การใช้รังสีเหนี่ยวนำให้เกิดปฏิกิริยากราฟต์พอลิเมอไรเซชันของกรดอะคริลิกบนแป้งมันสำปะหลังเพื่อสังเคราะห์พอลิเมอร์ที่มีความสามารถในการดูดซึมสูง

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บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์ที่จะสังเคราะห์พอลิเมอร์ที่มีความสามารถในการดูดซึมสูง โดยใช้รังสีเหนี่ยวนำให้เกิดปฏิกิริยากราฟต์พอลิเมอไรเซชันของกรดอะคริลิกบนแป้งมันสำปะหลัง โดยศึกษาปัจจัยสำคัญสำหรับการสังเคราะห์โคพอลิเมอร์ เช่น ปริมาณรังสี และปริมาณมอโนเมอร์ เพื่อหาสภาวะที่เหมาะสมสำหรับปฏิกิริยากราฟต์พอลิเมอไรเซชันที่ให้ค่าการดูดซึมน้ำสูงสุด นอกจากนี้ได้ทำการวิเคราะห์หา water retention, germination percentage และ germination energy เพื่อประเมินความเป็นไปได้ สำหรับการนำพอลิเมอร์ที่มีความสามารถในการดูดซึมสูงไปประยุกต์ใช้ในทางเกษตรกรรม โดยเฉพาะอย่างยิ่งในพื้นที่แห้งแล้ง ได้ทำการวิเคราะห์ลักษณะสมบัติของกราฟต์โคพอลิเมอร์โดย FTIR ผลการทดลองพบว่าทรายที่ผสมกราฟต์โคพอลิเมอร์ร้อยละ 0.1 โดยน้ำหนักสามารถดูดซับน้ำได้มากกว่าทรายที่ไม่ผสมกราฟต์โคพอลิเมอร์ ผลการทดลองแสดงให้เห็นว่าพอลิเมอร์ที่มีความสามารถในการดูดซึมสูง มีผลอย่างมากต่อการงอกของเมล็ดและการเจริญเติบโตของต้นอ่อน

คำสำคัญ : พอลิเมอร์ดูดซึมมาก รังสี กรดอะคริลิก แป้งมันสำปะหลัง

Superabsorbent Prepared by Radiation Induced Graft Copolymerziation of Acrylic Acid onto Cassava Starch

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Abstract

Superabsorbent was synthesized by radiation-induced graft polymerization of acrylic acid onto cassava starch. Parameters such as the absorbed dose and the amount of monomer were investigated in order to determine the optimum conditions for the grafting polymerization. Water retention, germination percentage and germination energy were determined in order to evaluate the possibility of superabsorbent in agricultural applications, especially in arid regions. The graft copolymer was characterized by FTIR. Results indicated that the sand mixed with 0.1%wt superabsorbent can absorb more water than the sand without superabsorbent. The germination energy of corn seeds mixed with 0.5% superabsorbent was obviously higher than those without superabsorbent. These experimental results showed that the superabsorbent has considerable effect on seed germination and the growth of young plants.

Keywords: Superabsorbent, Radiation, Acrylic acid, Cassava starch

1. Introduction

The northeastern part of Thailand is the largest region of the country covering about 170,000 square kilometers, which is one-third of the country. The rainfall characteristics in this area are dominated by the southwest monsoon from the Indian Ocean and tropical cyclones from the South China Sea. This zone suffers from quite a large number of drought days, and more importantly, the rainfall is highly irregular. The water holding capacity of soils in the Northeast is generally low because of poor level of organic matter and clay contents. Erratic rainfall and low water holding capacity of soils often create water stress, affecting the stability of rice production as well as other crops. The low fertility of the soils generally results in low crop productivity while the erratic rainfall leads to the instability of rice fields.

The application of superabsorbent polymers to agricultural development especially in the arid rural areas where water is scarcely available has provided a very strong impact on the socioeconomic revolution. In fact, the physical properties of such superabsorbents are indeed very attractive to farmers and reforesters. When sufficient water is in contact with the superabsorbent granules, they transform themselves into water-laden gel chunks. These gels then act as a local reservoir, releasing water vapor into soil and plants as needed and also maintain moisture at balance. In addition, these superabsorbents also prevent the leaching of nutrients as well as generate more nutrients within the soil to seeds, which allows faster germination, promotes earlier emergence, improves stand and gives a greater crop yield.

Natural polymers such as starches, cellulose, chitin and chitosan are natural materials with high potential for various applications from medical to environmental and agricultural due to their unique properties, especially biodegradability and biocompatibility. Thailand ranks ninth in the world's producer of cassava starch roots and it's the world's largest exporter of cassava products.

The production of cassava starch often exceeds the export and consumption scale which results in Thailand's surplus of unused cassava starch. The development of superabsorbent by radiation processing is therefore a promising method to increase the values of cassava starch which is abundant and inexpensive. The use of this natural polymer as a superabsorbent can definitely alleviate the lack of water in the arid rural areas of Thailand and also decreases the import of expensive synthetic superabsorbent from foreign countries.

Radiation processing has been widely utilized to synthesize a large number of new materials. This is simply due to the fact that radiation processing is convenient, environmental-friendly, effective, able to initiate reactions at ambient temperature, easier to control compared with chemical processes and requires no initiators. It has been proven that radiation processing can also be utilized for the synthesis of superabsorbents.[1-4]

This research project aims to apply the use of radiation processing to synthesize superabsorbent. The superabsorbent will be synthesized from poly acrylic acid-grafted cassava starch. Various factors will be investigated in order to determine the optimum conditions for the grafting polymerization. The criteria are emphasized by the optimum conditions of important parameters to give a maximum amount of water absorption.

2. Experiments

Cassava starch containing 12.8% moisture was supplied by Siam Quality Starch Co. Ltd., Thailand. Acrylic acid (AA) of 99% purity from Aldrich was used without further purification. Methanol, a commercial grade from BDH, was fractionally distilled. In a gelatinization reactor, 10 g of cassava starch was mixed with 190 ml of distilled water. The mixture was continuously stirred at 450 rpm using a mechanical stirrer under nitrogen atmosphere. The mixture was gradually heated from ambient temperature to 80^{o}C and held at this temperature for one hour. The mixture was left to cool down to room temperature to yield the gelatinized starch. The obtained gelatinized cassava starch was mixed with acrylic acid monomer. The mixture was stirred under nitrogen atmosphere at room temperature for 30 min to form a homogeneous mixture. The gelatinized starch-acrylic acid mixture was transferred into glass bottle and purged with nitrogen gas for 5 min. Then, it was irradiated under gamma ray from Co-60, Gamma Chamber 5000 of 14,000 curies from Department of Atomic Energy, Government of India, Mumbai. After irradiation, the mixture turned into a gel.

Finally, the gel was dried in vacuum oven at 50°C for 24 h. The crude product was weighed and extracted with methanol in a Soxhlet extractor for 24 h to remove poly(acrylic acid) (PAA) homopolymer. Then, pure copolymer was dried in a vacuum oven at 50°C for 24 h.

Homopolymer percentage was determined. The gel samples were immersed directly in distilled water for 72 hours at ambient temperature to reach the equilibrium state of swelling. The weight of the swollen gel (W_s) was then measured. The swollen gels were later dried at 50°C until the weight of the dried gels (W_d) remained constant. Equilibrium Degree of Swelling (EDS) was identified. The degree of grafting was determined by the percentage increase in weight. The dried superabsorbent with particle diameters between 0.7 and 0.3 mm was left to swell in distilled water for some time and then, the swollen superabsorbent was weight after removal of excess water. The percentage of water absorption at the certain time was calculated. Water retention was calculated from the following method. A 500 g of dry sand mixed with 0.5 g superabsorbent was placed in a container, and the other 500 g sand without superabsorbent was place in an identical container. One litter of water was added into both containers, and then the containers were kept under identical conditions at room temperature (about 30 ± 3°C) for 15 days. The initial mass of the mixture in the two containers were measured after removal of excess water and their masses were recorded daily to compare the water retention of superabsorbent. Water retention was then evaluated. Germination percentage of the seeds was also calculated. The same amount of soil with 15% moisture was placed into two identical baskets (30 x 25 x 12 cm). The depths of the soil were 10 cm. One basket was irrigated with 1500 ml of water, while the other was irrigated with 1500 ml water mixed with 10 g superabsorbent. The same amount of healthy corn seeds was placed in each basket. Germination percentages were calculated to testify that the seed qualities of two samples are identical and germination energies were determined to compare the effect of the superabsorbent on seeds germination. Germination percentage of the seeds was then analyzed. Infrared spectra were taken from a Bruker Tensor 27 FTIR spectrophotometer equipped with an attenuated total reflection (ATR) accessory. The scanning used was 16 times at a resolution of 4 cm^{-1}.

3. Results and Discussions

The FTIR spectra of cassava starch grafted PAA and cassava starch are shown in Fig. 1. The FTIR spectrum of cassava starch shows the characteristic absorption bands of starch at 3300 and 1650 cm^{-1} due to O-H stretching and bending modes, respectively. Additional characteristic absorption bands of cassava starch appear at 2916, 1150 and 1016 cm^{-1} due to C-H stretching, tertiary C-OH, and C-H bending, respectively .While that of cassava starch grafted PAA shows similar pattern with an extra band at 1730 cm^{-1} attributed to –COOH group in the acrylic acid.

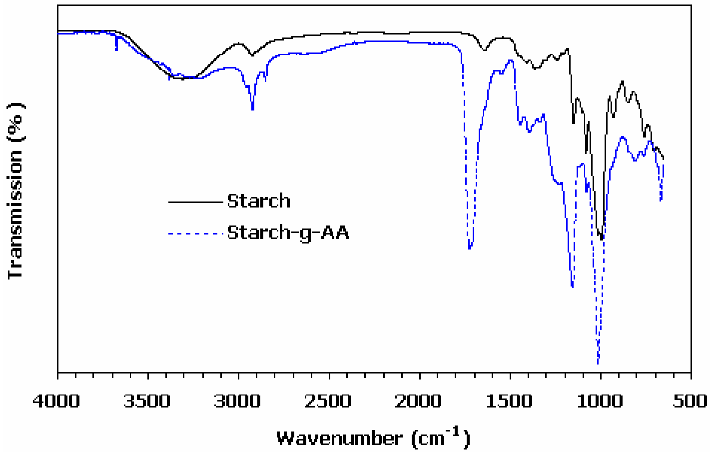

Fig. 1 FTIR spectra of starch grafted PAA and cassava starch.

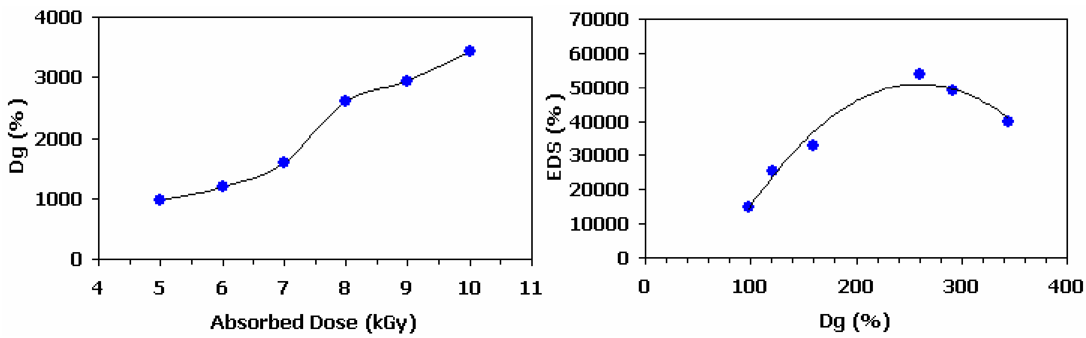

Fig. 2 Effect of total dose on degree of grafting

and effect of degree of grafting on equilibrium degree of swelling.

The effect of absorbed dose on the degree of grafting is shown in Fig. 2. The degree of grafting increased with increasing absorbed dose. An increase in dose enhances the formation of radicals, resulting in higher degree of grafting. There is a limited crosslinking density for the maximal EDS according to Flory's theory.[5] When the crosslinking density is less than the appropriate density, the EDS of superabsorbent increases as the degree of crosslinking increases. However, when the crosslinking is higher than the appropriate one, the EDS of superabsorbent decreases as the crosslinking density increases.[6] It can also be observed from Figure 2 that the effect of % Dg on % ESD of superabsorbent has the same trend as that of absorbed dose on % EDS of the superabsorbent, which is shown in Figure 3.

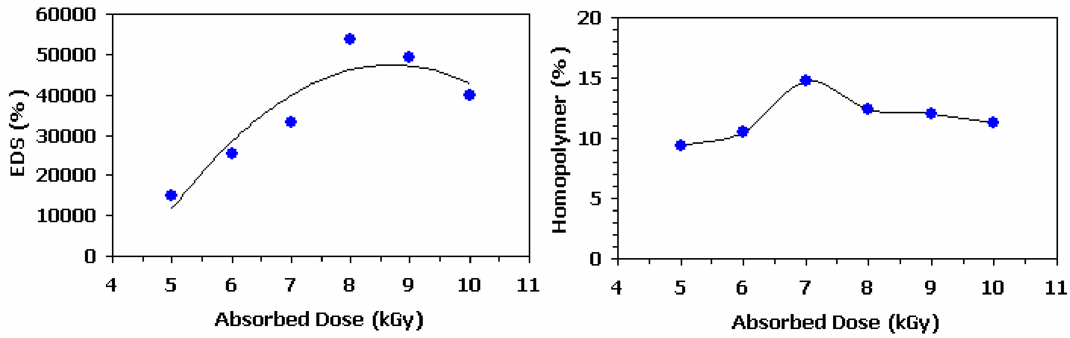

Fig. 3 Effect of absorbed dose on equilibrium degree of swelling

And effect of absorbed dose on % homopolymer.

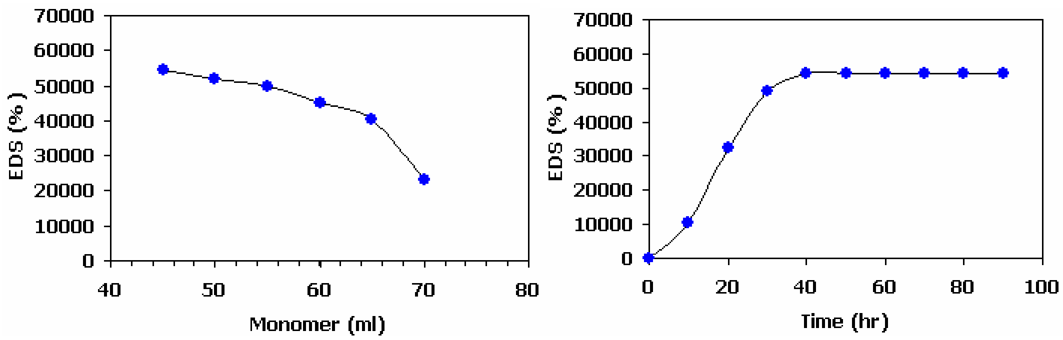

Fig. 4 Effect of the amount of monomer on equilibrium degree of swelling

and the swelling kinetics of superabsorbent.

From Fig. 3, it can be seen that % homopolymer increases with increasing absorbed dose up to 7 kGy, then decreases with increasing dose. At the absorbed higher than 7 kGy, % homopolymer decreases. This is due to the fact that high dose can induce ample active grafting sites on the cassava starch backbone for the grafting monomer. The effect of the amount of monomer on equilibrium degree of swelling is presented in Fig. 4. The equilibrium degree of swelling decreases with increasing the amount of monomer. This is due to the fact that the networks of the superabsorbent become denser with high monomer concentration, and therefore, would retain a lot of heat produced by polymerization. Hence, the temperature of the reaction system would increase and in turn accelerate the chain termination and transfer speeds. The high reaction temperature decreases the water absorbency of the superabsorbent[7]. Fig. 4 also shows the swelling kinetics of superabsorbent.

The equilibrium degree of swelling initially increases with time, but started to level off at 40 hr, indicating that the superabsorbent attained the equilibrium in 40 h.

The water retention of the sand mixed with superabsorbent, and the sand without superabsorbent were studied. The masses of two samples were compared within 15 days. The results were presented in Fig. 5. Initially, the sand mixed with 0.1 wt% superabsorbent can absorb more water than the sand without superabsorbent. After seven days the sand without superabsorbent had nearly given off all water, while the sand with 0.1% wt superabsorbent still retained 50 % water.

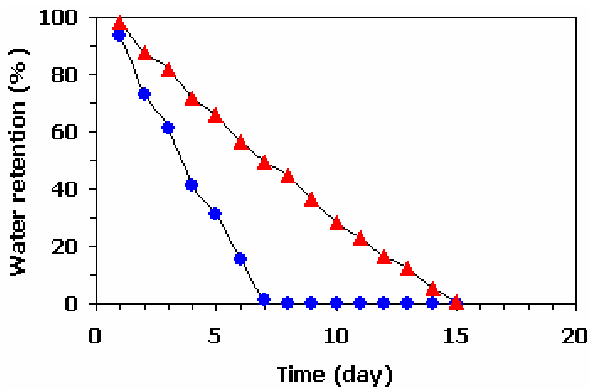

Fig. 5 Water retention of sand with (triangle) and without (circle) 0.1 wt% superabsorbent.

Table 1 Effect of superabsorbent on germination of corn seeds.

Superabsorbent content (%)	Germination percentage (%)	Germination energy (%)
0	63.0 $\pm$0.2	49.0 $\pm$0.1
0.5	98.0 $\pm$0.2	89.5 $\pm$0.1

The germination energy of the corn seeds with 0.5 wt% superabsorbent (Table 1) was obviously higher than that of the seeds without superabsorbent. This is attributed to the fact that superabsorbent can not only absorb large amount of water but also have good water retention capability, which supplies plentiful water to promote the seed growth. The germination percentage of seeds with 0.5 wt% superabsorbent was also higher than that of the seeds without superabsorbent. After 15 days, soil with 0.5 wt% superabsorbent showed a favorable effect on weights of leafages and roots of plants (Table 2).

Table 2 Effect of superabsorbent on growth of young corn plants.

Superabsorbent Content (%)	Plant Height (cm)	Leafage Weight (g)	Root Weight (g)
0	18.3 ± 0.1	5.5 ±0.1	1.2±0.1
0.5	27.5 ± 0.1	10.6 ±0.1	2.7 ±0.1

5. Conclusion

From the preliminary study, it can be concluded that the superabsorbent has potential for applications in agriculture, especially in arid regions. The experimental results showed that the superabsorbent may have considerable effect on seed germination and young plant growth.

6. References

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