actuators, water blocking tapes, medicine for the drug delivery systems and absorbent pads where water absorbency or water retention is important [3, 7, 8, 9].

## II. MATERIALS AND METHODS

### A. Synthesis of Swelling Polymer

The swelling polymer was synthesis from rice husk: 5g cellulose from rice husk was finely ground and the distilled water was charged. This mixture is stirred for 15 min until a clear solution is obtained. The reactor was immersed in a thermostated at 80°C. Then, 2.75ml acrylic acid and 0.01g methylene bis acrylamide were added and stirred for 15 min. After that, 0.05g ammonium per sulfate was added, stirred for 10-15 min obtained gel. Cooled at room temperature and poured to excess non-solvent acetone and remained for 6h to dewater. Then, acetone was decanted and the product was cut into small pieces (diameter ~ 5mm). Again, the fresh acetone was added and remained for 24h. The filtered gel was dried at 45°C for 6h. After grinding, the powdered polymer was stored away from moisture and heat.

### B. Characterization of Swelling Polymer

The structure of swelling polymer was analyzed by the following modern methods: Infrared spectroscopy (FT-IR) was obtained by Nicolet Magna 550, the samples powdered were prepared in KBr pellets. X-ray diffraction (XRD) technique using a Bruker B8 Advance X-ray powder diffractometer. The elemental composition was determined by Energy dispersive analysis of X-rays (EDX, Varian Vista Ax). The size and morphology of materials was examined using scanning electron microscopy (SEM, Hitachi S-4800FEG)

### C. Measurement of Swelling Ratio (SR)

The swelling polymers ( $W_o$ , g), which was put into a tea-bag of nonwoven fabric, was immersed in water for 24h. The treated bag was allowed to hang on a holder for 10 min to separate the swollen sample ( $W_s$ , g) from the unabsorbed water (Feng Hua, 2001). Degree of swelling ratio was defined as follows:

$$SR (g/g) = (W_s - W_o) / W_o$$

Influence of pH on the swelling behavior of the swelling polymers was studied. Monitor the polymer's ability to release water under dry conditions in air

### D. Survey the Moisture Retention of the Swelling Polymer on Mustard Green

The experiment was conducted in greenhouse, covered roof, planted in pots. Each pots was germinated 3 seeds, watered fully, trimmed excess leaves only 1 plant per pot after germination. The experiments were arranged in complete randomized block, each formula (CT) was 3 times repeated, each replicate has 30 trees. Fixed the amount of 300g of potting media and fertilizer are the same for each of the experiments. The amount of irrigation water in CT2 and CT3 were 20% decreased compared to CT1.

CT1: Alluvial soil: Rice husk char (2: 1).

CT2: 97% [Alluvial soil: Rice husk char (2: 1)] + 3% swelling polymers.

CT3: 95% [Alluvial soil: Rice husk char (2: 1)] + 5% swelling polymers.

Monitoring of indicators: Germination percentage (%) was statistic at 10 days after sowing. Plant height (cm), leaf area ( $cm^2$ ), water content in media (g), water content in tree (%) was measured at 40 days after sowing. After 40 days sowing, stop watering and monitor the amount of water in the tree

### E. Methods of Data Analysis and Processing

The data was processed by biological statistical method using IRRISTAT and excel software.

## III. RESULTS AND DISCUSSION

### A. Characterization of Swelling Polymer

The FT-IR method allows for identifying some information of the material structure. The FT-IR method is based on the interaction of light in the infrared region with the bonds in the sample. The light with the certain wavelength will vibrate certain links. So that energy absorption is closely related to the molecular structure

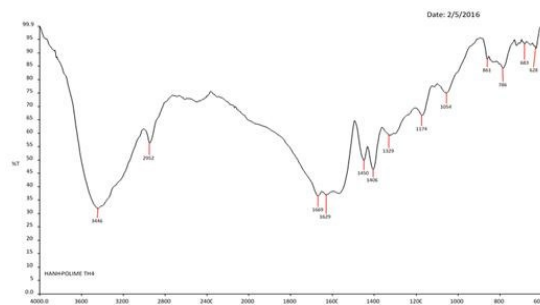


Fig. 2. FT-IR spectrum for swelling polymer

In this Figure, a bands appear in the IR spectrum that could indicate a polymer degradation process. The increase of the band at  $3446cm^{-1}$  signals a vibration of  $-OH$  groups. The increase of the band  $2952 cm^{-1}$  signals a vibration of the C-H stretching of new methylene groups in the polymeric unit. The pick at  $1669 cm^{-1}$  is due to the  $>C=O$  bending. The pick at  $1450cm^{-1}$  is due to the  $-CH_2-$  bending. The band at  $1329 cm^{-1}$  corresponds to a vibration of C-O stretching The peaks in the region from  $1174-861 cm^{-1}$  are due to  $-C-O-$  stretching, the  $-C-O-C-$  pyranose ring skeletal vibration gives a prominent band at  $1054cm^{-1}$  and the  $-CH_2-$  rocking vibration at  $786cm^{-1}$  corresponds to the methylene groups. Accordingly, the garft reaction was occurred.

In the Fig. 3a, all the samples exhibit typical cellulose diffraction angles ( $2\theta$ ) around  $15^\circ$ ,  $16^\circ$  and  $22^\circ$ . In the Fig. 3b, these vertices still remain but not clear, suggesting that the crystal phase in the cellulose has decreased. That mean, the grafting reaction have been formed.

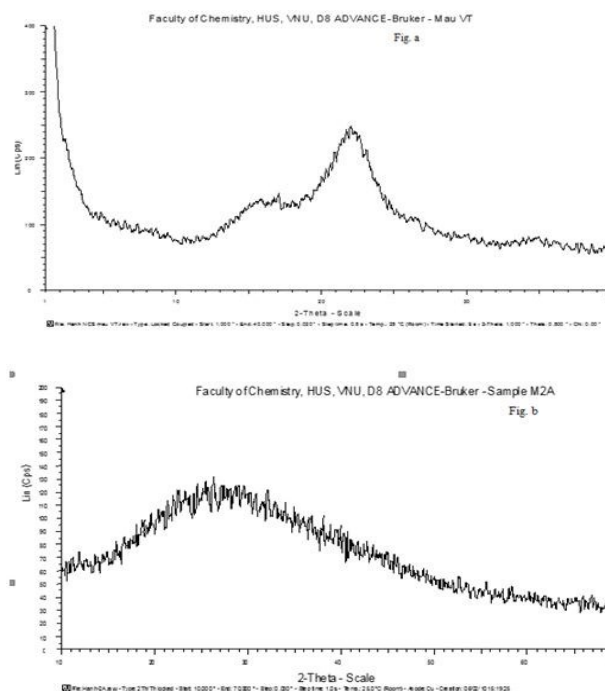


Fig. 3. XRD patterns of cellulose (a) and polymer (b)

The EDX method allows to determine the composition of elements in the materials. In EDX spectrum of the swelling polymers (Fig. 4), the swelling polymer which prepared from rice husk material has high carbon

compounds, with amount of carbon about 40.68%. This is a short chain cellulose component, which is the source of organic nutrients for plant growth. In addition, the composition also contains some other elements Si (8.03%), N (0.20%), P (0.06%), K (0.27%), Zn (0.11%), Fe (0.04%).... These are micronutrients essential for plant

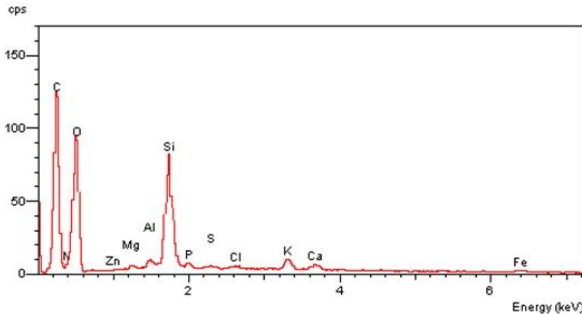


Fig. 4. EDX spectrum of swelling polymers

The SEM micrographs of the husk shows that the husk has a fibrous structure, characteristic for cellulosic fibers. Cellulose is a carbohydrate compounds, made from hundreds, thousands of  $\beta$ -D-Glucose units, forming straight chains. The hydrogen atom on this circuit forms a hydrogen bond with the oxygen atom on the adjacent chain, keeping the cellulose bonds tightly bonded to each other, thus creating a strong network structure. So that, rice husk only capable of absorbing moisture due to interaction with water, unable to swell to keep large amounts of water

Swelling polymer are synthesized from finely grated rice husks. With a short chain, flexible cellulose circuit, combined with bridges of acrylic acid, MBA between the vessels, makes the product a spatial, spatial structure that stores a large amount of water

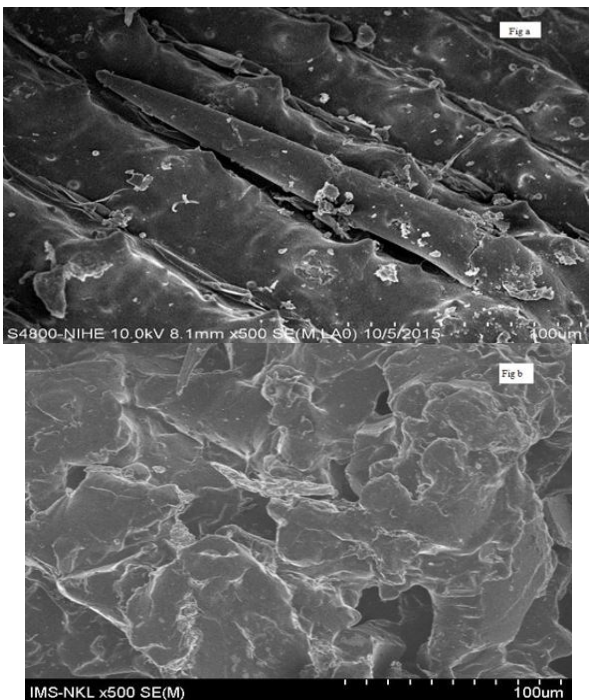


Fig. 5. SEM micrographs of polymer: (a) rice husk, (b) polymer

### B. The Swelling Ratio of Polymer

The swelling ratio of polymer in distilled water: The swelling polymers was synthesise on the copolymerization reaction by the grafting of acrylic acid onto the cellulose.

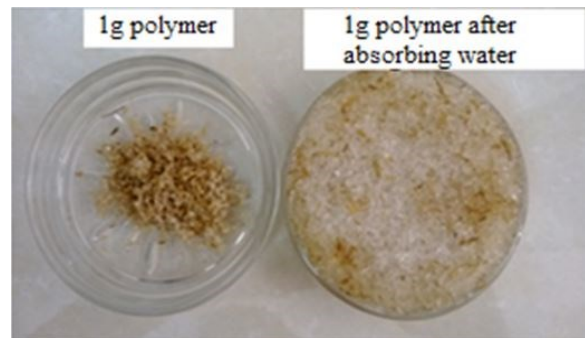
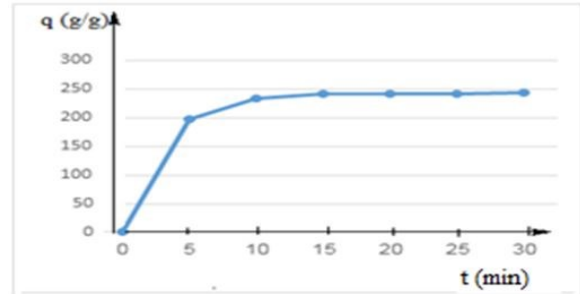


Fig. 6. The swelling of polymers

The product has high moisturizing capacity, maximum swelling polymer in distilled water is about 250 gram per gram polymer (Fig.6). Thus, this synthetic products that have high water retention, It ability can be used to store and regulate water for crops, especially in drought areas and lack of water.

The mechanism of water absorption of synthesis polymers was explained by the fact that polymer chains containing some functional groups  $-\text{COOH}$  and  $-\text{OH}$  are present in the structure of acrylic acid and cellulose. The  $-\text{COOH}$ ,  $-\text{OH}$  groups are hydrophilic, so when introduced into the water, there is a hydration interaction between the functional groups on the polymer and the solvent. These effects reduce energy and increase the entropy of the system. Because of the hydrophilic nature, polymer chains tend to disperse indefinitely in water, which also increases entropy. The presence of mesh material forming a three-dimensional space network, the elastic force of the polymer network blocking the unlimited dissolved. In the system, there exists a balance between the network elasticity and the unconfirmed trend of the circuit. For ionic polymers, neutralized circuits contain the same charge. The charge neutralization is maintained when the negatively charged  $-\text{COO}^-$  groups are balanced with positively charged  $\text{Na}^+$  ions. When exposed to water,  $\text{Na}^+$  ions are hydrated to reduce their gravitational pull on the  $-\text{COO}^-$  groups (due to high dielectric constant of water). This process allows free  $\text{Na}^+$  ions to move freely within the network to form osmotic pressure inside the gel. However, the  $\text{Na}^+$  ions are flexible but cannot move away from the gel because they are still weakly absorbed by the  $-\text{COO}^-$  groups along the polymer main chain and

resembles being trapped by a semi-permeable membrane. Therefore, the dynamic force of the process is the difference in osmotic pressure inside and outside the gel [3, 8].

Effect of pH on the swelling ratio of the swelling polymers (Fig. 7): When the polymers are immersed in buffer solutions with low pH (pH = 3-4), the ionization of the carboxylic acid groups is very low, and the electrostatic repulsion between the ionized groups in the networks has hardly any contribution to the swelling of the hydrogels. This leads to a collapsed polymer network with a rather limited SR. A transition of the SR can be observed between pH 5 and pH 6, at this pH range, dissociation of the carboxylic acid groups occurs. Both the charge repulsion and the presence of free counter-ions in the gel, which cause a high osmotic pressure, contribute to the improved SR. [7].

At pH = 7- 9, the SR of the polymers is almost constant and maximum 252g/g because of the charge repulsion and elastic stress of the hydrogel networks. In alkaline buffer solutions, the carboxylic acid groups become progressively ionized. Therefore, the swelling polymers more rapidly because of a large swelling force created by the electrostatic repulsion between the ionized groups in the network.

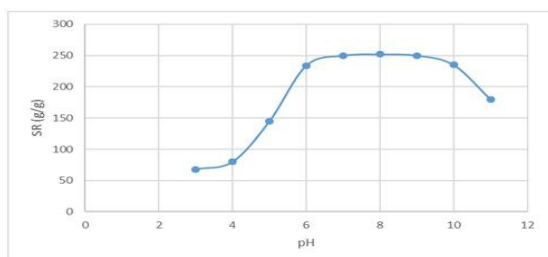


Fig. 7. Effect of pH on the swelling behavior of the swelling polymers

At pH = 10-11, the higher concentration of cation ( $\text{Na}^+$ ) will restrain the extending of the polymer networks, therefore the swelling of the polymer is inhibited.

The water release capability of swelling polymer (Fig. 8): Take 1 gram swelling polymer after absorbing water, to dry naturally in air. The amount of water absorbed in the polymer decreases in time, maintaining good humidity for about 30 days. After about 80 days, the amount of water in the sample remain about 6 grams per gram sample. Thus, this swelling polymer is able to retain water and gradually release water for tree to used

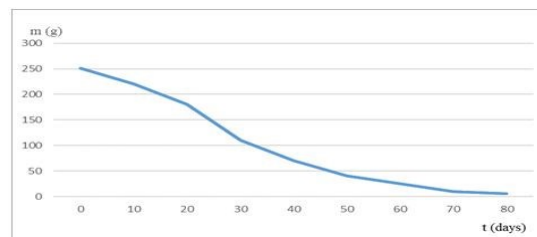


Fig. 8. The water release capability of swelling polymer Survey the moisture retention of the swelling polymer on mustard green

The use of humectants in agriculture has been a technological advance applied in many countries around the world since the 1980s. The effectiveness of this measure has been confirmed in the United States, Canada and China. .... with the renovations of the desert, the greening of barren hills in the United States, the application of Brazilian coffee fields, and sugar beets in Germany ... the results show that they are increased crop yields, reduced plant mortality, reducing the necessary care for plants, saving time and watering [8].

In this study, we were studied the effect of this polymers was synthesized from rice husks with acrylic acid on the growth and development on mustard gree.

Table 1. The moisture retention of the swelling polymer on mustard green

CT	Seed germination (%)	Plant height (cm)	Canopy diameter (cm)	Number of leaf (leaf/tree)	Leaf area (cm <sup>2</sup> )	Water concentration in potting media (g)	Water concentration in leaf (%)
CT1	78.22	17.32	17.02	6.62	115.37	77.53	93.03
CT2	90.16	20.44	19.78	6.91	180.69	118.24	93.32
CT3	93.87	21.87	22.14	7.05	187.51	143.81	93.35
LSD (5%)	1.83	1.06	0.44	0.84	13.08	7.84	0.98
CV %	4.01	2.20	1.96	3.75	5.37	3.13	2.10

The results showed that in CT2 and CT3, when adding 3% and 5% swelling polymer, the rate of seed germination increased 11.94 to 16.56% compared to CT1. After 40 days sowing, the plant height and leaf area of CT2, CT3 were both higher than CT1- the control formula. In turns, the plant heigh increase 18.63- 26, 27%, the leaf area increase 56,62- 62,53%

This can be explained in CT2 and CT3 by the addition amount of swelling polymer, which is capable of good moisture retention, providing adequate moisture for seed germination. This is shown by analyzing the water content in the potting media and the water concentration in leaf.

Although CT2, and CT3 had an irrigation water content of 20% lower than CT1, the water content in potting media was always higher than 152.51% (CT2) and 185.49% (CT3) compared to CT1. And water content in the leaf remained stable at 93.03-93.35% in accordance with Ministry of Health – Institute of Nutrition studies [10]

In addition, the swelling polymer is made from rice husk, this material provides a large of organic components, micronutrients in the rice husks, increasing the organic nutrients content, then that make the plants development better. This product has been researched and tested by author and partners. It has good results. Nguyen

the Hung shows that potting media has 25% moisturizing agent by volume which is suitable for spinach and the potting media has 20% moisturizing agent by volume which is suitable for celery [11]. Nguyen Thi Hong Hanh experimented in mustard green, the results show that the treatment with additional 5% of moisturizing polymer by weight that has the rate of germination 91.11%, more than 13.7% compare with the control treatment and the yield reached were about 61.41 g/plant. It was larger than the control treatment were 33.01 g/plant [12]

Survey the water retention capacity on conditional lack of water (Fig.9) The result show that: In CT1- the control media, without swelling polymer, water content in the tree decreases from 98.42% at 0 day to 37.26% at 7 days and 22.18% at 14 days stopped watering. In the CT2 and CT3, with present of the swelling polymer, water content in the tree decreases slowly. This swelling polymer can be retain water and release them for tree to used so that can maintained at over 80% after 14 days stopped irrigation

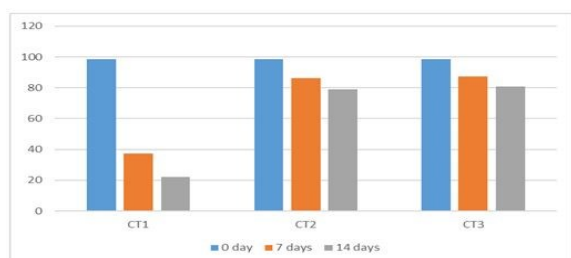


Fig. 9. The amount of water content in the tree after 0 day, 7 days and 14 days stopped watering

#### IV. CONCLUSIONS

The swelling polymers was synthesized from cellulose by the graft reaction of acrylic acid onto the cellulose chains. Some physical methods (IR, XRD, SEM, EDX...) were used to determine the structure of the products, that indicated the graft reaction was occurred. The products have high swelling, about 250 gram per gram polymer in distilled water and they swell well in acidic and basic solutions from pH = 3-11. Within the pH = 6-10 range, the swelling of polymers is stable, so that, the swelling polymer can be used for all acid and alkaline soils. The results of experimental on mustard green, this swelling polymer can make the rate of seed germination increased 11.94-16.56%, the plant height increase 18.63- 26.27%, the leaf area increase 56.62- 62.53% compare with the control treatment. This swelling polymer is capable of maintaining moisture for trees under conditions of lack of water.

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