SYNTHESIS OF CASSAVA STARCH-BASED WATER-ABSORBING POLYMER FOR AGRICULTURAL APPLICATION

การสังเคราะห์โพลิเมอร์ดูดซึมน้ำจากแป้งมันสำปะหลังเพื่อใช้ในเกษตรกรรม

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ABSTRACT

Superabsorbent polymer was synthesized by using native cassava starch. Cassava starch was chemically modified into poly (starch-g-acrylonitrile) under a grafting copolymerization of acrylonitrile onto the 80°C gelatinized starch via a redox initiation mechanism using Ce(IV) as initiator in an acid medium. In addition to the cassava starch-g-acrylonitrile, a homopolymer of polyacrylonitrile (PAN) was a by-product which was later removed by extraction with dimethyl-formamide. The purified graft copolymer was subsequently saponified with an 8.5% KOH solution at 85°C to convert the nitrile groups into a mixture of acrylamide and carboxylate groups which were responsible for water absorbency.

Water absorption of the newly synthesized copolymer was carried out in deionized water and in $MgCl_2$ *solutions. The water absorption capacity in pure water was ranged from 120 to 270 time its original dried weight. Water absorption capacity in saline solutions decreased dramatically with increasing the salt concentrations. Water retention in sand and in mixed sand-copolymer at different copolymer concentrations were also performed. Increasing the concentrations of the copolymer in sand increased the water retention capacity.*

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บทคัดย่อ

แป้งมันสำปะหลังที่มีในท้องถิ่นได้รับการดัดแปลงโครงสร้างให้เป็นแป้งที่มีโพลิอะคริโลไนทริลโดยผ่านปฏิกิริยากราฟท์โคโพลิเมอไรเซชันของอะคริโลไนทริลในแป้งที่ผ่านการทำเจลาทิไนซ์ที่อุณหภูมิ 80° ซ. ด้วยสารเริ่มปฏิกิริยาของซีเรียม (IV) ในสารละลายกรด ซึ่งนอกจากจะได้กราฟต์โคโพลิเมอร์แล้วยังได้สารโฮโมโพลิเมอร์ของโพลิอะคริโลไนทริล (PAN) ด้วย ซึ่งสามารถขจัดออกไปโดยการสกัดด้วยไดเมทิลฟอร์มาไมด์ นำสารโคโพลิเมอร์ที่บริสุทธิ์แล้วมาทำสะพอนิฟิเคชันด้วยสารละลายด่างโพแทสเซียมไฮดรอกไซด์ความเข้มข้นร้อยละ 8.5 ที่อุณหภูมิ 85° ซ. โดยเปลี่ยนหมู่ไนทริลไปเป็นสารผสมของอะคริละไมด์และคาร์บอซิเลตซึ่งเป็นส่วนที่กำหนดความสามารถในการดูดน้ำ

การทดสอบคุณสมบัติการอมน้ำของสารโคโพลิเมอร์ที่สังเคราะห์ได้ใหม่นี้ในน้ำกลั่นและในแมกนีเซียมคลอไรด์ได้ผลดังนี้คือ ความสามารถในการดูดน้ำกลั่นมีค่าตั้งแต่ 120 ถึง 270 เท่า ของน้ำหนักสารโพลิเมอร์แห้ง ในขณะที่การดูดน้ำในสารละลาย $MgCl_2$ ลดลงอย่างเด่นชัดเมื่อปริมาณเกลือเพิ่มขึ้น จากการเปรียบเทียบ การอมน้ำในทรายธรรมดา และทรายที่ผสมสารโพลิเมอร์นี้ในอัตราส่วนต่าง ๆ กัน สามารถสรุปได้ว่าเมื่อเพิ่มปริมาณสารโคโพลิเมอร์ในทรายจะเพิ่มความสามารถในการอมน้ำให้มากขึ้น

INTRODUCTION

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

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 act then as a local reservoir, releasing water vapor into the soil and plants as needed and also maintaining an even moisture balance. These materials improve the available water holding capacity by up to 50%, thus reducing water consumption in an ordinary way. In addition, these superabsorbents also prevent the 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 greater product. In transplanting application, coatings of superabsorbents to bare roots of vegetables, trees, ornamentals, seedings and so on, prior to transplanting help prevent roots from drying, reduce wilting, prevent transplant shock, increase plant survival by decreasing recovery time and improve root development.

Besides, the removal of suspended water from organic solvents is an important potential use for hydrolyzed starch-g-polyacrylonitrile. Its uses as a dehydrating agent for ethanol-gasoline mixture to avoid the azeotropic distillation step that is necessary to remove final traces of water from ethanol has been carried out. It can also be used to absorb water from aqueous solution of polymers, such as proteins, in order to concentrate the polymers under mild concentrations.

Superabsorbents or high-water absorbing polymers are those derived from biomaterials which can be made from starch and cellulose. They can be prepared by graft copolymerization of vinyl monomers initiated either by certain metal ions such as salts of cerium (IV), manganese (III), ferric (III), etc; or by radical initiators such as benzoyl peroxide, or by radiation from Co^{60} source.

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 since they produce low crop yields. Furthermore, crop production is unstable because of the erratic nature of the rainfall of the region. On the other hand, one of the major limiting factors of soils in the Northeast is low water holding capacity which is mainly due to low organic matter and clay contents. The most practical means to increase water retention capacity is to add organic matter. In order to give plants nutrients as well as increase soil aeration and water absorption, the addition of high-water absorbing materials can be another useful means in developing the Northeast part 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. Quite often, the production of cassava starch exceeds the export and consumption scale. This situation causes the country cassava surplus. The surplus is certainly a waste and usually destroyed in order to keep the stable pricing of the product.

This research aims at :

- developing a cheap and reliable process for manufacturing of high-water absorbing polymer, based on cassava starch, which can be transferred to the industry for a large scale production;
- using the Country's surplus and unused cassava starch;
- improving farm productivity in the Northeastern region during the dry season.

MATERIALS AND METHODS

Cassava starch produced from tapioca cultivated in summer was obtained from Thai Wah Co. Ltd. It contains 12.80% moisture, 0.07% ash, 32.57 ppm SO_2, pH value of 5.80 and viscosity at 66–77°C of 780 BU.

Acrylonitrile (AN, 98% pure) was provided by Siam Resin & Chemical Co. Ltd. It was purified by fractional distillation at atmospheric pressure through a 14-inch vigreux column and stored in the refrigerator under nitrogen gas.

Methanol, commercial grade from BDH was also purified by fractional distillation at atmospheric pressure.

Other chemicals used were of analytical grade, employed without further purification.

1. Gelatinization of cassava starch

Into a 1,000 cm^3 4-necked round bottom flask, 10 g of cassava starch was mixed with 292 cm^3 of triply distilled water. The system was heated at around 80° ± 3°C for 1 h under nitrogen atmosphere to form a gelatinized starch slurry.

2. Grafting of acrylonitrile onto cassava starch

The gelatinized starch was then cooled to about 40°C. Two portions of 5 g of acrylonitrile were added into the gelatinized starch containing 0.55 mmol of 8.0 cm^3 ceric ammonium sulphate in 0.5 and 1.0 N HNO_3, respectively. The mixture was stirred under nitrogen atmosphere at 40°C for 3 h. The reaction product was subsequently precipitated with methanol, filtered, and washed with methanol again before being dried at 65°C for 3 h.

The dried samples were investigated for its acidic activity under an infrared spectrometer. The length of the C≡N peak at 2,243 cm^{-1} was measured. The better acidic activity based on the length of the C≡N peaks, was used to determine the effect of starch(g)/AN(g) ratios on grafting and water absorption.

Effect of starch/AN ratios on grafting

Various amounts of acrylonitrile: 5, 10, 15, 20, 25 and 30 g were added to each of 10 g of the cool gelatinized starch in the presence of 8.0 cm^3 solution of 0.55 mmole cerium ammonium sulphate and the chosen acidity of nitric acid (found 1.0 N). The reaction steps were repeated as mentioned earlier. The dried samples were inspected with an IR spectrometer.

3. Homopolymer extraction by N,N-Dimethylformamide (DMF)

In a 500-cm^3 Erlenmeyer flask, 5.0 g of the dried starch-g-polyacrylonitrile, ground into a powder form, was stirred in 250 ml of DMF at room temperature for 24 h.

The extracted product was filtered, washed with methanol, and dried for 30 h at 65°C. Then 100 cm^3 of the clear extract was precipitated in an excess amount of methanol, then filtered and washed again with methanol. The precipitate was dried for 3 h at 65°C and weighed to determine the amount of the homopolymer, polyacrylonitrile, All products were detected with the IR spectrometer. The IR analyses were carried out with 0.04 g of dried product mixed with 2.00 g dried KBr. Calibration of the spectrometer was held constant for all analyses.

4. Copolymer characterization

Saponification of starch-g-polyacrylonitrile

A suspension of 10 g DMF-extracted starch-g-polyacrylonitrile as added to 200 cm^3 of an 8.5% potassium hydroxide solution. The mixture was stirred with a magnetic stirrer and the saponification was carried out at 85°C for 2 h. It developed to deep red solution and changed to light yellow at the later stage. It was then allowed to cool to room temperature and precipitated with alcohol. The product was then filtered and washed thorougly with methanol until pH 7 was reached. The paste was dried in the 65°C oven for 30 h to remove any residual methanol. The dried product was ground into a powder form.

Determination of percent add-on

In a 250-cm^3 Erlenmeyer flask equipped with a condenser, 1.00 g DMF-extracted polymer was stirred in 100 cm^3 of 1 N H_2SO_4 and the mixture was refluxed for 60 min. Filtered the water-insoluble polymer, washed until pH of the washed solution was 7, and then dried. The weighed percentage polyacrylonitrile (PAN) in the graft copolymer or so called "percentage add-on" was computed from the weight difference between the graft copolymer and the soluble starch which was removed by acid hydrolysis.

Determination of percentage conversion

The experimental procedures described in sections 1 through 2 were carried out. The weight of the grafted copolymer and homopolymer was regarded as the total amount of polymer obtained from the weight of monomer charged.

Determination of homopolymer formation

The weight obtained from section 3 was the amount of polyacrylonitrile produced as a by-product.

Determination of grafting efficiency

The experimental procedures of sections 2 through 3, which gave the weight difference between the total weight of polymer and the weight of homopolymer produced was regarded as the percentage grafting efficiency.

5. Water absorption/retention capacities of the copolymer

In deionized water

A 0.1 g of dried and saponified starch-g-polyacrylonitrile was immersed in a weighed amount of triply-distilled water. After one hour, the slurry was filtered through a wetted and weighed no. 41 filter paper in a funnel by normal gravity force. Corrections were made for the water retention of the filter paper, i.e., the wetted filter paper will reduce, to a certain extent, the capillary effect of the filter paper. The amount of water retained by the starch-g-polyacrylonitrile was calculated as in gram per gram of dry modified starch.

In magnesium chloride solutions

The same experimental procedure as described in section 1 was carried out, except a series of $MgCl_2$ solutions of 0.5 and 1% W/V was used instead of deionized water.

In sand alone and sand with saponified starch-g-polyacrylonitrile

To determine the water retention capacity of the river sand itself, a known quantity of water was drained at approximately rate of 2 cm^3/min to a layer of 20 g river sand. Then drained away any excess unabsorbed water and weighed.

A sandwich comprising 10 g of the river sand, 0.1 g of the starch-g-polyacrylonitrile and another 10 g of the sand was made in a sequential order to observe the water retention capacity of sand in the presence of the superabsorbent. The experiment was then carried out exactly the same technique as the determination of water retention capacity of the sand alone.

Likewise, 0.2, 0.3 and 0.4 g of the starch-g-polyacrylonitrile were mixed with the sand by repeating the earlier experimental procedure.

The weight difference between the two experiments indicates the efficiency of water retention capacity of the sand by incorporating the starch-g-polyacrylonitrile.

6. Scanning electron microscopy of the copolymer

The dry and ground copolymers synthesized with various ratios of starch(g)/AN(g) were investigated by the simple technique of scanning electron microscopy and x-ray microanalysis to observe the morphology of the superabsorbent and the elements left from the reaction steps, such as the potassium cation from the saponification and the cerium ion from the grafting copolymerization.

RESULTS AND DISCUSSION

Infrared (IR) analyses

At present, IR spectroscopy was used as a tool to follow up changes in graft copolymerization. The IR spectra of cassava starch, and the copolymers after grafting, after extraction, and after saponification were given in Figures 1-4, respectively. The IR spectrum of cassava starch in Figure 1 gave absorption bands at 3,400 and 1,000-1,100 cm^{-1}, characteristic of amylose containing in the starch.

The absence of the C≡N group at 2,243 cm^{-1} and the strong asymmetrical stretching band at 1,570 cm^{-1}, and a weak symmetrical stretching band 1,430–1,390 cm^{-1}, characteristics of the $-C=O^{-}$ group indicated the occurrence of grafting. The absence of the primary amine may be due to a relatively low concentration, and/or the usually low intensity of the NH stretching band and overlapping with the existing one(s) of the starting materials.

Grafting of acrylonitrile onto cassava starch

Effect on nitric acid normality on grafting efficiency

Since 0.5 and 1.0 N HNO_3 were used as a medium for ceric ammonium sulfate for grafting acrylonitrile onto cassava starch, the IR spectra of the graft copolymer indicated that the acid normality of 1.0 N HNO_3 catalysts solution gave a relatively higher C≡N stretching peak at 2,243 cm^{-1} (peak length 3.9 cm).

According to the result, the subsequent experiments were carried out in a reaction medium of 1.0 N HNO_3. The higher acidity of nitric acid activates the activity of the catalyst which enhances the complex formation between the Ce(IV) and the cassava starch. Higher acidity than 1 N is not needed since the acid is produced stoichiometrically under the cleavage of glycolic C_2 and C_3. Too high an acid content is undesirable due to the interference of the excess anions on water absorption. That is the overall glycol cleaving rate is governed by the concentration of Ce(IV), the amount of nitric acid and the glycol concentration[3].

Effect of starch/acrylonitrile ratios on grafting

Upon investigation of the IR spectra of the starch-g-polyacrylonitrile by the ratios of starch(g)/AN(g) : 10:5, 10:10, 10:15, 10:20, 10:25 and 10:30, it was found that the peak lengths of the nitrile stretching absorption at the wavelength of 2,243 cm^{-1} were increased with increasing the acrylonitrile concentrations. Since the preparation of the pellets from these samples were carefully made, and the condition of the IR spectrometer was kept constant, it is quantitatively and technically justified. After the DMF extraction of the products, the peak lengths of all ratios were decreased which indicated of the removal of the homopolymer, polyacrylonitrile. All the nitrile peaks disappeared after saponification which means that these peaks were converted into the carboxamide and carboxylate groups which are capable of high water absorption. The proportional increase of the C≡N stretching absorption peak at 2,243 cm^{-1} after grafting as the acrylonitrile content increased is illustrated in Figure 5. Table 1 shows the change in peak lengths of the nitrile stretching absorption due to grafting, extraction, and saponification of the polymers.

Determination of homopolymer content and percentage grafting efficiency.

Although the synthesis of starch-g-polyacrylonitrile involves a free-radical pathway, contributed by the redox initiator, free-radicals formed on starch caused by chain transfer reactions produce a significant amount of homopolymer which is removable by dimethylformamide. PAN is soluble in such a solvent while the starch-g-polyacrylonitrile remains unchanged. This renders the decrease in the peak lengths of nitrile groups of the graft copolymer as shown in Table 1.

Grafting efficiency is a term used to explain the extent of graft copolymerization. Usually, high grafting efficiencies are desirable since a highly grafted copolymer will Ultimately yield a material with a higher water absorption efficiency. The amounts of polyacrylonitrile and grafting efficiency of the experiment were presented in Table 2 that :

1) The higher the acrylonitrile content, the greater the homopolymer produced.

2) Grafting efficiency decreased with increasing the concentrations of acrylonitrile because less initiator is available to the polysaccharide chain and becomes more favorable to chain transfer to the increasing amount of acrylonitrile.

It is noted that increasing vicosity of the medium causes the stirring problem. The efficiency of the stirring system such as the stirring rate, the geometry of the propeller should be seriously taken into account for effective stirring.

The stirrer could only move at the center bottom of the reaction flask especially at high acrylonitrile contents, due to gel effect or Trommsdorf-Norrish effect. Under this situation, the diffusion efficiency of radicals to the reactive grafting sites would surely be reduced. This behavior allows the polymer growing chains to become larger which eventually will decrease the number of chain terminations. Thus, the viscosity increased which was accompanied by the higher molecular weight.

In addition, the data presented in Table 2 should be treated only as a guideline for the polyacrylonitrile formation as the technique for filtering the very viscous and sticky polymers, especially at a high acrylonitrile content, caused a material loss due to very strong adhesion with the filter paper. Although the polyacrylonitrile produced as a by-product may not be desirable for water absorption, it is indeed a very good packaging film with high barrier effects such as moisture protection, the applications of which should not be overlooked in the future for the agroindustry of Thailand.

Determination of percent conversion of monomer and percent add-on

The conversion of acrylonitrile and the percent add-on increased with increasing the amounts of acrylonitrile charged (Table 3), the results indicated that the more concentrate the monomer, the more it could react with the starch substrate free radicals as well as could polymerize via chain transfer reaction to form polyacrylonitrile. The 10/10 ratio of starch(g)/AN(g) gave a very interesting indication of economical and practical viewpoints in that only increasing the acrylonitrile content by 5 g, the amount of percent add-on increased by more than 4 times and the amount of homopolymer produced as a by-product was only 6.6% (Table 2) ; while the conversion of polymerization was as high as 41%, the amount of which was normally expected for the radical chain polymerization. It is of great interest to see the extent of water absorption capacity of the copolymer itself and in the soil, and chemical environment.

Water absorption

In deionized water

Water absorption capacity of the starch-g-polyacrylonitrile increased with the acrylonitrile contents (Figure 6). Water absorption capacity of the copolymer was in the same trend as the percent add-on and grafting efficiency. A linear relationship between water absorption and the amount of acrylonitrile was observed at the low acrylonitrile contents from 5% to 20%. The absorption curve reached a plateau when the acrylonitrile concentrations exceeded 20%. The similar trend of water absorption and percent add-on is observed and shown in Figure 7.

These results correlate quite well with the mechanistic model of the enhanced water absorbency of acrylate-grafted polysaccharides[6] that is identical to the same as that described by Grignon and Scallman for the swelling of cellulose gels.[2] The swelling is considered to be caused by osmotic pressure differential resulting from a difference in concentration of mobile ions between the interior of the gel and the external solution.

The concentration of mobile K^+ ions in the polymer gel, resulting from the saponification step is higher than those in deionized water which comprises only hydrogen and oxygen atoms. As the ionic groups cannot move out of the gel, the solution within the gel is regarded as separated from the external solution by a semipermeable membrane which confines to the potassium carboxylate and carboxamide groups, but gives free passage of water. The gel swells as a result of the entry of water in an attempt to reduce the osmotic pressure differential due to the difference in ion concentrations. Swelling continues until the osmotic pressure differential is equal to the resistance to further expansion, i.e., when the ion concentration between inside and outside the gel has reached equilibrium.

Okieimen and Ebhoaye[4] suggested that the water absorption properties of cellulosic materials are thought to result from interaction through hydrogen bonding of the hydroxyl groups on the cellulose with water molecules.

In conclusion, the effect of water absorption depends on the frequency of interposition of the grafted polymer chains on the cellulosic starch backbone, and the nature of the grafted polymer. In other words, the amount of grafting chain or acrylonitrile is one of the determining factors as indicated in Figure 6.

It must be noted that the figures of water absorption capacity of the graft copolymer in deionized water change with multiple wetting-drying cycles. The loss of absorbency is probably due to a condensation type of crosslinking reaction occurring between hydroxyl, carboxamide or carboxyl substituents at the drying temperature[4].

In magnesium chloride solutions

In magnesium chloride solutions, a plateau indicating an osmotic pressure differential of zero, was reached with a maximum water absorption of only 19.6 g/g with 0.5% solution of magnesium chloride at 20% acrylonitrile content. The 1% solution gave similar result with the maximum water absorption of only 14 g/g. (Figure 8)

In generalization, the decrease in water absorption of starch-g-polyacrylonitrile in the presence of salt solutions, such as Ca^{+2}, Mg^{+2}, and fertilizers is mainly due to the fast approaching of zero osmotic pressure differential of the potassium carboxylate and carboxamide semipermeable membrane. It is also interpreted as due to the ionic strength resulted from electronic configuration on one hand, and on the other hand for divalent cations such as Mg^{+2} ions, the less absorption of the copolymer probable is the consequence of crosslinking by salt formation of carboxyl groups on the adjacent chain or chain segments. In addition, it has been suggested that the presence of sodium chloride, a monovalent cation, causes the grafted polyion chain to undergo configurational changes, resulting in the reduction of the swelling forces[4]. By far, the sound explanation for water absorption is the osmotic pressure differential concept. It is suggested, therefore, that more superabsorbent be incorporated in the saline or fertilized soil, the amount of which to be added needs more experimental works to indicate.

In sand alone and sand with saponified starch-g-polyacrylonitrile

The results of water retention capacity in sand are given in Table 4 and Figures 9-10. They clearly indicate that the water retention capacity depends definitely on the amount of starch-g-polyacrylonitrile used. The water retention of the medium increased dramatically, since that of sand was only 36.5 g/g.

Figures 9 and 10 show a linear relationship between water retention and polymer concentration. As the concentration increases, so does the water retention capacity. In the case of increasing the starch/acrylonitrile ratios, going from 10:5 to 10:30, water retention capacity increased as a consequence of the increasing amounts of acrylonitrile and the copolymer added.

Scanning electron microscopy of saponified cassava starch-g-polyacrylonitrile

In order to observe the changes in particle size and shape of the graft copolymer, cassava starch was investigated under a Fritsch Laser Particles Sizer, model Analysette 22. It is very unfortunate that under all the available techniques of this equipment, the graft copolymer cannot be investigated which is due to its absorptivity causing stickiness and coalescence on the surface of each individual particle, and finally becoming an aggregate center. The aggregator then adhered to parts of the unit which ceased the measurement. Therefore, only the particle size distribution of the starch could be illustrated in Figure 11. It was found that the average size was 16.8 micrometers with a mean square deviation of

11.91 micrometers at the measure reliability of 98.1%. Truncated, round and oval like are the shapes of this cassava starch viewed under a light microscope[5].

The electron micrographs of all ratios of cassava starch/acrylonitrile gave identical surface characteristic and pore structure. The micrographs indicated very soft, sticky and porous surface. The distributions of pores were very irregular and so did the depth of the pores. These pores, indeed, could accommodate huge amounts of water and solutions (Figure 10). Since the particle shapes of the starch-g-polyacrylonitrile were changed through the grinding process, therefore, no correlation between the pore size distribution and absorptivity can be deduced. X-ray microanalysis indicated the presence of huge amount of the potassium ion and very minute amount of the sodium, iron and cerium ions. However, the reliability of tracer element analysis should be perfomed by x-ray fluorescence technique.

Plant's test on mixture of sand and cassava starch-g-polyacrylonitrile

This study used an ornamental plant, Bai Plu Daang, a kind of Piperaceae, as an experimental species. The plant was dipped in a glass containing a slurry of 0.3 g graft copolymer in 90 cm^3 water. The glass was placed near the window where sunlight and wind could get on the plant. No further irrigation was provided. The plant could survive for 26 days until the water was nearly dried out. Repeated cycles were continued until the third cycle was reached with a decreasing nonirrigation period. Some leaves turned yellow and then faded away while simultaneously a number of new leaves and branches grew with healthy sign. Control experiments of Bai Plu Daang only in a glass containing only tap water were carried out in the same manner. The leaves turned yellow and soft after 14 days, then became wilting and fell away. The water in the glass became dry in the second week. This illustrates that the graft copolymer helps in maintaining the normal growth and vigor of plantation without wilting symptoms, even when the frequency of irrigation is considerably reduced.

CONCLUSION AND SUGGESTIONS

The investigation on the chemical modification of native cassava starch by a graft copolymerization has led to a new type of polymer with attractive water absorption properties. This novel material is a biodegradable high-water absorbing polymer. The results obtained are very significant in terms of the numerous applications possible: the product has already been used in agricultural, horticultural, silvicultural areas and in industrial goods such as sanitary napkins, baby diapers, etc. The results match well similar material, synthesized from different sources of substrate in industrial nations.

The findings can be summarized as follows:-

1. Cassava starch-g-polyacrylonitrile was synthesized and confirmed by infrared spectroscopy: the nitrile stretching band appeared at 2,243 cm^{-1} during grafting, and

disappeared during saponification; the characteristic bands appeared at 3,400; 1,000–1,100 cm^{-1} indicated the occurrence of grafting with cassava starch. The disappearance of all the nitrile groups, on the other hand, resulted in the appearance of carboxylate and carboxamide groups. The formation of two new functional groups also resulted in two new absorption bands. Firstly, the carboxylate group -COOK gave rise to two bands: a strong asymmetrical stretching band at 1,570 cm^{-1}, and a weak, symmetrical stretching band at 1,400 cm^{-1}. Secondly, the primary amide could not be detected, probably as a result of a relatively low concentration, and/or due to the usually low intensity of the -NH stretching band and overlapping with existing ones, the -OH stretching bands of the starting material. These two groups are capable of water absorption properties based on the differential in osmotic pressure due to the potassium carboxylate and carboxamide semipermeable membrane.

2. By increasing the acrylonitrile content, an increase in percentage of homopolymer and percent add-on was observed, while the percent grafting efficiency decreased. The formation of polyacrylonitrile as a by-product was undesirable in water absorption capacity.

3. Water absorption capacity of cassava starch-g-poly-acrylonitrile synthesized was in the range of 120 to 270 times its original dried weight depending upon the acrylonitrile contents from 5 g to 30 g based on 10 g cassava starch.

4. The starch/AN ratio of 10:10 is an attractive figure since it is economical to produce, yet still gives a water absorption value of 170. Most of the commercial available ones have water absorption figures of about 120 to 200.

5. Water absorption capacity of the graft copolymer in 0.5 and 1.0% magnesium chloride solutions gave a maximum value at 20 g/g and 14.5 g/g, respectively. An increase in ion content in water reduces the water absorption due to a decrease in the osmotic pressure.

6. Water retention capacity in the river sand was 36.5 g/g. Mixtures of sand with 0.5, 1.0, 1.5 and 2.0% cassava starch-g-polyacrylonitrile could increase water retention gradually upto a maximum of 232 g/g at 2% of the polymer synthesized from 30 g of acrylonitrile.

7. Scanning electron micrographs revealed the soft, sticky and porous surface of the graft copolymer as well as the irregular depth and size of the pores. This characteristic is capable of holding a huge amount of water.

Suggestion

Since this current research is only a guideline of the whole spectrum of this area, further experimental work on a wide range of factors should be proceeded. As the starch-based high-water absorbing polymer can be deteriorated by the following factors:

1. Multiple wetting-drying cycle causes less absorption;
2. Degradation by plants;
3. Decomposition by microorganism;
4. Degradation by ultraviolet radiation and heat;
5. Decrease in water absorption by salt solutions.

To develop a better and new high-water absorbing polymers to be used in agriculture and horticulture, the following properties are to be acquired:

1. Permanent water absorption stability;
2. Stable expanding, wetting, and non-shrinking drying.

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Table 1. The change in peak lengths of the nitrile stretching absorption due to grafting, extraction, and saponification of the polymers

Amount of acrylonitrile added (g)	Peak length of the C≡N peak		
	After grafting (cm)	After DMF extract (cm)	After saponification (cm)
5	3.9	1.9	0
10	5.2	5.0	0
15	6.7	5.0	0
20	7.5	7.4	0
25	7.4	6.8	0
30	9.4	8.1	0

Table 2. The amounts of polyacrylonitrile and the grafting efficiency of acrylonitrile on cassava starch

Starch(g)/AN(g)	Percent of Polyacrylonitrile	Percent grafting efficiency
10/5	5.51	94.45
10/10	6.61	93.39
10/15	11.67	88.33
10/20	15.27	84.73
10/25	18.00	82.00
10/30	19.40	80.60

Table 3. Effect of starch/acrylonitrile ratio on percent conversion and percent add-on

Starch(g)/AN(g)	Conversion of monomer (%)	Percent add-on (%)
10/5	40	8.5
10/10	44	36.5
10/15	60.8	42.8
10/20	64.5	50.5
10/25	66.4	69.0
10/30	77.8	75.0

Table 4. Water retention capacity of sand mixed with various concentration of saponified starch-g-polyacrylonitrile

Starch(g)/AN(g)	Water retention capacity(%) on polymer added in sand			
	0.5%	1.0%	1.5%	2.0%
10/5	50	68.2	81.3	96.8
10/10	60	85.8	93.3	109.1
10/15	66.4	100.3	122.3	137
10/20	68.5	102.8	158.2	186
10/25	81.2	130.0	174.6	220
10/30	85.2	135.8	182.7	232

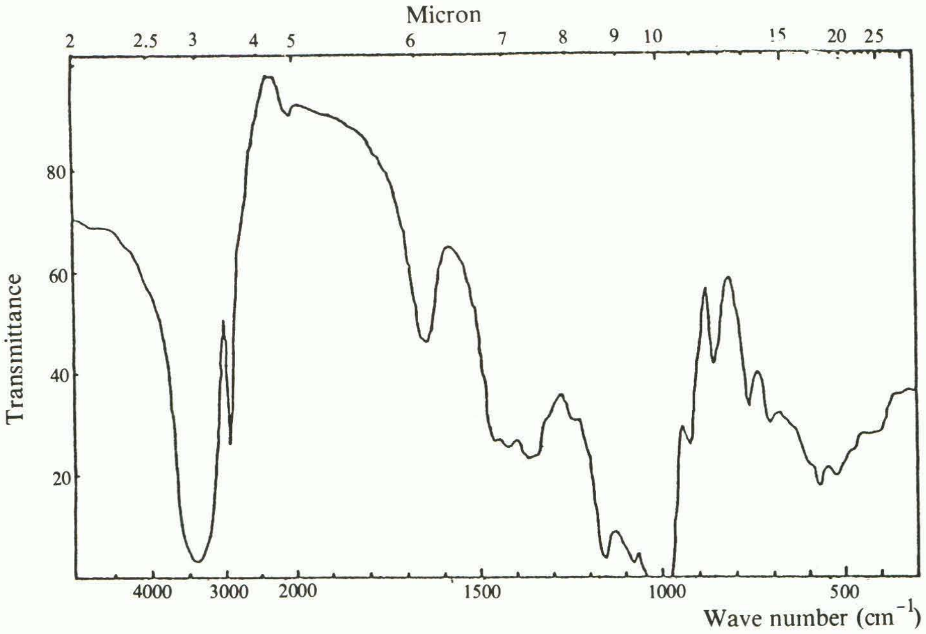

Fig. 1 Infrared spectrum of dried cassava starch

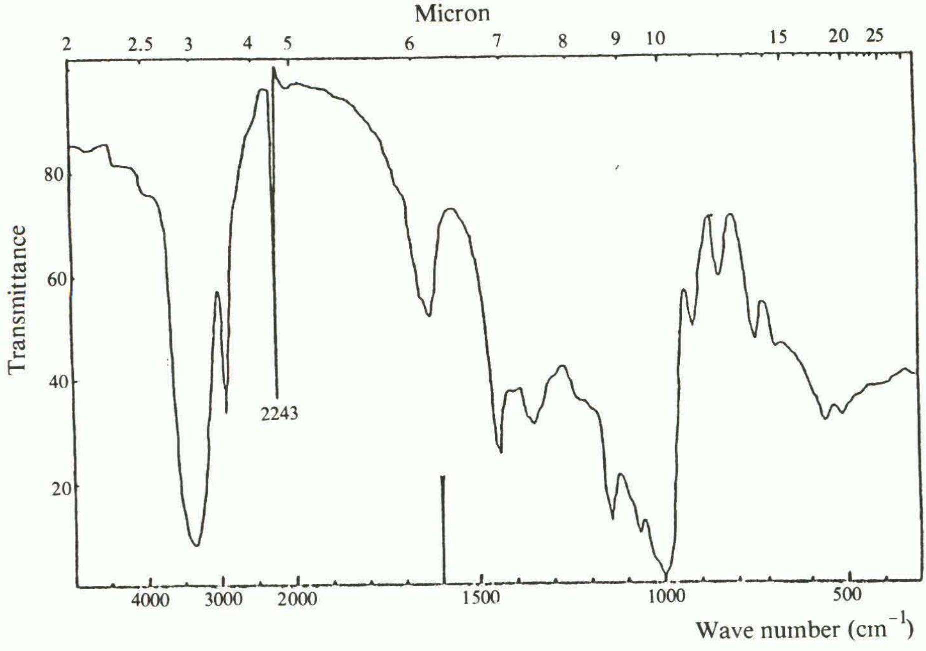

Fig. 2 Infrared spectrum of the graft copolymer after grafting

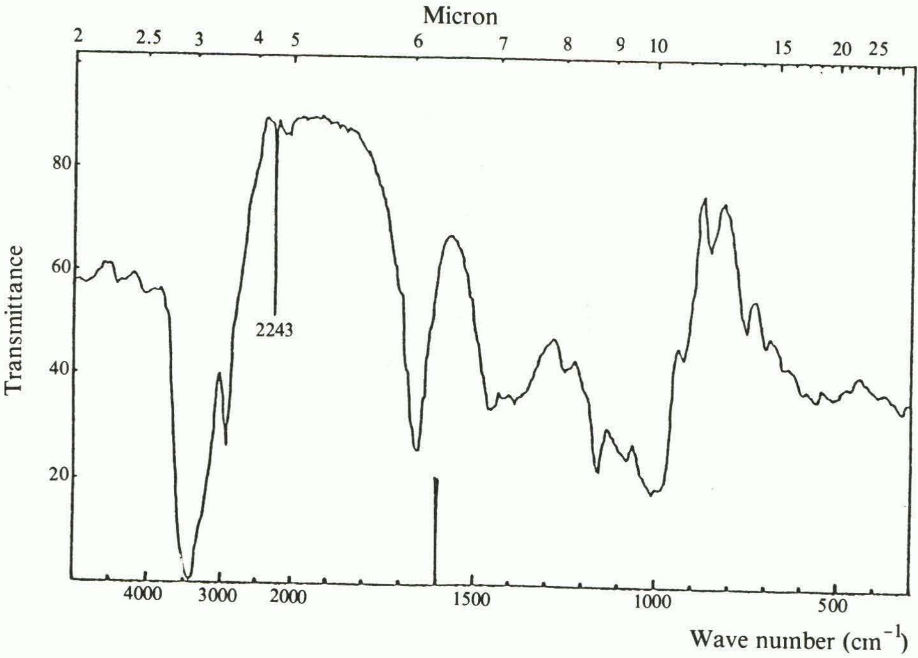

Fig. 3 Infrared spectrum of the graft copolymer after DMF extract

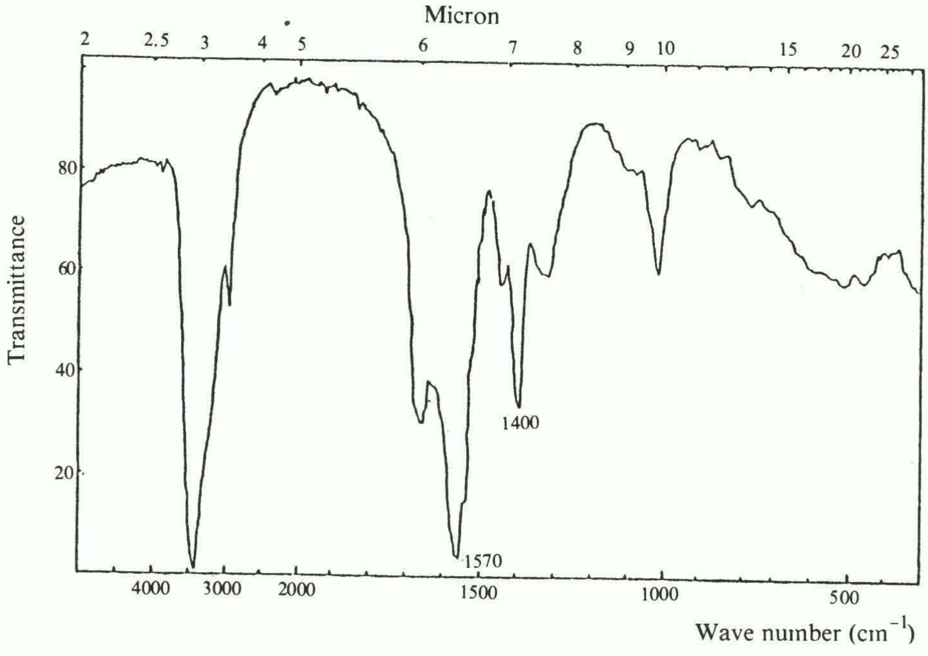

Fig. 4 Infrared spectrum of the saponified graft copolymer

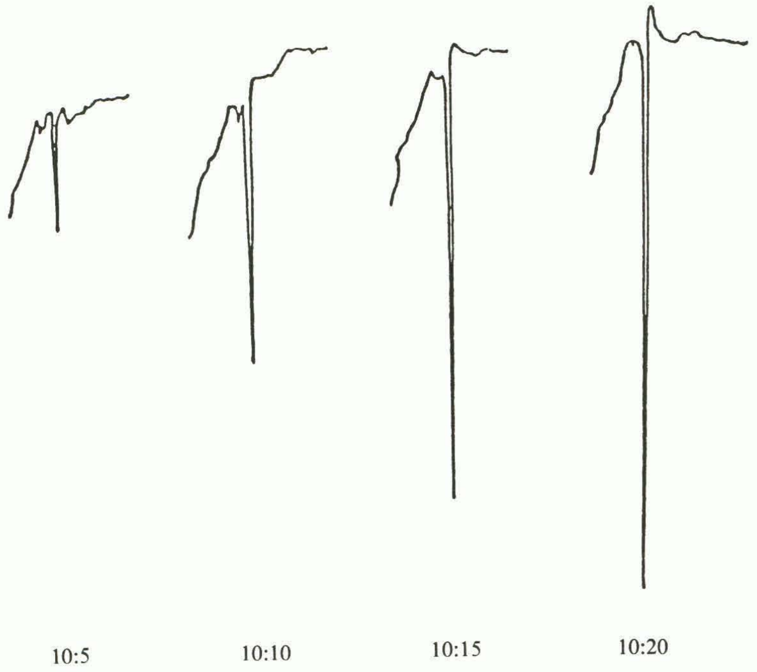

Fig. 5 The proportional increase of the C≡N stretching absorption peak at 2,243 cm^{-1} after grafting as the acrylonitrile content increased

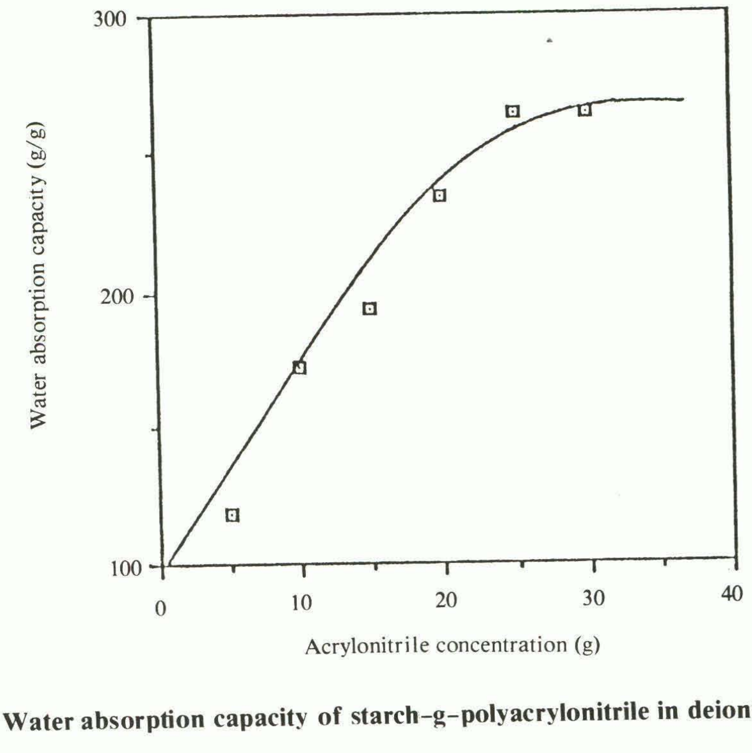

Fig. 6 Water absorption capacity of starch-g-polyacrylonitrile in deionized water

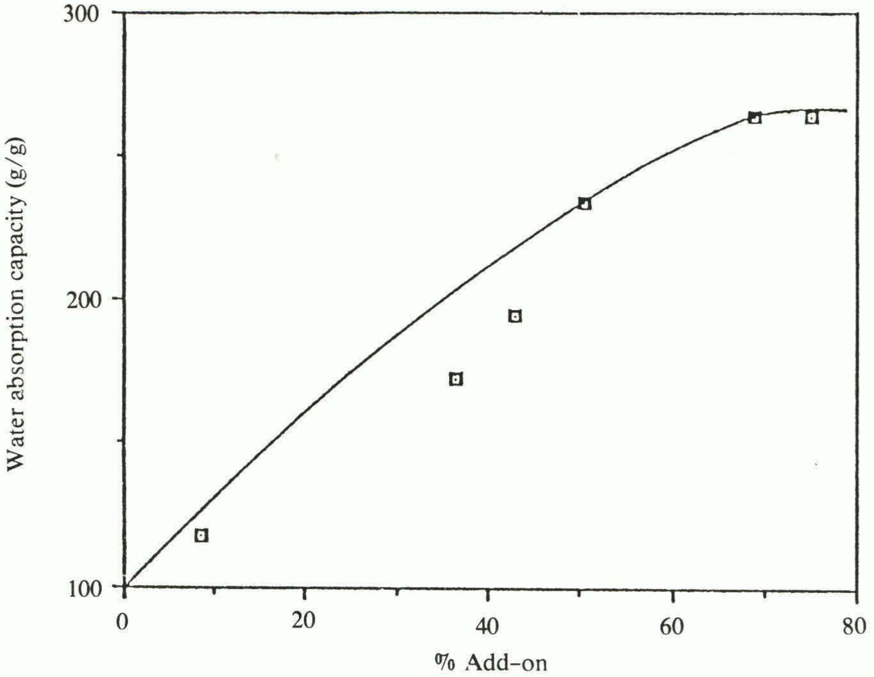

Fig. 7 Effect of percent add-on on water absorption capacity of starch-g-polyacrylonitrile in deionized water

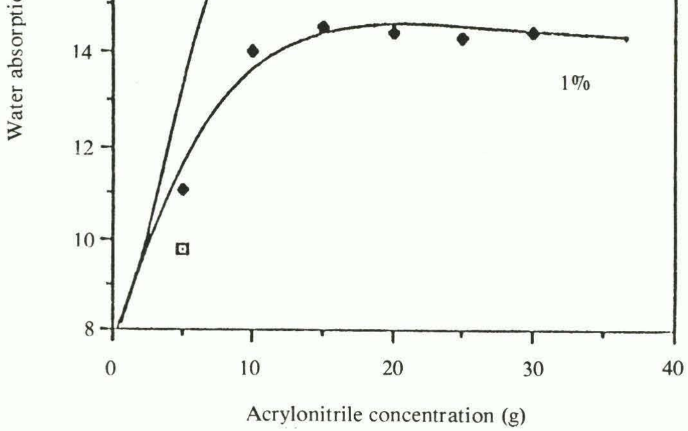

Fig. 8 Results of water absorption of starch-g-polyacrylonitrile in the presence of magnesium chloride solutions

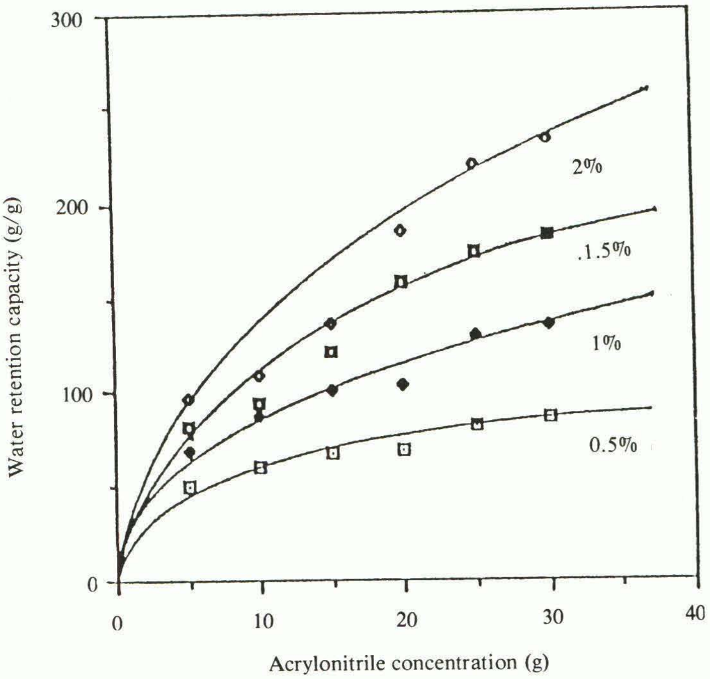

Fig. 9 Water retention capacity of sand mixed with various amounts of cassava starch-g-polyacrylonitrile at various acrylonitrile contents

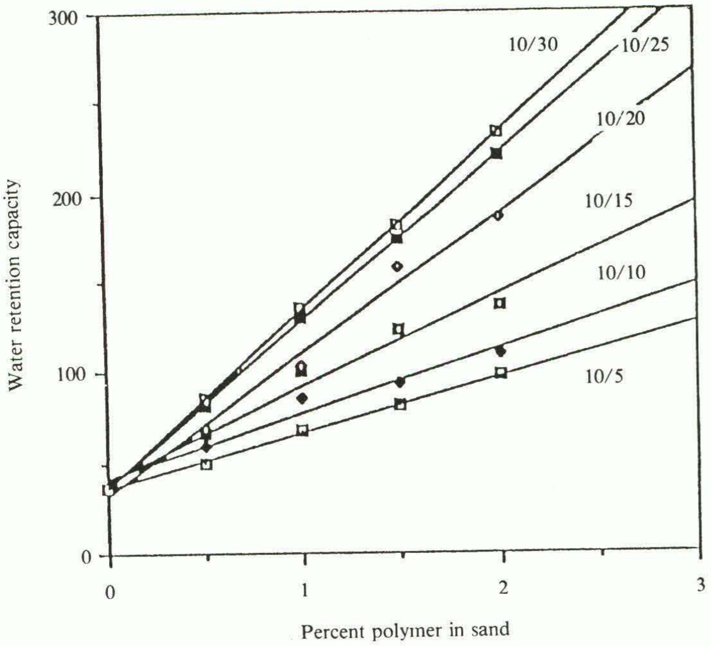

Fig. 10 Water retention capacity of sand mixed with cassava starch-g-polyacrylonitrile containing various acrylonitrile contents at different amounts of the copolymer added

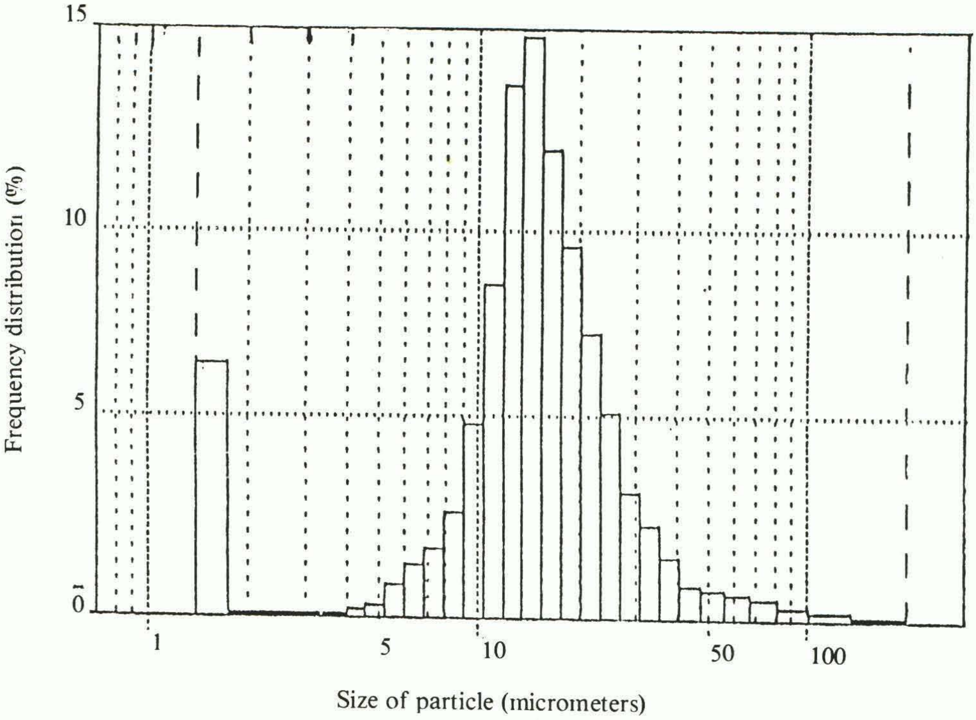

Fig. 11 Frequency distribution of cassava starch

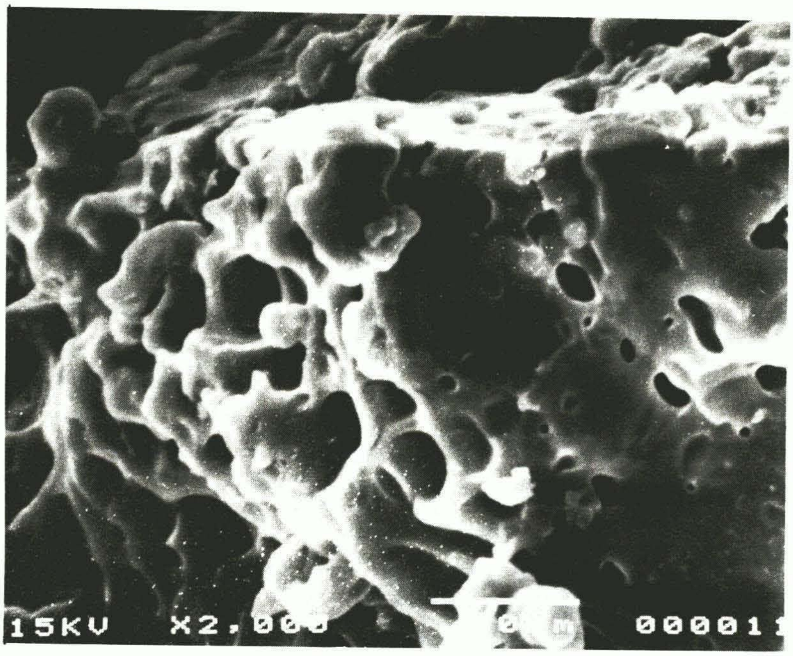

Fig. 12 Electron micrograph of the copolymer synthesized from 15 g acrylonitrile, magnification at 2,000 times