

ผลของรังสีแกมมาที่มีต่อตัวแปรของการเกิดกราฟต์ในแป้งมันสำปะหลังที่กราฟต์ด้วยพีเอเอชเอ็นและสมบัติการดูดของเหลว

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บทคัดย่อ

การคัดแปรสมบัติการดูดของเหลวของแป้งมันสำปะหลังพื้นบ้าน โดยทำปฏิกิริยากราฟต์โคโพลีเมอร์เซชันของแป้งมันสำปะหลังที่เจลาทีไนซ์แล้วที่อุณหภูมิ 85°C. และอะคริไลโนคริลด้วยการฉายรังสีแกมมาพร้อมกัน ใช้เปลวโลหะอะลูมิเนียมคลุมผนังด้านในของขวดปฏิกิริยา สามารถลดปริมาณไฮโดรเจนที่ปนเปื้อนให้น้อยกว่าร้อยละ 1.8 และมีความสามารถดูดน้ำกลั่นได้สูงถึง 865 ก./ก. ของกราฟต์โคโพลีเมอร์แห้ง ยืนยันปฏิกิริยาที่เกิดทั้งกราฟต์โคโพลีเมอร์เซชันและแซฟฟอนิฟิเคชันได้ด้วยเทคนิคทางอินฟราเรดสเปกโทรโฟโตเมตรี ได้วิเคราะห์เชิงเคมีทางโพลีเมอร์และสถิติถึงผลร่วมของตัวแปรทางรังสี ในส่วนของเวลาการฉายรังสีที่มีต่อขอบเขตการเกิดกราฟต์โคโพลีเมอร์เซชัน และตัวแปรการเกิดกราฟต์ซึ่งมีอิทธิพลต่อสมบัติการดูดน้ำและของเหลว

EFFECT OF GAMMA RAYS ON GRAFTING PARAMETERS AND LIQUID RETENTION PROPERTY OF CASSAVA STARCH-*g*- PAN

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ABSTRACT

Radiation modification on liquid retention properties of native cassava starch, gelatinized at 85°C, by graft copolymerization with acrylonitrile was carried out by mutual irradiation to γ -rays. A thin aluminum foil was used to cover the inner wall of the reaction

vessel so that the extent of homopolymer could be reduced to be less than 1.6% with a distilled water retention value of 665 g/g of the dry weight of the saponified grafted product. Confirmations of graft copolymerization and saponification reactions were made by the Infrared spectrophotometric technique. The combined effect of radiation parameters in terms of an irradiation time and a dose rate to the same total dose on the extent of grafting reaction expressed in terms of grafting parameters which directly influenced liquid retention values was evaluated in conjunction with statistical analysis.

Key words : Radiation, γ -rays, graft copolymerization, cassava starch, acrylonitrile, PAN, liquid retention properties.

INTRODUCTION

In recent years, a considerable amount of research by polymer scientists has focused on the development of high-water absorbing polymers for their applications in agriculture, horticulture, arboriculture, personal uses and medical cares.

High-water absorbing polymers are types of materials that can absorb/retain liquid/fluid greater than 15 times its dry weight and that cannot release the retained liquid out in a liquid/fluid form, but only diffuse through the gel membrane. By such a definition, this type of material is, of course, suitable for a whole range of applications. The application of high-water absorbing polymers to an agricultural development especially in the arid rural areas when water is scarcely available should have provided a very strong impact on socio-economic revolution. In fact, the physical properties of these polymers should be indeed very attractive to concerned governmental sectors, farmers and reforesters. When sufficient water is in contact with the polymer granules, they immediately transform themselves into water-laden chunks. These gels behave then as a local reservoir, release water vapor into the soil and plants as needed and also maintain an even moisture balance. These materials improve the available water holding capacity by up to 50% and thus reduce water consumption in an ordinary way. Additionally, these polymers also prevent leaching of nutrients as well as generate more nutrients within the soil to seeds which make them germinate faster, emerge earlier, improve stand and yield more products. In a transplanting application, coatings of the polymer to bare roots of vegetables, trees, ornamentals, seedlings and so on, prior to transplanting, help prevent roots from drying and thus reduce wilting; prevent transplant shock, increase plant survivals by decreasing recovery time, and improve root developments.

High-water absorbing polymers can be derived from both starch and cellulose, which are bio-materials and bio-degradable with a relatively long life. They can be synthesized by graft copolymerization of a vinyl monomer onto a starch/cellulose backbone initiated either by certain redox metal ions such as salts of cerium (IV), manganese (III), or H_2O_2 -ascorbic acid; or

by radical initiators such as benzoyl peroxide; and by radiation. The most preferred radiation technique is by employing a Co^{60} source to produce γ -rays as an initiator. This technique is used in the current research work.

The Northeast of Thailand is the largest region of the country covering about 170,000 square kilometers which is one third of the country. Most soils in the Northeast are infertile because they produce low crop yields. Most importantly, the crop production is unstable due to an erratic nature of rainfall of the region. Geographically, one of the major shortcomings of the soils in the Northeast is a low-water holding capacity which is mainly due to low organic matter and clay contents. The most practical means to increase the water retention capacity is to add organic matter. However, in order to give plants nutrients as well as increase soil aeration and water absorption, the addition of a high-water absorbing polymer can be another alternative in developing the Northeast of Thailand.

Cassava is a native crop of Thailand, which ranks ninth among the world's producers of cassava roots and Thailand is the world's largest exporter of cassava products. Very often, there are country's cassava surplus which is a waste and is often destroyed to keep the stable pricing of the products. This research currently aims at developing a cheap and reliable process to produce a bio-degradable high-water absorbing polymer based on the native cassava starch; improving the graft copolymer yields by reducing the extent of the homopolymer through the use of radiation parameters in conjunction with grafting factors; and consequently evaluating water and liquid retention capacities of the polymer.

MATERIAL AND METHOD

Material

Cassava starch produced from tapioca cultivated in summer was donated by Thai Wah Co.,Ltd. It contains 12.8% moisture, 0.07% ash, 32.57 ppm SO_2 , a pH value of 5.80 and a viscosity value at 66-77°C of 780 BU. Acrylonitrile of at least 98% purity was provided by Siam Resin & Chemical Co., Ltd. It was purified by fractional distillation at atmospheric pressure through a 14-inch vigreax column and stored in the refrigerator under nitrogen gas. Methanol, a commercial grade from BDH, was also purified by fractional distillation at atmospheric pressure. Sodium-free potassium hydroxide, N,N'-dimethyl formamide, magnesium chloride hexa-hydrate and sodium chloride were all from Carlo, Erba, of an analytical grade.

Nicolet 5 DX Fourier Transform Infrared Spectrophotometer was used for recording infrared peaks of the products in KBr pellets. Energy Dispersive X-ray Fluorescence Spectrometer, Model EDXRF XR-200 was used for detecting elements by means of X-ray fluorometry, and Canon-Fenske viscometer No. 100 for viscosity-average molecular weight

determination. The radiation source is a dry system of Co^{60} , the Gammabeam 650 of 13,000 curies from the Atomic Energy of Canada Limited.

Method

1. Gelatinization of Cassava Starch

In a 1,000 cm^3 3-necked round bottom flask, 10 g of moisture free cassava starch was added and mixed with 200 cm^3 of triply distilled water. The paste was heated at around 85 ± 3 $^\circ\text{C}$ for one hour under nitrogen atmosphere and a stirring rate of 400 rpm to form a paste-like slurry which permitted a complete gelatinization to take place. The gelatinized starch was then cooled to about 35°C .

2. Graft Copolymerization of Acrylonitrile onto Cassava Starch

A thin aluminum foil weighed about 30.4 g was inserted into the reactor and wrapped around as an inner wall of the reactor.

5 cm^3 of acrylonitrile was added in the cooled gelatinized starch. The mixture was then stirred under de-oxygenated nitrogen atmosphere at room temperature for 20 minutes. The well-stirred mixture was subsequently subjected to γ -ray irradiation at a dose rate of 56.2 grays/minute to the total dose of 5.058 kilograys for one and a half hours at a pitch diameter of 32 cm. The reaction temperature was controlled at about 30°C by a water-bath circulation. A small portion of the irradiated product was investigated by X-ray fluorometry to check for the contamination of aluminum in the product.

3. Removal of Homopolymer

A hard gel-like paste was then ground to a powdery form with a grinder. It was then mixed with 450 cm^3 of DMF and was stirred for 24 hours. The supernatant was decanted and the paste was washed with 1:1 aqueous methanolic solution. The mixture was filtered and the methanolic solution was evaporated and dried at 65°C for 3 hours. The dried product was weighed to determine the amount of polyacrylonitrile. Both products were subjected to an IR spectrophotometer to check for the occurrence of homopolymerization at the wave number of $2,243 \text{ cm}^{-1}$ indicating the nitrile stretching group. In order to quantify the homopolymer formed, the subsequent extraction of homopolymer and the completion of saponification, an identical amount of this product (0.04 g) in a dry powdery form was mixed with 2.00 g of dry KBr, analar grade. Calibration of the spectrometer was held constant for all analyses.

Another duplicate experiment was carried out without an insertion of thin aluminum foil to wrap around the inner wall of the reaction vessel. All products obtained after graft copolymerization and DMF extraction were also subjected to an X-ray fluorometer.

4. Precipitation and Washing

The gel-like material was gradually formed during the irradiation. After the completion of irradiation, 250 cm³ of methanol was then poured onto the gel and stirred thoroughly to become slurry which was then left overnight. Filtration followed and the product was washed again thoroughly with another 250 cm³ of methanol. The graft copolymer was subsequently dried in a vacuum oven at 65°C for 8 hours. The dried sample was subsequently investigated by an infrared spectrophotometer.

5. Saponification

10 g of DMF-extracted product was added to 200 cm³ of an 8.5% KOH solution. The mixture was stirred continuously with a magnetic stirrer and the saponification was carried out at 85°C for 2 hours. A deep red solution developed and changed to light yellow at the later stage which indicated the completion of the saponification. The product was subsequently allowed to cool to room temperature to precipitate with methanol. It was then filtered and washed thoroughly with methanol until the pH 7 was reached. It was dried in the 65°C vacuum oven for 30 hours to remove any residual methanol. The dried product was ground to a powdery form. It was again subjected to IR analyses.

6. Characterization of Copolymer

The copolymer obtained above was normally characterized as for the magnitude of water absorption in triply distilled water. The grafting parameters involved were characterized in terms of percent add-on, viscosity-average molecular weight, percentage of homopolymer formation, grafting efficiency, grafting ratio, grafting frequency and percent conversion which were described elsewhere [1].

7. Water Absorption Capacity of the Graft Copolymer

0.2 g of the newly synthesized high-water absorbing polymer was immersed in 250 cm³ of triply-distilled water. After the polymer was fully swollen, another 50 cm³ of triply-distilled water was added. The polymer was left at room temperature for another 30 minutes to ensure complete absorption. The gel was filtered by using a 100-mesh aluminium

sieve, size 7.4 x 2 cm, until no more water drained off. The drained water was then weighed and the water absorption or water retention was computed using the following equation.

$$\text{Water retention} = \frac{300(\text{g}) - \text{weight of filtered water (g)}}{0.2 \text{ g of high-water absorbing polymer}} \quad (1)$$

8. Influential Parameters Affecting Radiation-induced Graft Copolymerization

Two parameters of importance were studied as follows:-

8.1 Total Irradiation Dose

A Fricke dosimeter was used to check the consistency of the absorbed dose of γ -rays on a scheduled basis. The experiment was carried out according to the method described above in 2, except that various total dose were regulated by the irradiation times as the following: 1/2, 3/4, 1.0, 1 1/4, 1 1/2, 1 3/4, 2.0 and 2 1/2 hours. Noted that the distance of the pitch diameter was 32 cm and dose rate at 56.2 grays-minute⁻¹.

8.2 Dose Rate

The experimental procedure was prepared and carried out as described above in 2 except that various dose rates were varied by the distances of pitch diameter as follows:- 25, 32, 40, 45, 50, 60, 70 and 80 cm which gave the following irradiation times (in hr:minsec) as the following : 0:28:50, 0:45:0, 1:1:05, 1:17:05, 1:35:25, 1:54:25, 2:14:30, 2:56:30, and 3:48:0 to the total dose rates of 11.09, 14.33, 18.80, 22.10, 26.50, 32.80, 41.40, 56.20 and 87.60 grays-min⁻¹. Noted that, all of these combinations gave a total dose of 2.529 kilograys.

RESULTS AND DISCUSSION

The current technique of radiation-induced graft copolymerization is the mutual or simultaneous irradiation which generally gives a substantial amount of homopolymer. After being subjected to the IR spectrophotometer, evidences of changes in the graft copolymerization of acrylonitrile onto cassava starch from cassava starch to the starch-g-PAN before and after DMF extractions, and after KOH saponification were illustrated in Figures 1-4. Besides the general peaks of the C-H stretching, there are a board and strong absorption band of free hydrogen-bonded and polymeric hydroxyl groups in the range of 3010-3600 cm⁻¹. Sharp absorption bands at 1650, 1170, 1080 and 990 cm⁻¹, assigned to be the -C-O- stretching of the chelated aldehyde group as in an enolic form, the anti-symmetric -C-O-C- stretching, -C-O- stretching and skeleton vibration, respectively, were the main frame of the products which indicate the characteristic bands of polysaccharide, and the existence of graft copolymerization. A strong asymmetrical stretching band at 1570 cm⁻¹, and a weak symmetrical stretching band at 1400 cm⁻¹ are for the carboxylate group, -COOK- and

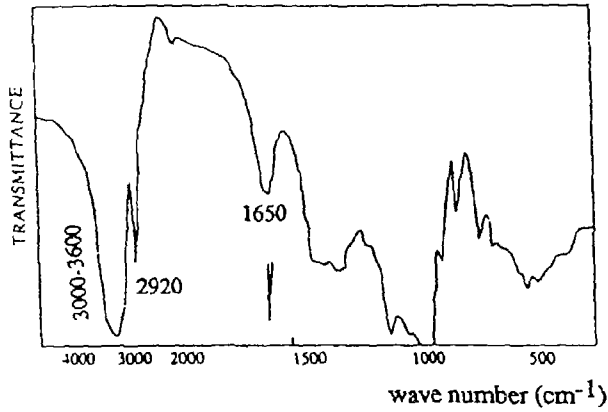


Figure 1 Infrared spectrum of native cassava starch

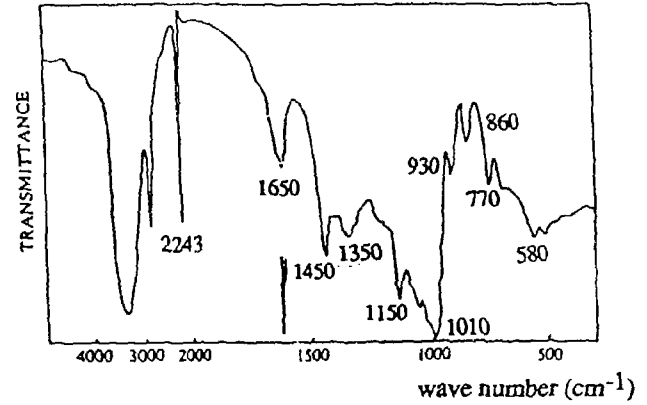


Figure 2 Infrared spectrum of cassava starch-g-PAN before DMF extraction

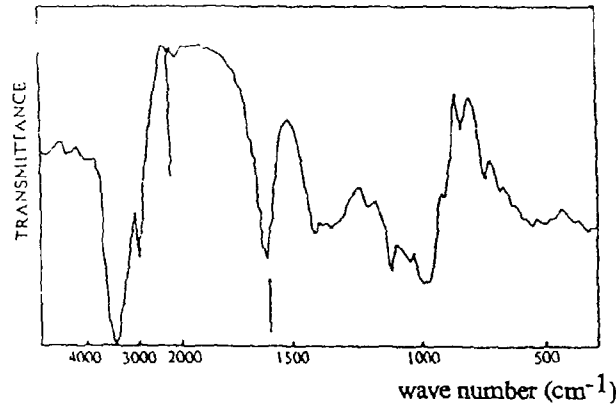


Figure 3 Infrared spectrum of cassava starch-g-PAN after DMF extraction

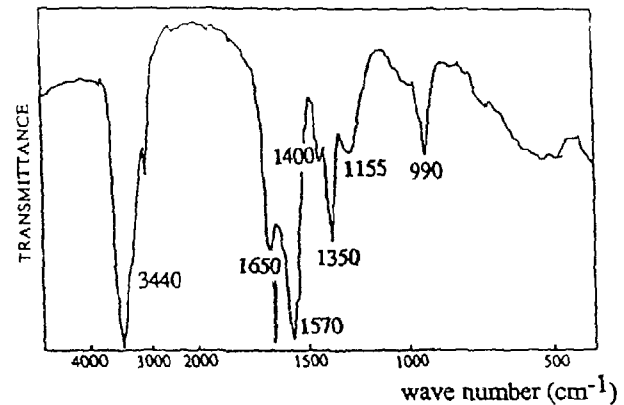


Figure 4 Infrared spectrum of cassava starch-g-PAN after KOH saponification

the carboxamide group, $-\text{CONH}_2-$, confirming the presences of both non-ionized and ionized carboxyl groups. The disappearance of the nitrile stretching peak is another indication of the conversion of the $-\text{C}\equiv\text{N}$ group into a mixture of carboxamide and carboxylate groups.

REDUCTION OF HOMOPOLYMER

It must be mentioned that the reaction temperature of these experiments was not controlled as it was just a preliminary test to envisage the effect of aluminium on homopolymer. Considering the extent of homopolymer, polyacrylonitrile, formed, it was found that the first experiment gave a 35% polyacrylonitrile content while the second one in which there was no insertion of aluminum foil gave 64%. This result indicates that aluminium can reduce the extent of homopolymer formation by a factor of 1.8. Additionally, there is no evidence of the contamination of aluminium ion from the foil to the product. The energy dispersive X-ray fluorescence spectrum does not indicate any peak of aluminium ion. It does also imply that the aluminium reactor may replace the normally used glass reactor. With a proper control of all reactions, it is expected the homopolymer can be reduced appreciably to less than 0.5%.

The ions of copper and iron were used as an electron transfer process from a propagation polymer to a d-orbit of the cation [2]. Consequently, the current result probably implies that the role of aluminium atoms on suppression of homopolymer formation of acrylonitrile is due to a redox reaction between the hydroxyl radicals and the aluminium or an electron transfer from the polymer growing chain to a p-orbital electron of the aluminium atom, thus reducing the chance of homopolymer formation.

General speaking, γ -rays produce active sites (free radicals) at the C-2 or C-3 hydroxyls of the fully swollen starch backbones. Grafting reaction emanates from these sites to which acrylonitrile molecules diffuse from the aqueous phase. Competitively, H^\bullet , OH^\bullet and e^-_{aq} from the aqueous phase can also initiate the homopolymerization

EFFECT OF TOTAL DOSE ON GRAFT COPOLYMERIZATION OF ACRYLONITRILE ONTO CASSAVA STARCH

The effects of total dose on grafting parameters and water retention of the saponified starch-g- PAN were depicted in Table I.

Homopolymer and Grafting Efficiency

Since γ -irradiation usually involves the generation of β -electrons from which dissociation, electron-capture, electron-ejection and excitation reactions occur. The resulting species can be both ions and free radicals. As water as the reaction medium and the reaction

temperature at $30\pm 10^\circ\text{C}$ certainly eliminate any participation of ions, it is only the free radicals initiating the reactions. As a general rule, $G(\text{AN}^\bullet)$ value of 5-5.6 and $G(\text{Amylose}^\bullet)$ value of 5-14, depending on water content, favor the grafting reaction of acrylonitrile onto the starch. At higher doses, $G(\text{H}^\bullet)$, $G(\text{OH}^\bullet)$, and $G(\text{e}^-_{\text{aq}})$ of 0.55, 2.8 and 2.7 at pH 4-7 can initiate homopolymer formation rather than grafting reaction [3]. The H^\bullet and OH^\bullet are the frequently chain transfer agents to polymer growing chains of both the starch $^\bullet$ and PAN $^\bullet$, the latter of which should graft onto the active sites of the starch backbones, but terminate the grafting reaction instead, as well as these H^\bullet and OH^\bullet terminate the active sites of starch backbones (starch $^\bullet$). The higher the homopolymer formation, the lesser the grafting efficiency. The height of the $-\text{C}\equiv\text{N}$ peak at 2243 cm^{-1} after DMF extraction indicates the grafting efficiency.

Table I

Effect of Total Dose on Graft Copolymerization of Acrylonitrile onto Cassava Starch

TD ^a (KGy)	HM ^b (%)	C ^c (%)	PAO ^d (%)	GR ^e (%)	GE ^f (%)	VMW ^g $\times 10^{-4}$	CF ^h (AGU /chain)	WR ⁱ (g/g)
1.686	12.3	51.7	19.8	24.7	58.1	8.00	2,004	88
2.529	3.4	58.0	28.9	40.6	89.1	7.07	1,075	235
3.372	18.4	73.0	27.4	37.8	55.5	6.83	1,115	164
4.215	22.9	75.1	26.0	39.2	46.7	6.74	1,183	150
5.058	26.1	76.2	22.6	29.1	38.9	6.56	1,390	145
5.901	33.8	85.8	19.7	24.5	30.9	6.37	1,603	117
6.744	39.3	90.6	18.2	22.3	21.9	6.03	1,673	90
8.430	42.0	90.9	14.1	16.4	16.3	5.83	2,194	83

^a total dose, ^b Homopolymer, ^c Conversion, ^d Percent add-on, ^e Grafting ratio, ^f Grafting efficiency, ^g Viscosity-average molecular weight, ^h Grafting frequency, ⁱ Water retention, noted that filtration of retained water was through a 100-mesh aluminum screen and the dose rate of $56.2\text{ grays}\cdot\text{min}^{-1}$.

Conversion

An increase in the total dose enhances the formation of radicals in the reaction mixture: monomer, starch and water. All molecules are activated to induce a higher conversion for both homopolymer formation and grafting reaction, nonetheless at a greater extent to the homopolymer formation at the disposal of graft copolymerization.

Percent Add-on and Percentage of Grafting Ratio

At the irradiation doses lower and higher than 2.529 KGy, percent add-on and percentage of grafting decrease. At the lower end of irradiation dose, fewer radicals emitted produce a small number of PAN growing chains to be grafted on a fewer active sites of the

starch, as there is not enough radicals to initiate ample active sites on the starch backbone. At the higher doses, the greater amount of polyacrylonitrile is formed as homopolymer at the expense of polyacrylonitrile which should otherwise be grafted to the starch backbone. For percent add-on and percentage of grafting ratio, they are in the same trend.

Viscosity Average Molecular Weight and Grafting Frequency

Increasing the total dose from 1.688 to 8.430 KGy, the molecular weight decreases gradually. Two main reactions can be elaborated on this result. The higher the irradiation dose, the more the free radicals are generated to produce a substantial number of short chains of polyacrylonitrile grafted on the starch backbones which result in the short grafts, and may give too high a grafting frequency and/or too high a homopolymer formation due to high collision frequencies. Additionally, the higher doses induce degradation of the starch backbone, resulting in several small molecules of different natures, a waste of the reactions.

In this respect, the lower the viscosity-average molecular weights, the shorter the grafted chain lengths. A relatively low grafting frequency gives a higher water-retention value due to its chain flexibility, as a result of the greater number of AGU units between two grafted chains of PAN.

STATISTICAL ANALYSIS OF CORRELATION BETWEEN THE EFFECT OF TOTAL DOSE ON GRAFTING PARAMETERS AND WATER RETENTION VALUE

An SPS program was employed to evaluate the correlation coefficient between grafting parameters and water retention value of the starch-g- PAN. The importance of each grafting parameter to water retention value is in the following order :- Percent add-on (0.90048), grafting ratio (0.87730), grafting efficiency (0.81596), homopolymer (0.72234), grafting frequency (-0.86184) .

It is then noteworthy that the first three parameters involve directly the nature of grafting reaction which governs the extent of water retention. The last two have a negative effect on water retention from which the percentage of homopolymer formation has a stronger impact, as its formation usually takes place at the expense of graft copolymerization. The higher grafting frequencies usually make the polymer to become constrained to absorb fluid. It is of much interest that conversion does not show much influence in water retention ($r = -0.458846$).

EFFECT OF TOTAL DOSE ON WATER RETENTION

Total dose has directly imposed a significant effect on grafting parameters as described above. High water retention values can be correlated to the lowest percentage of homopolymer, the higher values in grafting efficiency, percent add-on, and grafting ratio. High homopolymer formation and grafting frequencies decrease the water retention value significantly.

EFFECT OF DOSE RATE ON GRAFT COPOLYMERIZATION OF ACRYLONITRILE ONTO CASSAVA STARCH

The previous experiments suggested the appropriate total dose of 2.529 KGy which was used in this part of the work. To study the dose rate, a correlation between a pitch diameter and the dose rate was established in an exponential form. Table II shows the effect of dose rate on grafting parameters and a water retention value.

Table II

Effect of Dose Rate on Grafting Parameters and Water Retention Value

DR ^a (Gy/min)	HM ^b (%)	GE ^c (%)	GR ^d (%)	C ^e (%)	PAO ^f (%)	VMW ^g x 10 ⁻⁴	GF ^h (AGU /chain)	WR ⁱ (g/g)
11.09	0.5	98.8	72.6	82.0	40.1	14.04	1,302	368
14.33	0.5	98.7	64.7	79.8	39.3	13.23	1,262	398
18.80	0.8	97.9	63.9	78.4	39.0	12.06	1,165	445
22.10	1.3	97.3	63.0	76.1	38.6	11.45	1,122	369
26.50	1.8	95.3	59.0	71.2	37.1	9.97	1,043	339
32.60	2.1	94.3	57.5	70.6	36.5	9.85	1,057	318
41.10	2.2	92.7	41.8	58.1	34.2	9.08	1,078	312
56.20	3.4	89.1	40.6	58.0	28.9	7.07	1,075	235
87.60	7.7	74.8	33.7	18.3	28.0	6.96	1,102	175

^aDose rate, ^bHomopolymer, ^cGrafting Efficiency, ^dGrafting Ratio, ^eConversion, ^fPercent add-on, ^gViscosity-average molecular weight, ^hGrafting Frequency, ⁱWater Retention, and the total dose of 2.529 KGy.

Effect of Dose Rate on Percentages of Homopolymer Formation, Grafting Efficiency, and Conversion

A free radical is a molecular fragment with an unpaired electron. It is usually unstable and ready to combine to be a more stable species. When a dose rate of γ -rays is high, the

generation of free radicals is enormous accordingly. Recombinations of primary radicals into any inert species in the bulk medium are very significant. As a theoretical consequence, at a higher dose rate, there are a great deal of free radicals generated, yet there are only a few free radicals available to start the graft copolymerization. Most radicals undergo recombination, or they are trapped in solvent cages and initiate homopolymerization [4].

The lower dose rates which produce a smaller amount of homopolymer and a higher grafting efficiency may probably suggest a diffusion control mechanism of homopolymer formation as that only a few radicals produced can encounter each other to form homopolymer. Simultaneously, the monomer radicals and/or molecules are available at all grafting sites on the starch backbones. Grafting reaction takes place in the accessible regions of the starch and grafting efficiency is, therefore, enhanced.

Considering the conversion, the higher the dose rate, the lower the conversion. It is worthwhile mentioning that a constant total dose was used in the experiment which was a product of a dose rate controlled by a distance of pitch diameter and an irradiation time. The result of such a conversion does not obey the Reciprocity Law for the whole range of dose rates especially at high dose rates. Normal conversion of monomer in a free radical polymerization is of around 70%. The optimum dose rate and appropriate irradiation time shall permit a high conversion with a maximum water retention value, i.e. more graft copolymers.

Effect of Dose Rate on Percent Add-on and Percent Grafting Ratio

A declining trend of both percent add-on and percent grafting ratio is found when increasing the dose rates. The small quantity of free radicals produced from a low dose rate is more effective towards a grafting reaction than a homopolymer formation. There are a small number of free radical population in the aqueous phase to collide among themselves which would, otherwise, results in a greater amount of homopolymer formation. The free radicals are consequently allowed to diffuse to the starch backbones to be grafted on.

Effect of Dose Rate on Viscosity-average Molecular Weight (\bar{M}_v) and Grafting Frequency

Increasing the dose rates decrease the \bar{M}_v values. A few free radicals of both acrylonitrile and starch produced at lower dose rates initiate mainly graft copolymerization due to the lesser termination of free radicals with the polymer growing radicals, resulting in the longer chain length of the grafted polyacrylonitrile and consequently a larger \bar{M}_v value.

Grafting frequency was found relatively decreased with an increase in dose rate. The appropriate number of AGU per chain of the starch controls the chain flexibility for absorbing fluid. Too high a dose rate will initiate too many active sites on the starch backbones which lead to too many grafted chains, i.e. a higher grafting frequency or the small number of AGU units between the two grafted PAN chains.

STATISTICAL ANALYSIS OF CORRELATION BETWEEN THE EFFECT OF DOSE RATE ON GRAFTING PARAMETERS AND WATER RETENTION VALUE

The following grafting parameters affecting water retention by the influence of dose rate were statistically evaluated.

Percent add-on (0.93469), grafting efficiency (0.90611) \bar{M}_v (0.86811), Conversion (0.8898), grafting ratio (0.86717) and homopolymer (-0.90719).

The result of the statistical evaluation excludes the role of grafting frequency ($r = 0.49258$) on water retention. The extent of conversion has a significantly negative effect on water retention, i.e. the percent of conversion in such kinds of reactions should, at least, reach a certain level of somewhat 70%.

EFFECT OF DOSE RATE ON WATER RETENTION

Dose rate of γ -rays influences the grafting parameters very significantly especially at the high dose rate. High water absorption is affected positively by percent-add on, grafting efficiency, conversion and grafting ratio. Homopolymer has a strong negative effect on water absorption.

From Tables I-II, the appropriate amounts of the total dose of 2.529 KGy and the dose rate of 18.80 grays-min⁻¹ give the grafting frequently of 1,075 and 1,165, respectively. Therefore, the number of anhydroglucose units is in the magnitude of about 1,100. Statistical analyses disregarded the positive effect of this grafting parameter. Homopolymer is essentially an undesirable by-product which drastically reduces the extent of graft copolymerization and water absorption. It is necessary that homopolymer formation be eliminated during graft copolymerization.

With a proper control of the radiation factors of γ -rays in terms of total dose and dose rate, in conjunction with a good ratio of starch/acrylonitrile, a water retention value as high as 665 g/g of its dry weight can be achieved easily. This type of the high-water absorbing polymer can also be used in any environment such as in aqueous saline solutions under the condition that its water absorption/retention value in distilled water should be high enough to withstand the reduced osmotic pressure in saline solutions so that water absorption ability is still valid [5].

CONCLUSION

A high-water absorption polymer of hydrolyzed cassava starch-g- PAN can be synthesized by using γ -rays under the proper control of the total dose and dose rate which govern directly the grafting parameters and indirectly the water retention. Both the total dose and dose rate influence percent add-on, grafting ratio and grafting efficiency significantly from which high water retention values are favor, because the number of AGU units between the two grafted PAN chains must meet a certain value first before the starch can become a high-water absorbing polymer, beyond that point grafting frequency seems to be less significant to water absorption/retention ability. Conversion is not so important under the effect of total dose. Unlike the total dose, the influence of dose rate on conversion is very crucial at the two extreme ends, very low and very high due to the Reciprocity failure. Most importantly, the homopolymer formation is definitely an undesirable factor affecting the grafting reaction and the ability of water retention. The use of aluminium can reduce the homopolymer formation significantly. Its roles as a homopolymer suppressor is likely due to an electron transfer process of the hydroxyl radicals and the polymer growing chain to a p-orbital electron of the aluminium atom which consequently promotes the efficiency of grafting reaction. The total dose has a strong influence on homopolymer formation than its counterpart of dose rate.

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