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Radiation Graft Copolymerization of Rice Straw Cellulose-Acrylamide Monomer for Synthesis of Hydrogel and its Application for Chili

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Abstract: ***Agricultural productivity in Myanmar, comparing with other South East Asia countries, is considerably low because local agricultural systems still follow the traditional methods that utilise the available natural resources combined with improved cultural practices. To fulfil the major needs for improvement in agricultural productivity and to recycle the abundant agricultural wastes into useful products, current research is based on modification of rice straw cellulose through radiation copolymerization with acrylamide monomer for synthesis of hydrogel and to study its application for chili planting. Rice straw cellulose was prepared by soda process. Monomer concentration was varied from 1M up to 2M, and various radiation doses (10, 20, 30, 40, 50 kGy) were applied for graft copolymerization. Morphological structures of cellulose and grafted copolymer were analysed by Scanning Electron Microscope (SEM). Fourier Transfer Infrared (FTIR) was used to analyse the original cellulose and grafted copolymer. The effect of radiation dose and monomer concentration on grafting efficiency and swelling degree, and effect of hydrogel on plant growth were studied. Chili (Capsicum annuum L.) was used as cultivar for hydrogel application. Hydrogel obtained at 20 kGy using 1.5M of monomer concentration was found to be the optimum condition for growth of chili.***

Keywords: Rice straw cellulose, Radiation Copolymerization, Hydrogel, Chili

1. Introduction

There are three main soil groups which are agriculturally important in Myanmar. They are Alluvial, with 50% of total sown area, that are mostly found in river basin and delta regions, Black Soil, with 30% of total sown area, that can be found in dry regions, and Red Laterite, with 20% of total sown area, that are found in lower Myanmar associated with undulating topography [1]. Although Myanmar is an agricultural based country with 12 million hectares agricultural land, agricultural productivity is low compared with other South-East-Asia countries. It may be because present agricultural systems in Myanmar still follow the traditional methods that utilise the available natural resources combined with improved cultural practices [2]. In dry zone regions that are resource-poor areas, are suffering from scarcity of water because of low annual rainfall and thin vegetation cover. Also, in undulating land, composed mainly of clay and sandy loams, natural fertility is low [1]. Therefore improvement in utilization of water resources and nutritive fertilizers become important factors in the country. Studies show that about 40% to 70% of nitrogen and nitrogen compounds loaded in fertiliser cannot be absorbed by plant's root and are permeated into the environment [3]-[4]. One early approach to increase the fertilizer effectiveness and efficiency is modification of the product into slow-release fertilizer (SRF) form. As the rate, the pattern and the duration of release in SRF system cannot be controlled well, another effort is on the synthesis of controlled release fertilizer (CRF) based on coated or encapsulation fertilizer such as resin, rubber, formaldehyde and sulphur. But one problem is the higher cost of producing coated or encapsulated fertilizers compared with that of conventional fertilizers. These situations are a force led to applications of hydrogel-type controlled release fertilizers.

Hydrogels are three-dimensional cross-linked networks and they can be used in many kinds of applications including biotechnology, biomedicine, pharmaceutical, veterinary, agriculture and other fields. If they are used as a controlled release system, the lost amount of ingredients in fertiliser by permeation to the environment can be controlled by changing the network structure in them. There are also advantages of using hydrogels in CRF such as increment in fertiliser efficiency, reduction of soil toxicity, and enhancement in soil condition. Natural biopolymer such as cellulose, chitin, chitosan and starch are good precursors in hydrogel preparation for they are nontoxic, biodegradable, renewable and abundant in nature. Among these, cellulose extracted from rice straw is more favorable because of its great cross-linking ability in the presence of abundant hydroxyl (OH) groups [4].

Radiation grafting is one of the most favourable methods among different methodologies for graft copolymerization such as chemical, photochemical and high energy radiation initiation techniques. For it can enable easy handling at room temperature, provides large penetration in polymer matrix, gives the formation for initiating grafting rapidly and uniformly, and needs no further chemical initiation. As befitting one of the largest rice-producing countries in the world, rice straw is the most abundant waste in Myanmar. Major food crops grown in Myanmar are potato, onion, chillies, vegetables, and spices [2]. Among them chili (Capsicum annuum L.) is one of the most widely cultivated crops throughout the year in both dry and wet seasons in Myanmar. In this study, chili was used as cultivar for the application of radiation grafted hydrogel. Hydrogel was used to enhance soil water retention for the better growth performance in chili. The main aim of this research is to fulfil the major needs for improving agricultural productivity in the country and to recycle the abundant agricultural wastes into useful products by applying peaceful use of nuclear techniques for development in productive, profitable, and sustainable agricultural systems without the use of costly hazardous synthetic agricultural chemicals.

2. Materials and Methods

2.1 Materials

Rice straw was collected from rice fields in Pa Thein Gyi, Mandalay Region, Myanmar. Acrylamide monomer (analar grade), sodium hydroxide (flake type), acetic acid, ethanol, and bleaching powder were used.

2.2 Preparation of cellulose pulp from rice straw

Chaff and impurities were primarily cleaned and the straw was ground to get about 60 mesh particle sizes. The grounded straw powder was soaked in water for about 6 to 8 hours in order to remove water-soluble dirt and impurities. Cellulose pulp was made by soda process [5].

2.3 Graft copolymerization of cellulose-acrylamide using gamma radiation

Cellulose was mixed with distilled water and stirred at 400 rpm at room temperature for one hour. Different concentrations of acrylamide monomer (1M, 1.5M, and 2M) were prepared and added to the cellulose mixture. The mixture was stirred about 30 minutes to get homogeneous solution. 350 cm^3 containers were used for the mixed samples to be irradiated. Graft copolymerization of cellulose-acrylamide monomer was carried out using Gamma Chamber (Cobalt-60, GC-5000) with various radiation doses (10, 20, 30, 40, 50 kGy).

2.4 Application of hydrogel for chili plants

Chili (capsicum annuum L.), one of the major food crops in Myanmar, was used as cultivar for the application of radiation grafted hydrogel. Water retention in soil with and without radiation grafted hydrogel was studied and comparison between early plant growth performances were carried out using polyethylene bags under environmental conditions. The radiation grafted hydrogel was also applied as soil conditioner to enhance soil water retention for better growth performance in chili.

3. Analytical Methods

3.1 Scanning electron microscope (SEM)

Scanning electron microscope was used to study the morphological structures of cellulose and grafted copolymer by detecting qualitatively the presence of connected micro porosity.

3.2 Determination of grafting efficiency

Cellulose-acrylamide graft copolymers were washed with deionised water and separated. The product was dewatered with ethanol and dried in oven at 65°C for 24 hours. Grafting efficiency (GE) was determined by the following equation.

$$GE = \frac{W_h - W_s}{W_m} \times 100\% \qquad (1)$$

W_h is weight of cellulose-acrylamide graft copolymer, W_s is weight of cellulose, and W_m is weight of acrylamide monomer.

3.3 Determination of swelling degree

Hydrogel is firstly immersed in deionised water for 48 hours at room temperature. After swelling, the copolymerized hydrogel is filtered and the swelling degree (SD) of the product is calculated by the following equation.

$$SD = \frac{W_{ss} - W_d}{W_d} \times 100\% \qquad (2)$$

W_{ss} is weight of hydrogel in swollen state and W_d is weight of dried hydrogel [6]-[7].

3.4 Fourier transformed infrared spectroscopy (FTIR)

The FTIR spectrum was used to identify functional group of the active components based on the peak value in the region of infrared radiation. The FTIR spectra of the original rice straw cellulose and grafted cellulose-acrylamide copolymer were recorded by FTIR spectrophotometer (IR-Prestige-21, Shimadzu, Japan) in the wave number range 550-4000 cm^{-1}. The FTIR spectrum was taken in transmittance mode.

3.5 Water retention test for hydrogel

The soils used were firstly dried in oven for 2 days at 60°C to remove moisture form soil. The radiation grafted hydrogel was mixed in container with 200 g of soil. The mixture was irrigated with the proper amount of water (100 ml), and the container was weighed at different set intervals. This measurement was carried out at room temperature. The weight loss of the mixtures against time was calculated at interval time and the water retention capacity of hydrogel was obtained. Controlled experiment without hydrogel was also performed as reference. Water retention percentage of soil treated with hydrogel was determined as the following equation.

$$WR(\%) = \frac{M_t - M_i}{M_i} \times 100\% \qquad (3)$$

Where, M_i is the initial weight of mixture, and M_t is the weight of mixture at certain interval time.

3.6 Plant growth performance

For this experiment, equal amount of soil was placed in bags, and two types of bags were set; the one without the addition of hydrogel and the one that contained radiation grafted hydrogel obtained using 20 kGy and 1.5M of monomer concentration. The hydrogel was mixed thoroughly with soil in bags. Equal amounts of chili plant seeds were placed in all bags and were exposed to environmental condition. Water irrigation remained constant at starting day for all the bags.

The growth patterns of both types of plants were observed at different time intervals and the average of plant height was determined.

4. Results and Discussions

4.1 Scanning electron microscopes of rice straw cellulose and grafted copolymer

The morphology of rice straw cellulose and grafted copolymer hydrogel were examined by means of scanning electron microscope (SEM) with the aim of detecting qualitatively the presence of connected micro porosity. According to the figures, it can be seen that interconnected micro porosity seems to be present after irradiation grafting of acrylamide monomer onto the cellulose backbone. Interconnected pores provided more available regions for the diffusion of water molecules, and thus, the hydrogel may demonstrate a higher water absorption capacity. The scanning electron microscopes of rice straw cellulose and radiation grafted copolymer are shown in the following figures.

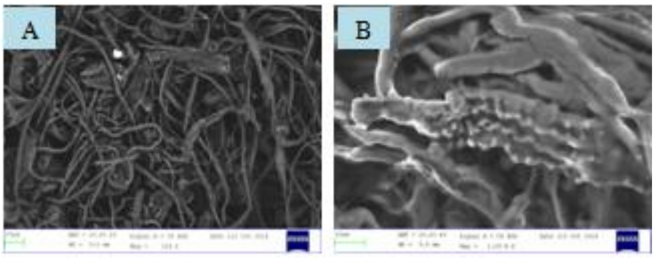

Figure 1: SEM pictures of (A) original rice straw cellulose, (B) cellulose-acrylamide grafted copolymer

4.2 Effect of radiation doses on grafting efficiency and swelling degree

The grafting efficiency and swelling degree were investigated with different irradiation doses (10, 20, 30, 40, 50 kGy) by using a fixed monomer concentration as shown in Table 1.

Table 1: Effect of radiation dose on grafting efficiency and swelling degree

Radiation doses (kGy)	*Grafting efficiency (%)*	*Swelling degree (%)*
10	90.815	834.45
20	91.220	950.50
30	91.539	725.33
40	91.694	760.85
50	92.034	742.92

In Table 1, it can be seen that the grafting efficiency increased with increasing radiation dose. An increase in the radiation dose enhances the formation of radicals in the reaction mixture of acrylamide monomer, cellulose, and water. The higher radiation dose can induce enough active grafting sites on the cellulose backbone for the grafting of monomer. Therefore increasing the total dose reduces the homopolymer content and increases the grafting efficiency. It was also found that the swelling of hydrogel increased with increased radiation dose from 10 to 20 kGy. However, the swelling degree decreased by increasing radiation dose from 20 to 30 kGy. These could be explained that the increasing radiation dose enhances the number of free radicals on the cellulose chain and, therefore, form more cross-linking between cellulose chains. Higher in crosslink density reduces the free volume available for swelling by increasing the tightness of the network structure [3].

4.3 Effect of monomer concentration on grafting efficiency and swelling degree

The effect of acrylamide monomer concentration on the grafting efficiency and swelling degree was investigated at 20 kGy of gamma radiation dose and the results are shown in Table 2.

Table 2: Effect of monomer concentration on grafting efficiency and swelling degree

Concentration (M)	*Grafting efficiency (%)*	*Swelling degree (%)*
1	90.179	1030.59
1.5	90.850	1008.35
2	91.220	950.50

The results show that the grafting efficiency increased with the increasing monomer concentration from 1M up to 2M. This behaviour can be attributed to the increase of monomer concentration in the surrounding of cellulose backbone and it can enhance chances for molecular collisions of the reactants [3]. It can also be seen that, at higher concentration of monomer, the free radicals come closer than lower concentration of monomer and that tends to form more cross-links in the cellulose chains. Therefore, with increased cross-link density, swelling degree decreased due to reduced vacant space of network for free solvent to enter into it.

4.4 Characterization of rice straw cellulose and grafted copolymers using Fourier Transformed Infrared spectroscopy (FTIR)

The FTIR spectrum of the original cellulose of rice straw is shown in Figure 2 and the spectrum of radiation grafted copolymer is presented in Figure 3. In FTIR studies, the mid-infrared spectrum (4000-400 cm^{-1}) can be approximately divided into four regions; X-H stretching region (4000-2500 cm^{-1}), the triple-bond region (2500-2000 cm^{-1}), the double-bone region (2000-1500 cm^{-1}), and the fingerprint region (1500-600 cm^{-1}) [8]. Fundamental vibrations in the 4000-2500 cm^{-1} region are due to O-H, C-H and N-H stretching. O-H stretching produces a broader band and N-H stretching is usually observed between 3400 and 3300 cm^{-1} [8].

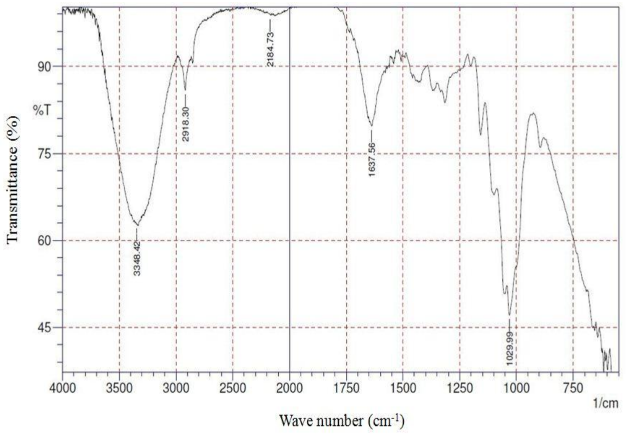

Figure 2: The FTIR spectra (4000-550 cm^{-1}) of the original rice straw cellulose

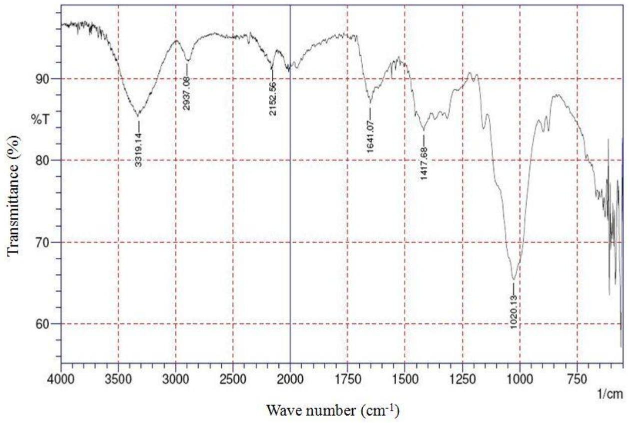

Figure 3: The FTIR spectra (400-550 cm^{-1}) of radiation grafted copolymer

According to the results of FTIR spectroscopy, spectra of both rice straw cellulose and grafted cellulose showed nearly the same profile. However, the intensities of the absorption bands were different. In Figure 2, the absorption peak at 3348.4 cm^{-1} is assigned to the stretching of –OH groups, which was diminished after graft-copolymerization. It can be explained that the partial hydrogen bone of cellulose was destroyed enhancing the new formation of cross-links with acrylamide monomer. The changed spectra can be seen with the peaks at 3319.14 cm^{-1} in Figure 3. These bands indicated the N-H stretching of the amide bands, which are characteristics of the –CONH$_2$ group present in the acrylamide monomer [9]-[3]. The another obvious characteristic of the grafted cellulose spectrum which is distinguished from the spectrum of the original cellulose in Figure 2 (2184.73 cm^{-1}) was the sharp presence of absorption bands at 2152.56 cm^{-1} in Figure 3, which indicated the presence of amide secondary amine group [9]-[3]. These changes provided strong evidence of the grafting of acrylamide monomer onto cellulose. The absorption bands at 1637.56 cm^{-1} in original cellulose and 1641.07 cm^{-1} in grafted copolymer are assigned to the functional group that is present in the lignin. The presence of spectral bands in the range of 1000-1500 cm^{-1} indicated the characteristic of aloxy group of cellulose. The bands observed in the finger print region at 1020.13 cm^{-1} in Figure 3 are typically related to the structural characteristics of cellulose and hemicelluloses.

4.5 Water retention in soil

Water retention test in soils with and without the addition of radiation grafted hydrogel was carried out under room temperature and results are shown in Figure 4. It can be clearly seen that water retention in soil decreased as the time was prolonged, and the soil containing hydrogel possess higher water retention over controlled one. This result indicates that the radiation grafted hydrogel can enhance the water retention capacity in soil, and they can be applied in dry fiends as water-managing materials to transformed dry area into green and fertile land.

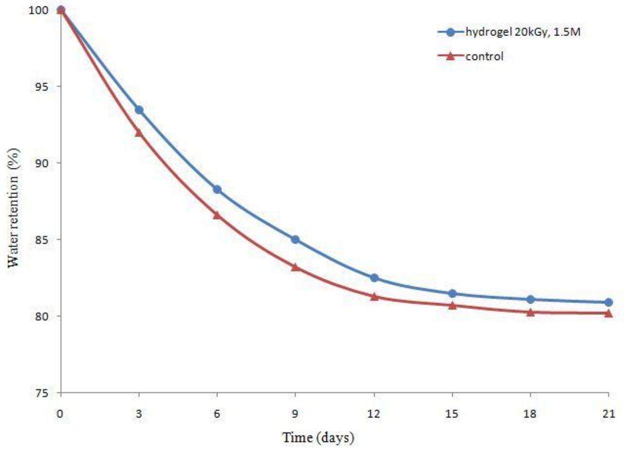

Figure 4: Water retention test in soil for radiation grafted hydrogel

4.6 Effect of hydrogel on plant growth

Seed germination and seedling development are the critical phases in an early growth and establishment of any plants. The successful establishment of agricultural crops are depends on the moisture available in the soil but poor soil moisture level could restricted the growth, particularly in arid and semi-arid environments [10]-[11]. From an economic point of view, agricultural hydrogels should be evaluated through the growth of the plants in height, and the results are shown in Table 3 and Figure 5.

Table 3: Comparison of plant height between hydrogel treatment and control soil

Cultivation period	*Average plant height (cm) (hydrogel treatment)*	*Average plant height (cm)(Controlled)*
Week 6	10.5	5
Week 12	80.2	55.8

Figure 5: The growth difference (week 6) of chili plants in (A) without hydrogel, (B) with hydrogel, and (C) growth difference in week 12

5. Conclusion

Comparison of the morphological structures of rice straw cellulose and radiation grafted copolymer hydrogel showed that cellulose and acrylamide monomer were well grafted after gamma irradiation. Therefore rice straw cellulose was modified by using radiation grafting technique. FTIR analysis also showed that acrylamide had been grafted onto cellulose. The higher the radiation dose the higher the grafting efficiency of cellulose-acrylamide hydrogel. However, swelling degree was found to have different characteristics with radiation doses. The increasing of acrylamide monomer concentration increased the grafting efficiency but decreased the swelling degree. The radiation grafted copolymer hydrogel showed considerably good swelling behaviour and it was tested on chili plants. Based on water retention test, it was found that radiation grafted hydrogel has good water retention ability which promotes the plant performance and delaying the wilting time. The addition of radiation grafted hydrogel as water absorbent and soil conditioner reduced in irrigation requirement, longer plant survival and increased the probability for plant's growth by retaining and supplying the soil with water. The radiation grafted hydrogel found applicable in agricultural, especially in drought prone areas or water stress condition where the availability of water is less.

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