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Proceedings of the FNCA 2007 Workshop on Application of Electron Accelerator

- Radiation Processing of Natural Polymer -

22～26 November 2007, Hochiminh, Vietnam

(Eds.) Masao TAMADA and Tamikazu KUME

Environmental Polymer Group
Quantum Beam Science Directorate

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Japan Atomic Energy Agency

日本原子力研究開発機構

独立行政法人日本原子力研究開発機構　研究技術情報部　研究技術情報課
〒319-1195　茨城県那珂郡東海村白方白根２番地４
電話 029-282-6387, Fax 029-282-5920, E-mail:ird-support@jaea.go.jp

Intellectual Resources Section, Intellectual Resources Department,
Japan Atomic Energy Agency
2-4 Shirakata Shirane, Tokai-mura, Naka-gun, Ibaraki-ken 319-1195 Japan
Tel +81-29-282-6387, Fax +81-29-282-5920, E-mail:ird-support@jaea.go.jp

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（Eds.） Masao TAMADA and Tamikazu KUME$^+$

Environment and Industrial Materials Research Division
Quantum Beam Science Directorate, Japan Atomic Energy Agency
Watanuki-machi, Takasaki-shi, Gunma-ken

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This workshop was co-sponsored by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan and the Ministry of Science and Technology (MOST), Vietnam. The Vietnam Atomic Energy Commission and Japan Atomic Energy Agency (JAEA) jointly executed the workshop in cooperation with the International Atomic Energy Agency (IAEA). The main objectives of the workshop were the following:

- to discuss for the promotion of the commercial applications of radiation processing of natural polymer
- to prepare the work plan for the FNCA activities for 2007-2008.

The workshop was attended by experts on radiation processing from Bangladesh, China, Egypt, India, Indonesia, Japan, Korea, Malaysia, Pakistan, Philippines, Sri Lanka, Thailand and Vietnam.

The radiation processing of natural polymer is divided into crosslinking, degradation and graft polymerization. The radiation crosslinked polysaccharides are mainly used to prepare hydrogel for healthcare and environment. Hydrogels were commercialized in India, Korea, and Malaysia and are going to be commercialized in Philippines and Vietnam as wound dressings. Radiation degraded polysaccharides (alginate and chitosan) are commercialized in China and Vietnam in aquaculture and agriculture, respectively. Indonesia successfully carried out field test of radiation degraded chitosan as plant growth promoter. Also the radiation degraded chitosan was demonstrated to preserve post harvest fruit and to extend the shelf life of papaya in Pakistan and Sri Lanka, respectively. Radiation graft polymerization onto polysaccharide is applied for production of soil conditioner in Vietnam. Several applications of grafting technique were also reported.

Manuscripts submitted by presenters were compiled in the proceedings.

Keywords: Radiation, Natural Polymers, Polysaccharide, Crosslinking, Degradation

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$^+$*Takasaki Advanced Radiation Research Institute*

FNCA2007 電子加速器利用ワークショップ論文集
-天然高分子の放射線加工-
2007 年 10 月 22 日～10 月 26 日､ベトナム、ホーチミン

日本原子力研究開発機構 量子ビーム応用研究部門 環境・産業応用研究開発ユニット
（編）玉田 正男･久米 民和[+]

（2008 年 10 月 9 日受理）

本ワークショップは、文部科学省 (MEXT) 及びベトナム科学技術庁 (MOST) が共催し､国際原子力機関 (IAEA) の協力のもとベトナム原子力委員会 (VAEC) と日本原子力研究開発機構 (JAEA) が共同実施した。本ワークショップの目的は、アジア原子力協力フォーラム (FNCA) 参加各国の天然高分子の放射線加工の実用化状況を議論し、今後のプロジェクトの計画を策定することであった。ワークショップには FNCA 加盟 9 カ国のプロジェクトリーダー及び放射線加工の専門家が出席した。さらに､RCA プロジェクトリード国フィリピンのコーディネーターと RCA の非 FNCA 加盟国であるインド、パキスタンスリランカ及びエジプトから 4 名の専門家が出席した。

天然高分子の放射線加工は、放射線架橋、分解及びグラフト重合がある。多糖類の放射線架橋は、ヘルスケア及び環境のためのハイドロゲルの製造に使用されている。ハイドロゲルが、インド、韓国及びマレーシアで実用化され、フィリピン及びベトナムで商品化されようとしている。放射線によって分解したキトサンは、ベトナム及び中国で農業及び水産養殖で使用されている。インドネシアでは、分解多糖類の植物生長促進剤効果が実証試験された。また、果物の賞味期間延長効果が、パキスタン及びスルランカから報告された。多糖類への放射線グラフト重合が土壌保水剤としてベトナムで実用化された。放射線グラフト重合のさまざまな応用も報告された。

本論文集は、天然高分子の放射線加工に関する各発表者からの投稿原稿を編集したものである。

高崎量子応用研究所（駐在）： 〒370-1292 群馬県高崎市綿貫町 1233
[+]高崎量子応用研究所

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1. Project Report

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1.1 Review of Present Status of the Activities on FNCA Industrial Application Project -Application of Electron Accelerator-

Tamikazu Kume

Project Leader of Japan

Takasaki Advanced Radiation Research Institute, Japan Atomic Energy Agency

1. Name of the Project

Application of Electron Accelerator -Radiation Processing of Natural Polymer-

2. Objective of the Project

The objective of the project is to develop technology of electron beam (EB) irradiation system that has a variety of applications and good safety features. A self-shielded low energy accelerator system offers interesting option as their initial investment is much lower than a Co-60 facility. Moreover, its operation is much simpler and safe.

The main objectives in phase 2 (FY2006-2008) are:

1) To specify the advantage of radiation processing in modification of natural polymers
2) To carry out promotional activities of the developed product to market
3) To develop new products on Radiation Processing of Natural Polymers

3. Project Review FY2006

The current project aims at wider application of electron accelerator in industry. The project also aims at implementing practical application with the hope of benefiting the participating countries through not only the information exchange but also joint study by sharing experimental data. The proposed program will promote the use of low energy electron accelerator. However, the high energy electron beam accelerator as well as γ-rays will also be encouraged.

The project consists of two parts on the technical aspect of radiation processing of natural polymer, i.e. a) Radiation crosslinking of hydrogel of natural polymers for healthcare and environment and b) Radiation degradation of natural polymers for plant growth.

The project leader in many member countries except Malaysia and Japan was changed to the expert on radiation processing of natural polymers.

The results and outcome of the workshop are:

a) A National Executive Management Seminar on Application of Electron Accelerators for Radiation Processing of Natural Polymer was held on the first day of Workshop in Malaysia and attended by 120 participants from industries, universities, research institutes and members of FNCA Workshop (Fig. 1).

Fig. 1 FNCA Workshop in Malaysia, December 2006.

b) An exhibition that consists of posters and product display was held and participated by China, Japan, Indonesia, Korea, Malaysia and Vietnam.

c) The workshop has prepared a table on current status of research and development on radiation processing of natural polymer in each FNCA member country. The status of R&D is categorized into three stages namely laboratory (L), developmental (D) and commercial (C). Workshop agreed to further collect and compile data on the products that have been successfully commercialized.

d) The subjects and participating countries were selected as follows:

1) Radiation degradation of natural polymers

Material	Agriculture	Medicine and Healthcare
Alginate	Vietnam	
Chitosan	Indonesia, Thailand, Vietnam, China	China, Indonesia, Korea, Malaysia, Thailand, Vietnam
Carrageenan	Philippines,	

2) Radiation modification of polysaccharide and its derivatives

Material	Hydrogel for wound dressing	Hydrogel for medical, sanitary use
Chitosan	China, Vietnam	Korea, Malaysia
Carrageenan	Indonesia, Korea, Philippines	
Starch	Malaysia (Sago), Thailand (Cassava)	
CMC		Japan

e) Based on the success by many FNCA member countries in the development and commercialization of radiation crosslinking of hydrogel from natural polymer and radiation degraded natural polymer for agriculture applications, a manual on radiation processing of natural polymer was proposed. The participants were agreed to the proposed preparation of FNCA Guidelines on Development of Hydrogel and Oligosaccharides by Radiation Processing. The Guidelines consist of general description on radiation processing of natural polymer and the specific process for the crosslinking of hydrogel and degradation of natural polymer.

f) All participating member countries welcome the offer made by Japan to provide expert mission to assist FNCA member countries in relation to radiation processing of natural polymer. The mission will visit at least two countries consecutively for duration of 2-3 days per country in February 2007 within the fiscal year 2006.

g) Workshop has also requested FNCA representative from Japan to discuss with the IAEA/RCA representative on the possible cooperation in the future activity.

h) With regards to the question of patent within the FNCA member states, all participating member countries agreed that such issue is a complex one and it requires time and further deliberation in future.

i) The experience of FNCA member states in the commercialization of their R & D either a success or failure will be documented. The data will be evaluated and discussed in the next FNCA workshop in 2007. In view of the time constraint on the implementation of current project activities, the workshop proposed that the FNCA program on the Application of Electron Accelerator be extended for another year until 2008.

j) Three year plan of EB Workshop in phase 2 (Table 1) was proposed and accepted as follows:

FY 2006: “Radiation crosslinking and degradation” in Malaysia
FY 2007: “Economic evaluation” in Vietnam
FY 2008: “Technical transfer to end user” in China

4. Achievement of Phase 1 (FY 2001 ~ FY 2005)

Through the following workshop in phase 1, the experience, data and technical information on the application of low energy electron accelerators derived from this project are shared with other members of the FNCA countries (Fig. 2 ~ Fig. 5).

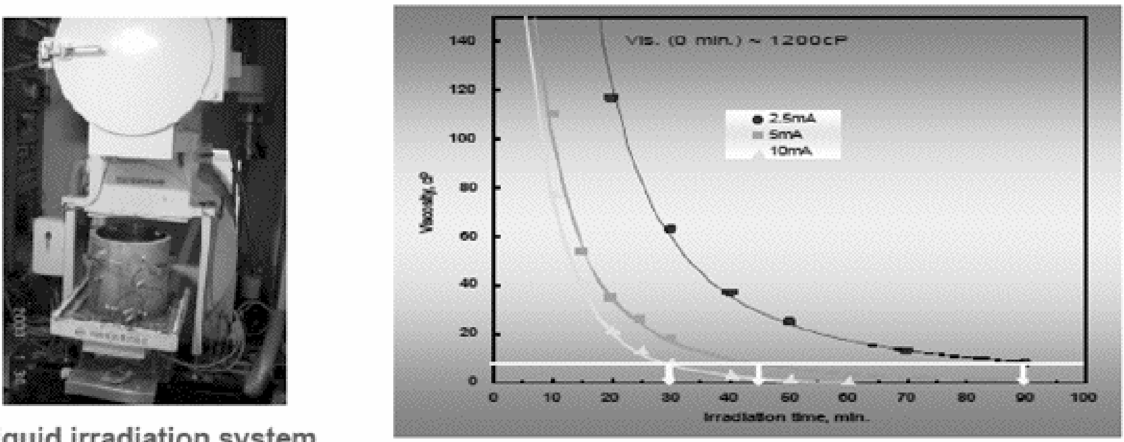
1) FY 2002: Liquid sample (degradation of natural polymer) at JAERI-Takasaki (Japan)
2) FY 2003: Solid sample (crosslinking of thin film) at MINT (Malaysia)
3) FY 2004: Gas sample (flue gas) at CAEP/Tsinghua University (China)

4) FY 2005: Waste water (textile wastewater) at KAERI (Korea)

The proceedings of these workshops were published as JAERI-Conf 2002-013, 2003-016, 2004-007, 2005-005 and JAEA-Conf 2006-005.

Table 1 Three Year Plan of the FNCA Project on Application of Electron Accelerator.

	FY2006	**FY2007**	**FY2008**	Notes
1. Overall Schedule	The 7th FNCA Meeting (November 25, 27, Kuantan, Malaysia) The 8th CM (February 7-9, 2007, Japan)	The 8th FNCA Meeting (Autumn 2007, Japan) The 9th CM (February 2008, Japan)	The 9th FNCA Meeting (?) The 10th CM (February 2009, Japan)	
2. Electron Accelerator Workshop	December 2006, Malaysia (December 12-16, 2007)	October 2007, Vietnam	Autumn, 2008 (?)	Launch of New Project from FY2009
1) Main Subject of Workshop	**Radiation Crosslinking and Degradation of Natural Polymers**	**Economic Evaluation**	**Technical Transfer to End User**	
2) Contents of Workshop	• Program formulation • Preparation of Table on Current Status of R&D • Information Exchange on Technical Transfer • Open Seminar and Exhibition	• Study on Irradiation System for Agriculture and Aquaculture • Compile the Data for Commercialized Products • Cost Evaluation • Open Seminar and Exhibition	• Study on Technical Transfer to End User • Study on New Application • Evaluation of project and Proposal of New Project • Open Seminar and Exhibition	
3. Expert Mission	Philippines and Thailand (February 2007)	Vietnam and Malaysia (July 2007)		
4. Preparation of Guideline	Outline and data collection	Preparation of documents	Publication	
5. Database of Irradiation Facilities (EB and γ)	Update	Update	Update	
Participating Countries : Bangladesh, China, Indonesia, Korea, Malaysia, the Philippines, Thailand, Viet Nam and Japan (total 9 countries)				



Liquid irradiation system using low energy EB (250keV, 10mA)

Effect of irradiation time & beam current on viscosity of alginate solution (5g/dL)

Fig. 2 FY 2002: Liquid sample (degradation of natural polymer) at JAERI-Takasaki (Japan).

Fig. 3 FY 2003: Solid sample (crosslinking of thin film) at MINT (Malaysia).

Fig. 4 FY 2004: Gas sample (flue gas) at CAEP/Tsinghua University (China).

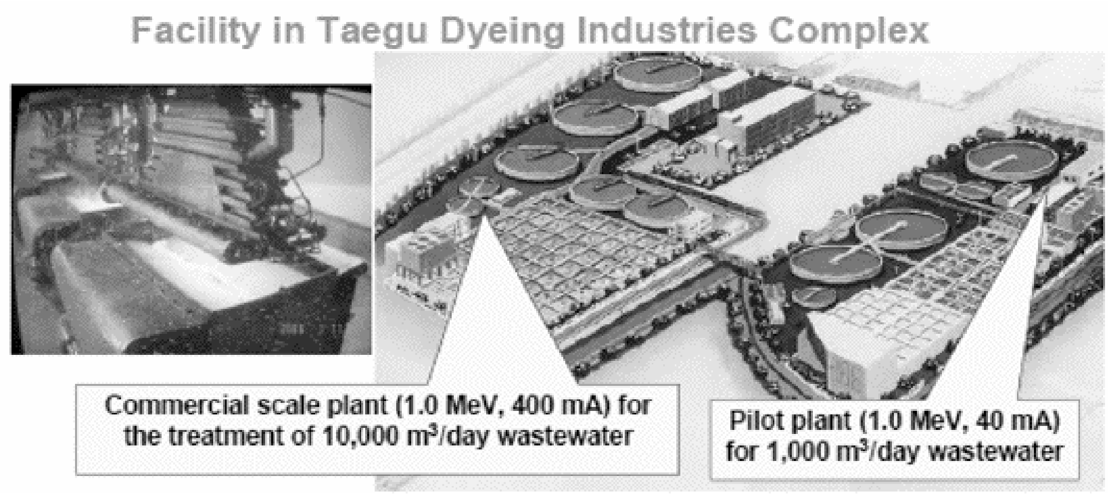


Fig. 5 FY 2005: Waste water (textile wastewater) at KAERI (Korea).

1.2 Provisions of FNCA Guidelines on Development of Hydrogel and Oligosaccharides by Radiation Processing

Hisaaki Kudo

Nuclear Professional School, Graduate School of Engineering, The University of Tokyo

Abstract

For FNCA Guideline of electron beam industrial application, this brief report provides examples of protocol and cost analysis, in the case of carboxymethyl cellulose (CMC)-dry gel, where contribution is allocated to Japan.

1. Introduction

As agreed last year at the workshop in Kuala Lumpur, Malaysia December 2006, this group shall prepare a written material as a product of this FNCA activity, namely, a guideline. The guideline was tentatively named as “FNCA Guidelines on Development of Hydrogel and Oligosaccharides by Radiation Processing”(to be arranged). The structure and contents (tentative) of the guideline is given somewhere else 1). The main body consists of Part 1 (generic aspects of radiation processing, etc.) and Part 2 (specific, crosslinking section and degradation section). In regarding with how to prepare the Guideline, to show technical details (know-how, protocol) is planned. Another important point is cost-analysis, compared with methods that do not use radiation, such as chemicals, or enzymes, etc. There are various materials and applications of radiation processing of natural polymers, and for each material/application, responsible country is allocated. This report is a trial to provide examples of protocol and cost analyses in the case of carboxymethyl cellulose (CMC)- dry gel, where contribution is allocated to Japan.

2. Example of Protocol

For Part 2 (specific), the protocols for each material should be shown. However, if we consider a material, many applications can be possible; in the case of CMC, such as bed-sore-mat, coolant, and dry-gel. Accordingly, the protocol differs somewhat from one to another. Then hereafter the protocol in the case of CMC-dry gel are described as following 2~6), though whether the items are sufficient or not (less sufficient or over sufficient) should be further considered (the following structure is based on the initial proposal 1)):

2.1 Raw material

2.1.1. Suppliers, grade and material history

Suppliers: From Daicel Co. Ltd.

Grade: Analytical grade

Material history: As received
2.1.2. Visual examination: Examined
2.1.3. Componential analysis: Undone
2.1.4. Others: Degree of Substitution (DS) is 1.3-1.4

2.2 Pre-treatment

2.2.1. Grinding or pulverization
  Grinding: Undone
  Pulverization: As received
2.2.2. Dissolution: Aqueous solution of 20wt% is prepared.
2.2.3. Others: Nothing special

2.3 Irradiation

2.3.1. Irradiators/Facilities: Co-60 γ-rays at JAEA Takasaki
2.3.2. Packaging: In air
2.3.3. Dose rate: 10kGy/h
2.3.4. Dose: 5kGy
2.3.5. Temperature: Room Temperature
2.3.6. Others: Electron beam (1mA at 1MeV) is also appropriate for irradiation.

2.4 Post treatment

2.4.1. Visual examination: Examined
2.4.2. Componential analysis: Undone
2.4.3. Product performance evaluation: Undone, but swelling ratio etc. was tested during developing process.
2.4.4. Others: Sliced, and drying below 80 ˚C for 3-24h (depending on thickness) in air, for example, 3h for 1mm-thikness, 24h for 1cm-thickness

2.5 Products

2.5.1. Grinding or pulverization
  Grinding: Nothing special
  Pulverization: Pulverized into 1-3mm diameter particles (CMC dry gel)
2.5.2. Dissolution: Not specified
2.5.3. Packaging: Not specified
2.5.4. Description: Nothing special
2.5.5. Instruction manual: Manufacturer had prepared
2.5.6. Others: Nothing special

2.6 Strategies

2.6.1. Safety considerations: Material Safety Qualification Tests Required

2.6.2. Environmental considerations: Biodegradability
2.6.3. Cost analysis: 100Japanese Yen (JPY)/100g-piece (discussed in later section)
2.6.4. Comparison with other procedures/products: Non-radiation-method poly(acrylic acid) (PAAc) products/ Radiation method is expensive
2.6.5. Publications/Patents: Scientific Publications and Patents (in United States and Japan)7)
2.6.6. Advertisement for end-users: Exhibitions, Techno-information events
2.6.7. Technology transfer: JAEA made technology-transfer to end-users
2.6.8. Marketing: Exhibitions, Techno-information events, Consultations
2.6.9. Others: Nothing special

2.7 Others: Nothing special

These inputs should be put together in tables of Excel™ sheet; it may be convenient to assure uniformity among different materials/applications. Expected is that such or similar description of protocol will be contributed by other participating countries for each application.

3. Example of Cost Analysis 2)

It is obvious that many factors influence on cost analyses. Even if we focus on a specific material, factors can vary widely depending on application. Therefore, similarly to the protocol, cost analyses should be made by application (not by materials). For the case of CMC-dry gel, cost for each step is given as below:

(1) Raw Material: 600JPY/kg-polymer (ca. 5US dollar; 1USD = ca.120JPY)
(2) Pre treatment: 0.4JPY/kg-Polymer, as 20wt% aqueous solution is prepared, 4kg (4liter) water is necessary per kg-polymer. Typical fare of water is given in Table 1 (though this fare table is not for industrial use) for the case of Tokai-mura, Ibaraki-prefecture, Japan. Although the unit cost of water considerably depends on the contract (diameter of the faucet) and usage quantity, it may be reasonable to assure that 1m3 cost ca.100JPY (unit cost of water is 0.1JPY/kg-water).
(3) Irradiation: 400JPY/5kg-paste (1kg-polymer with 4kg-water), as the dose is 5kGy and unit cost is 80JPY/kg.
(4) Post treatment: Cost is not available, as the method is (simply) to slice and dry.
(5) Total cost of radiation-method: 1000JPY/kg-product; the difference between the total cost and summation of each step may be the manufacture's profit.
(6) Product performance: Excellent water absorbent
(7) Other method: The method to use PAAc has been known, and its cost is 350JPY/kg-product. A comparison shows that radiation method is more expensive.
(8) Stage of radiation method: it is commercialized but suspended.

Again, a competitive method using PAAc costs around 350JPY/kg-product in contrast with radiation-method of 1000JPY/kg-product. Therefore, though the radiation method is technically established and commercialized, its status is suspended. The analyses above are summarized as Table 2. Expected is that such or similar description of cost analysis will be contributed by other participating countries for each application.

Table 1 Fare of water (in the case of Tokai-mura, Ibaraki-prefecture, Japan)

Diameter of faucet in mm	Base Fare		Additional Fare	
	Quantity in m^3	Fare in JPY	Quantity in m^3	Fare in JPY
13	less than 20	2310	more than 21	147 per m^3
20		2415		
25		2520		
30		3570		178.5 per m^3
40		4830		
50		5985		
75		9030		199.5 per m^3
100		12075		
150		17850		

1USD = ca.120JPY (as of 2007)

Table 2 Example of cost analyses for Carboxymethyl cellulose as dry gel (Japan)

Radiation effects		Crosslinking
Material		CMC
Responsible Country		Japan
Application		Dry Gel
Raw Material		600JPY/kg-Polymer
Pre-treatment	Method	20wt% aqueous solution
	Cost	0.4JPY/kg-Polym
	Unit Cost	0.1JPY/kg-Water
Irradiation	Dose	5kGy
	Cost	400JPY/5kg-Paste
	Unit Cost	80JPY/kg
Post-treatment	Method	Slice and Dry
	Cost	Not available
	Unit Cost	
Total cost of radiation-method		1000JPY/kg-Product
Product performance		Excellent Water Absorbent
Other method	Method	PAAc
	Cost	350JPY/1kg-Product
	Comparison	Radiation method is expensive
Stage of radiation-method		Commercialized, but suspended

4. Future Schedule

This report provides the protocol and cost analysis for CMC-dry gel, which is necessary to complete the Guideline. Similar contributions of protocols and cost analyses for other applications of natural polymers are highly expected. As one-year extension of this project was approved in Coordinators Meeting; deadline of the guideline is 2009 March. By the next workshop at Shanghai, China in 2008 autumn, data collection, compilation and draft preparation should be made, and by the end of Japanese fiscal year 2008 (2009 March) the final draft must be completed. The editors are ready to tackle this challenging task.

ACKNOWLEDGEMENTS: The author thanks Dr. F. Yoshii of Japan Atomic Energy Agency (JAEA), Quantum Beam Science Directorate, for valuable support.

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2. Progress in Radiation Processing of Natural Polymer

2.1 Hydrogel Wound dressing

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2.1.1 Synthesis of Hydrogels by Radiation and Their Applications in Korea

Young-Chang Nho, Youn-Mook Lim

Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute

Abstract

The radiation can induce chemical reaction to modify polymer under even the solid state or in the low temperature. The radiation crosslinking can be easily adjusted by controlling the radiation dose and is reproducible. The finished product contains no residuals of substances required to initiate the chemical crosslinking which can restrict the application possibilities. In these studies, hydrogels from a mixture of poly(*N*-vinyl pyrrolidone) (PVP), Carrageenan, poly(ethylene glycol) (PEG) and antibacterial agent were made by γ-rays irradiation for wound dressing. The physical properties such as gelation, water absorbability and gel strength were examined to evaluate the hydrogels for wound dressing. The applications of hydrogels in Korea were described.

1. Synthesis of Hydrogels for Wound Dressing

1.1 Introduction

Hydrogels are three dimensional, hydrophilic, polymeric networks capable of imbibing large amount of water or biological fluid. The network is composed of homopolymer or copolymer, and is insoluble due to the presence of chemical crosslinks (tie-points, junctions), or physical crosslinks, such as entanglements or crystallites. Hydrogels resemble natural living tissue more than any other class of synthetic biomaterials due to their high water contents and soft consistency which is similar to natural tissue. The chemical structures of the polymer affect the swelling ratio of the hydrogels. Hydrogels containing hydrophilic group swell to a higher degree compared to those containing hydrophobic groups. The interaction responsible for water sorption by hydrogels includes the process of hydration, which is connected with the presence of such chemical groups as -OH, -COOH, $-CONH_2$, -COHN-, $-SO_3H$, and the existence of capillary areas and differences in osmotic pressure. The force that makes hydrogel dissolve impossibly is connected with the existence of covalent bonds between individual polymer chains although they may also have a character of electrostatic or hydrophobic interactions.

Hydrogels to be used as burn wound dressings were invented by Rosiak et. al. and they have many interesting properties: immediate pain control; easy replacement; transparency to allow healing follow up; absorb and prevent loss of body fluids; barrier against bacteria; good adhesion; good handling; oxygen permeability; control of drug dosage and so on. They usually show good biocompatibility in contact with blood, body fluids and tissues. Hence, they are often used as contact lenses, burn wounds dressings, artificial cartilages or membranes as well as to coat the materials being applied in the contact with the living organism, e.g., coating of the surface of catheters, electrodes, vascular prostheses etc. Because of their ability to swell as well as to release trapped particles into the surrounding medium, hydrogels are often used as drug delivery systems. Gamma or electron beam irradiation, especially if combined with simultaneous sterilization of the product is a very convenient tool for preparation of hydrogels.

PVP hydrogels have excellent transparency and biocompatibility. PVP is used as a main component of temporary skin covers or wound dressings. Carrageenan is a seaweed polysaccharide and backbone of the polymer consists of alternating α-1,3-linked D-galactopyranose and β-1,4-linked 3,6-anhydro-D-galactopyranose. PEG is a colorless, transparent, and odorless sweet syrupy liquid. It is a humectant, i.e. "draws moisture". It is used in creams, lotions, facial treatments, masks and other body care products.

We are exposed to harmful microorganism such as bacteria and molds everyday. Irradiation is recognized as a very suitable tool for formation of hydrogels. Radiation process has various advantages such as easy process control, possibility of combining hydrogel formation and sterilization in one technological step, no necessity to add any initiators and crosslinkers possibly and difficult to remove. They make irradiation the method of choice in the synthesis of hydrogels.
In this work, attempts were made to prepare the hydrogels for wound dressing that consisted of PVP, Carrageenan, and PEG. The physical properties, such as gelation, swelling, were examined to evaluate the usefulness of hydrogels for wound dressing. The process for commercialization of hydrogels in Korea was described.

1.2 Experimental

1.2.1 Materials

Poly(*N*-vinyl pyrrolidone) (Mw. 1.3 × 10^6) was supplied by the Aldrich Chemical Company(WI, USA). Carrageenan and PEG were supplied by MSC (Korea) and Showa Company(Japan). The polyurethane membrane was supplied by the domestic maker. The polymers were used without further purification. Distilled water was used as a solvent in all experiments.

1.2.2 Preparation of hydrogels

PVP, Carrageenan and PEG was dissolved in distilled water of 90 ℃, and then cast to hydrogel sheet. The total concentration of PVP/Carrageenan/PEG was 4 ~ 10 wt%. The hydrogel sheet was cut to various sizes (5 x 5 cm, 5 x 10 cm, 10 x 10 cm, 10 x 20 cm, 20 x 20 cm). The cut hydrogel sheet was covered with the polyurethane membrane with adhesives on the one side. The hydrogels were packed with the laminate film which consisted of aluminum and plastics. The packed hydrogels were crosslinked and sterilized by 60-Co γ-rays irradiation.

1.2.3 Gel content

The gel content of the hydrogels was measured by extraction in hot distilled water of 50 ℃ for 48 h and vacuum dried at 50 ℃ for 48 h until they reached constant weight. The gel content was defined as in eq. (1); where Wd is the dried gel weight after extraction, and Wi is the initial weight of the polymer.

$$\text{Gel (\%)} = 100 \times Wd/Wi \qquad (1)$$

1.2.4 Degree of swelling

The degree of swelling could be described as water absorbability of the hydrogels. The gel samples were immersed in distilled water for 48 h at room temperature until the gel reached the equilibrium state of swelling. After the water on the surface of the swollen gels was removed with cellulose paper, the mass was determined. The dried gels were obtained by drying at 50 ℃ until they reached constant weight. The degree of swelling was defined as in eq. (2) ; where Ws is the weight of the swollen gels and Wd is the dried gel weight.

$$\text{Water absorbability (\%)} = 100 \times (Ws - Wd)/Wd \qquad (2)$$

1.2.5 Gel strength

A cylindrical hydrogel specimen, with a length of 4.0 mm and a diameter of 12 mm, was used for the compressive strength tests. The compressive strength tests were conducted by Instron model 4400 Universal testing machine at room temperature. A cylindrical hydrogel specimen was placed on the base and the probe was lowered until contact was made. The prove was then lowered at 10 mm/min until 70 % relative deformation, and then raised. The compressive strength used in this experiment is the value measured at 70% relative deformation. The mechanical properties of the hydrogels were obtained by determining the compressive strength.

1.2.6 Degree of water evaporation

The hydrogels of PVP/Carrageenan/PEG were prepared by gamma irradiation dose of 25 kGy. The degree of water evaporation was evaluated according to the time. The solid concentration of PVP/Carrageenan/PEG solution was 7 wt%. The hydrogels were placed on the grill of the apparatus which was set at 37˚C, and 70 % of relative humidity.

1.2.7 Healing test of the hydrogels for wound

Rats (200 g) were anesthetized with diethyl ether and ketamine, and then the dorsal fur was removed with electric clippers. The skin was cleansed with H2O2. After two wounds of 1 cm diameter in the dorsum were prepared, the skin of rats was disinfected with povidone iodine topical solution. Wounds of 1cm diameter formed in the skin on the backs of rats were covered with the hydrogel samples (1.5×1.5×0.3 cm) while no covering on the other side for checking a healing effect of the synthesized hydrogels. The synthesized hydrogels in these experiments were also compared with commercial urethane membrane to mimic the human skin. PVP/Carrageenan/PEG hydrogels made by γ-ray irradiation were used for the healing test of rats. Both the synthesized hydrogels and commercial urethane membrane were replaced with new ones every 3 days. Healing was evaluated as the percentage of the healed area from the original wound area. The healing test was repeated five times for each case, and then the healing effect was evaluated. At a certain postoperative day, macroscopic observation of wound status was made. This observation was repeated daily for 15 days. After all experiments, all the rats were sacrificed with an overdose of kentamine.

1.3 Results and discussion

1.3.1 Gel content

Polymer gels are created from polymer networks and solvents, i.e., the polymer network envelopes the liquid and prevents it from flowing out. In other words, the gel polymer network acts as a container that keeps a large amount of liquid. Some gels are crosslinked chemically by covalent bonds, whereas others are crosslinked physically by hydrogen or ionic bonds and by the physical entanglement of polymer chain. In general, gels formed by chemical bonding are irreversible gels, since they cannot be dissolved again. However, moderated heating can reversibly dissolve a physically crosslinked gel. Many natural polymer gels fall under the class of physical gels. The process of gelation upon cooling can be named as sol-gel phase transition. Carrageenans are linear, sulfated polysaccharides of the type (AB)n consisting of β-1,3-linked D-galactose and α-1,4-linked 3,6-anhydro-D-galactose. In general, carrageenan is known to form thermally reversible gels as a function of temperature and gel-inducing agents. The sol-gel phase transition of κ-carrageenan solutions occurs as a result of coil-to-helix conformational transition upon cooling. Hydrogels can be obtained by radiation techniques either by irradiation of solid polymer and aqueous polymer of monomer and polymer. In these studies, we prepared a series of hydrogels from γ-irradiation of PVP/PEG/carrageenan.

Figure 1 shows the gelation behavior of PVP/PEG/carrageenan hydrogels as a function of content of PEG. The content of carrageenan was fixed as 3wt%. The total concentration of PVP/PEG/carrageenan was in the range of 4 ~ 10 wt%. Gel content increased as the concentration of PVP increased, while gel content decreased as the concentration of PEG increased.

Figure 2 shows the swelling behavior of the hydrogels that were synthesized by gamma irradiation. Degree of swelling was in the range 4,000~16,500 %. Degree of swelling increased as concentration of PEG in PVA/PVP/PEG increased. The swelling percent was inversely proportional to the gel percent.

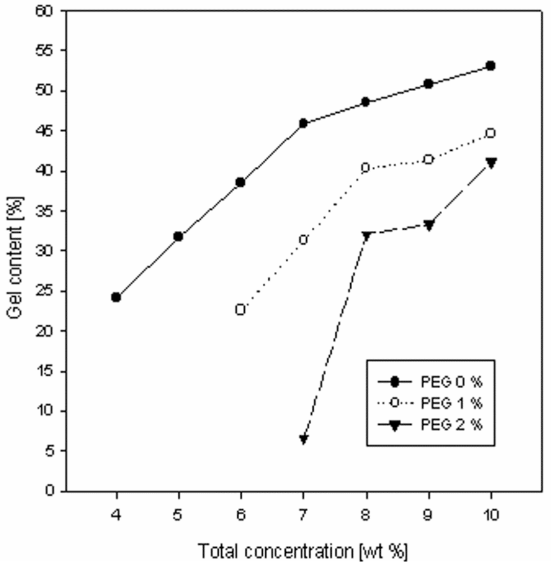

Fig. 1 Gel content of PVP/PEG/carrageenan hydrogels as a function of total solution concentration.

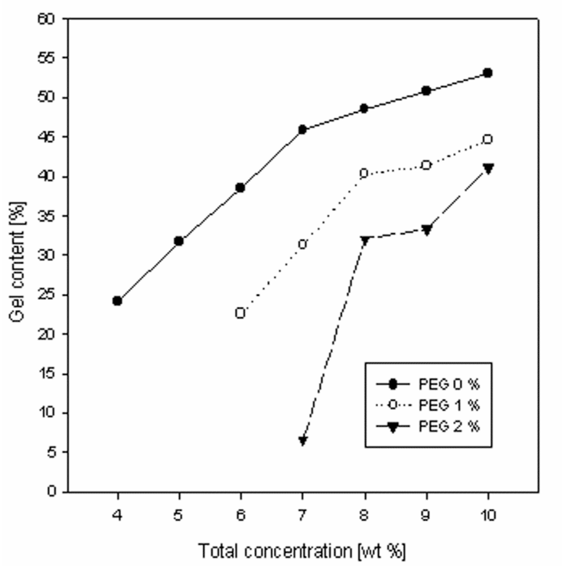

Fig. 2 Degree of swelling of PVP/PEG/carrageenan hydrogels as a function of total solution concentration.

Crosslinking by radiation transforms a linear polymer into a three-dimensional molecule, resulting in a significant increase in molecular mass, lower solubility in organic solvents, and improve mechanical properties. Degradation results in a decrease in molecular mass, and has the opposite effect on the physical properties of the polymer. Crosslinking and degradation occur simultaneously. However, the ratio of their rates depends on the chemical structure of the polymer, its physical state, and the irradiation state. Polymers are generally divided into those that predominantly crosslink and those that predominantly degrade. PVP are easily crosslinked in their homogeneous mixture with water. A natural product such as PEG tends to degrade on irradiation. Therefore, the addition of PEG in PVP solution results in the decrease in gelation of hydrogels.

1.3.2 Degree of water evaporation

To systematically measure evaporative water loss for the synthesized hydrogels, they were placed on the grill of water bath which is kept at a temperature of 37 ℃ and 70 % of relative humidity. Evaporative water loss was measured gravimetrically for the hydrogels which involve various contents of PEG, with or without the polyurethane membrane on of the surface of the hydrogels. The hydrogels were prepared by irradiation dose of 25 kGy. The evaporative water loss for the hydrogels was shown in Figure 3. Evaporative water loss continued to rise rapidly up to 5 h, and then leveled off. No significant differences were observed in the evaporation velocity between the compositions of hydrogels. However, the polyurethane membrane reduced the loss of water greatly. From this data, we can understand that it is critical to have the skin layer in hydrogels for the purpose of reducing the drying of hydrogels.

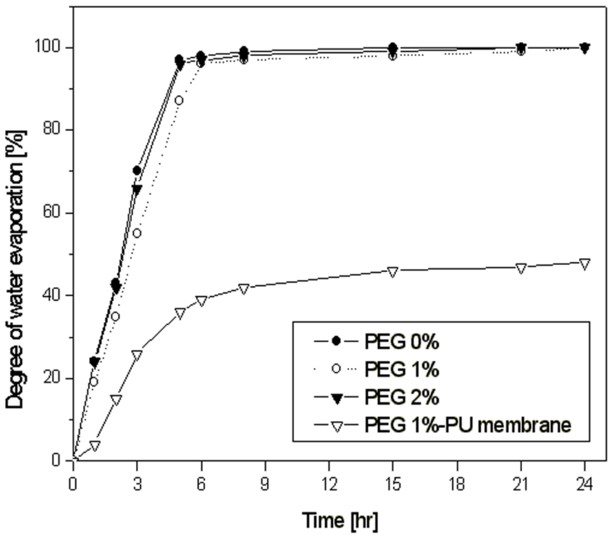

Fig. 3 Degree of water evaporation of PVP/PEG/carrageenan hydrogels with or without PU membrane as a function of time (total concentration 7 wt%).

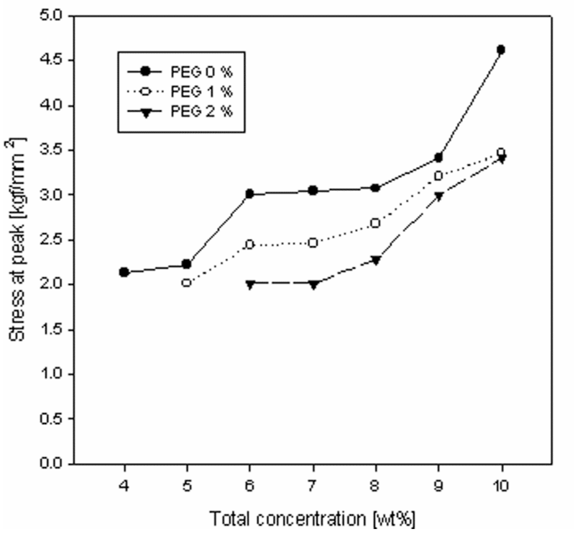

Fig. 4 Stress of PVP/PEG/carrageenan hydrogels as a function of total solution concentrations.

1.3.3 Gel strength

The compressive strength used in this experiment is the value measured at 70 % relative deformation. The gel strength of the hydrogels was obtained by determining their compressive strength. We measured the compressive strength for the hydrogels which were made by gamma irradiation (Figure 4). The compressive strength increased as the concentration of PEG in PVP/ carrageenan/PEG decreased. The content of PEG dose had a great influence on the compressive strength of hydrogels. It was shown that the compressive strength of hydrogel was proportional to the degree of gelation.

1.3.4 Healing test of the hydrogels for wound

A wound to the skin may pierce two layers, the epidermis and dermis as well as damaging appendages. The epidermis is repaired in three phases, migration of cells, proliferation and maturation, while new connective tissue is found in the dermis. PVP/ carrageenan/PEG hydrogels made by 60-Co γ-ray irradiation were used for the healing test of rats (Figure 5). Wound of 1 cm diameter formed in the skin on the backs of rat was covered with the hydrogel, on the other hand, with commercial urethane membrane to mimic the human skin. At the certain postoperative day, macroscopic observation of wound status was made. The wound with non-dressing dried quickly and was scabbed. The wound covered with commercial urethane membrane didn't dry as much as the wound of non-dressing and wasn't scabbed. However, the PVP/ carrageenan/PEG hydrogel had better curing effect than non-dressing and commercial urethane membrane. The observation was continued totally for 15 days.

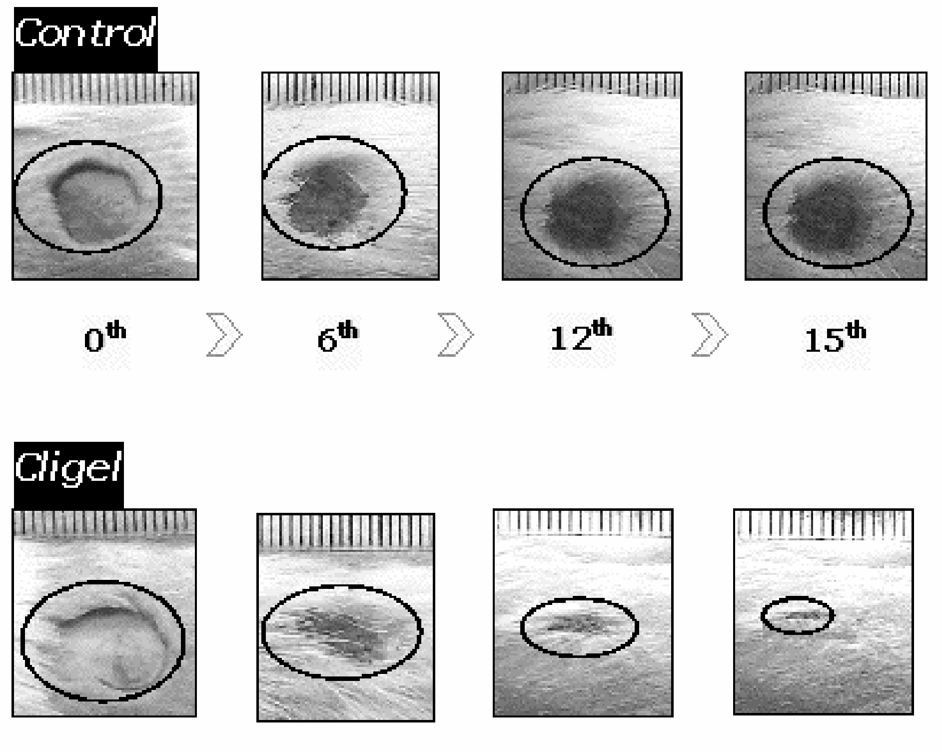

Fig. 5 Healing process of wound using (a) membrane (control), (b) Cligel.

1.4 Conclusions

In this work, attempts were made to prepare hydrogels for wound dressing which consisted of PVP/carrageenan/PEG. The hydrogels were made from physical crosslinking of carrageenan, and then chemical crosslinking of Co-60 γ-ray irradiation. Gel content and gel strength increased as concentration of PEG in PVP/ carrageenan/PEG decreased. Swelling degree increased as the concentration of PEG in PVA/PVP/PEG increased. Evaporative water loss continued to rise rapidly up to 5 h, and then leveled off. No significant differences were observed in the evaporation velocity between the compositions of hydrogels. However, the polyurethane membrane reduced the loss of water greatly. From this data, we can understand that it is critical to have the skin layer in hydrogels for the purpose of reducing the drying of hydrogels. The PVA/PVP/PEG hydrogel had better curing effect than no dressing and commercial urethane membrane.

2. Effect of Glycerin of Absorption of Wound Exudate of PVA Hydrogels

2.1 Experimental

PVA (Mw: 8.5 × 104) was supplied by Aldrich Chemical Co.. The water used as a solvent in all experiments was distilled water. Glycerin was also supplied by Aldrich Chemical Co.. PVA/glycerin was dissolved in distilled water of 95 ˚C, and the solutions were then poured into Petri dish at room temperature. The solution was kept at room temperature for 24 h in order to remove air bubbles. Hydrogels from a mixture of glycerin and PVA were made by "freezing and thawing", or exposing 60-Co γ-rays. PVA: glycerin ratio was in the range of 9: 1 ~ 7:3, and the solid concentration of the total PVA/glycerin solution was 25 wt%. Each cycle of "freezing and thawing" involved lowering the temperature to -76 ˚C, standing at this temperature for 10 min, then raising the temperature to room temperature.

2.2 Results and discussion

Figure 6 shows gelation behavior of the hydrogels which were synthesized by "freezing and thawing" and irradiation of γ-ray. PVA/glycerin ratio was in the range of 9:1 ~ 7:3, and the solid concentration of the total PVA/glycerin solution was 25wt %. Gel content increased as glycerin amount in PVA/glycerin decreased. It is well known that this procedure of PVA results in the formation of crystallites that serve as physical crosslinks to render the material insoluble in water. Gel content (%) in this experiment was continuously decreased as the amount of glycerin in PVA/glycerin increased because PEG is not crosslinked by "freezing and thawing" or radiation. Figure 7 shows the swelling behavior of the same hydrogels as shown in Figure 1. The swelling percent was inversely proportional to the gel percent because crosslinking density increases with increasing gelation.

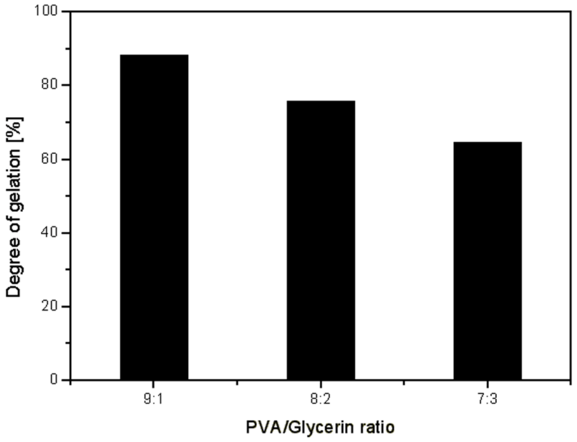

Fig. 6 Gelation of PVA/Glycerin hydrogels as a function of PVA/Glycerin ration.

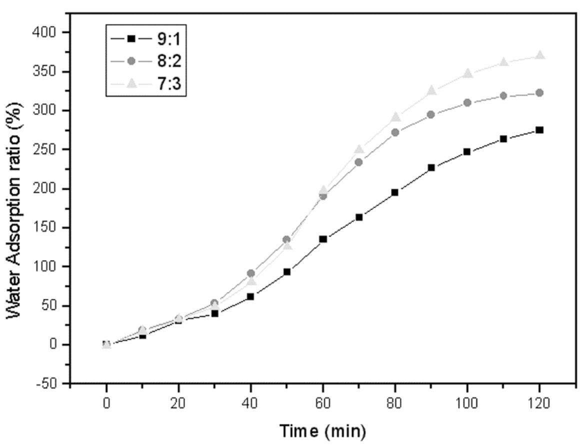

Fig. 7 Water adsorption ratio of PVA/Glycerin hydrogels as a function of time.

Figure 7 shows the swelling behavior of the same hydrogels as shown in Figure 1. The swelling percent was inversely proportional to the gel percent because crosslinking density increases with increasing gelation.

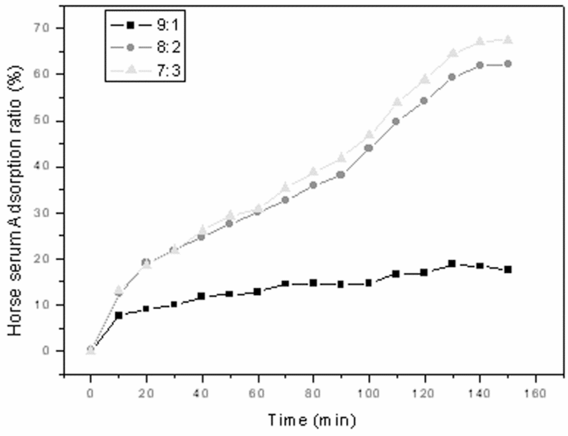

Fig. 8 Horse serum adsorption ratio of PVA/Glycerin hydrogels as a function of time.

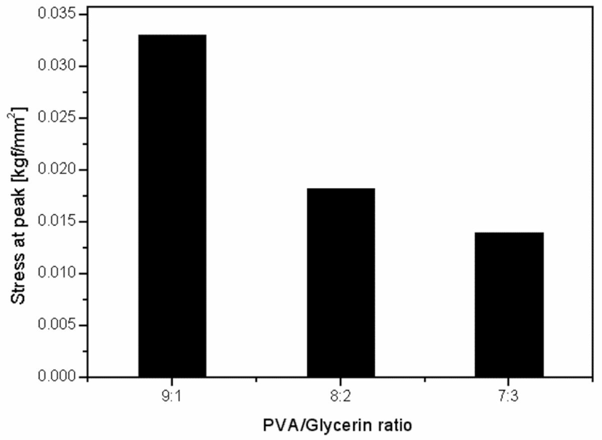

Fig. 9 Stress of PVA/Glycerin hydrogels as a function of PVA/Glycerin ratio.

3. Market Situation of Hydrogels in Wound Dressing in Korea

3.1 Benefit of hydrogels in wound dressing manufactured by radiation processing

It is recognized that radiation processing is well established in several industrial areas and that the success of these applications is based primarily on the technical and economical benefits. By the uses of radiation processing, volatile or toxic chemicals can be avoided, and strict temperature or moisture controls may not be needed. Irradiated materials are useable immediately after processing, and Radiation processing (curing, crosslinking etc) is generally fast and efficient. Hydrogels have many interesting properties: immediate pain control; easy replacement; transparency to allow healing follow up; absorb and prevent loss of body fluids; barrier against bacteria; good adhesion; good handling; oxygen permeability; control of drug dosage and so on. They usually show good biocompatibility in contact with blood, body fluids and tissues

3.2 Circumstance of hydrogels in wound dressing in medical market

Over the years, the market has moved from traditional (gauze based) products to advanced (moist wound healing) products. Various types of wound dressing for a range of uses are on the Korean market, following recent clearance from the Korean Food and Drug Administration (KFDA). It is known that wound dressing is indicated for venous stasis ulcers, diabetic ulcers, pressure sores, blisters, superficial wounds, abrasions, lacerations and donor sites. Main products on the markets are Medifoam (Ildong Pharmaceutical Co. Ltd., Korea), Duoderm (Convatec, A Bristol-Myers Squibb Company, Canada), Hydrosorb and Dermaplast (HARTMANN, Germany) Cligel (Hyundai Pharmaceutical Co. Ltd.). Among them, Medifoam made from hydrophilic polyurethane has the highest market share in the field of new type of wound dressing in Korea. The dressing is absorbent and does not stick to the skin. It is designed to absorb five times its own weight of wound exudate (fluid) by hydrophilic action. The properties between polyurethane foam and hydrogel dressings are compared. The absorption of wound exudate or water by hydrogel dressing is very low in comparison with polyurethane foam dressing. It is necessary to make an effort to enhance the absorption of wound exudate as well as to reduce the foul smell after detachment of hydrogel from wound. We tried to do some experiment to enhance the wound exudate of hydrogel.

4. Commercialization Process of Hydrogels for Wound Dressing in Korea

Anyone who intends to manufacture drugs or medical devices shall get a license from the Commissioner of the Korea Food and Drug Administration for each product, and each product shall be approved or notified. It is necessary to prepare the written reports as fellows.

1) Data on physico-chemical properties.
2) Data on Stability
3) Animal and clinical test
4) Data on the manufacturing processes, packaging, containers, cautions on handling, etc.
5) Data on batch analysis for hydrogels
6) Review process

The KFDA Commissioner shall handle the submitted “Registration of Hydrogel Manufacturing. A site inspection shall be notified to an applicant 20 days before inspection.

After a company submits the application for the registration of hydrogels manufacturing, appropriateness of submitted data shall be reviewed within 17 weeks. The KFDA Commissioner shall issue a registration certificate and notify publicly on the website provide that the submitted data and the result of the site inspection are deemed appropriate.

2. 1. 2 Pilot Scale Test and Commercialization of Sago Hydrogel for Face Mask and Wound Dressing

Khairul Zaman Hj. Mohd Dahlan, Kamaruddin Hashim, Zulkafli Ghazali

Malaysian Nuclear Agency

1. Introduction

Sago hydrogel has been successfully developed at laboratory scale and transferred to a local company for commercialization. Currently, sago hydrogel is used for making facial mask and is marketed as cosmetic skin care product. The application of sago hydrogel for wound dressing is currently undergoing a necessary process for clinical evaluation and official approval as pharmaceutical medical device. The following are the chronological events that lead to the commercialization of sago hydrogel.

1997 ~ 2002
- Laboratory research under bilateral project cooperation with JAERI.

2002
- Looking for industrial partner to transfer the technology in early 2001.
- File for patent in July 2002.

2003
- Signing Licensing and Technical Assistant Agreement with Rumbia Biotech Sdn. Bhd. on 3 September 2003.

2004
- Provide space for developmental work and pre-commercial trial production at Nuclear Malaysia beginning end of 2003.

2004
- Developed coating technique using prototype machine, identify suitable material and study product performance ~ Jan. to Nov. 2004.
- Modified sago hydrogel production building into GMP plant - Nov. 2004.
- Study demand, type and product performance at local market ~ Middle 2004 until now.

2005
- GMP plant starting operation - May 2005.

2007
- Marketed under MLM trade name Ecobelle beginning 2007.

Figure 1 illustrates chronologically the commercialization process of sago hydrogel facial mask.

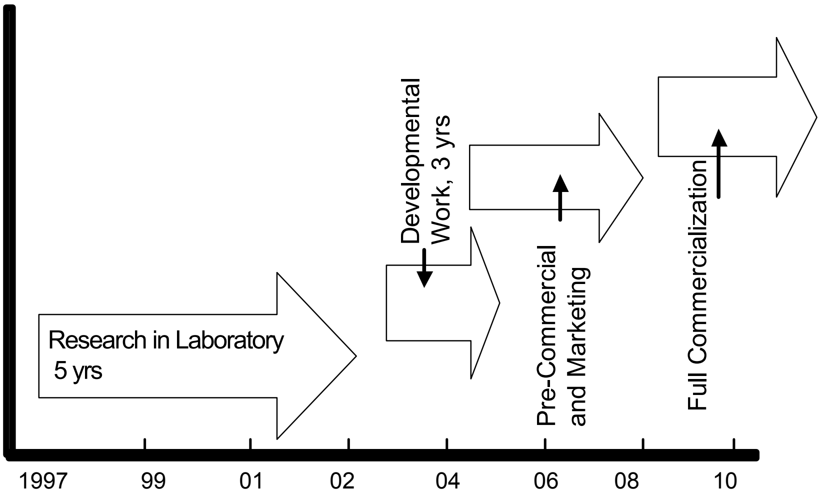

Fig. 1 Laboratory to market: Sago hydrogel commercialization process.

2. Pilot Scale Development

Sago hydrogel is produced by mixing of sago starch with water-soluble polymers. Figure 2 shows flow sheet of the process. The solution continuously stirred and heated until clear gel solution was formed. The gel solution was coated on the PE film at specific thickness and covered with cotton gauze. It then cut according to the size of facial mask and vacuum seal prior to irradiation. The product is irradiated at 25 kGy for crosslinking and sterilization processes. Figures 3 and 4 show the sago hydrogel facial mask produced by this process and electron beam processing of sago hydrogel facial mask, respectively.

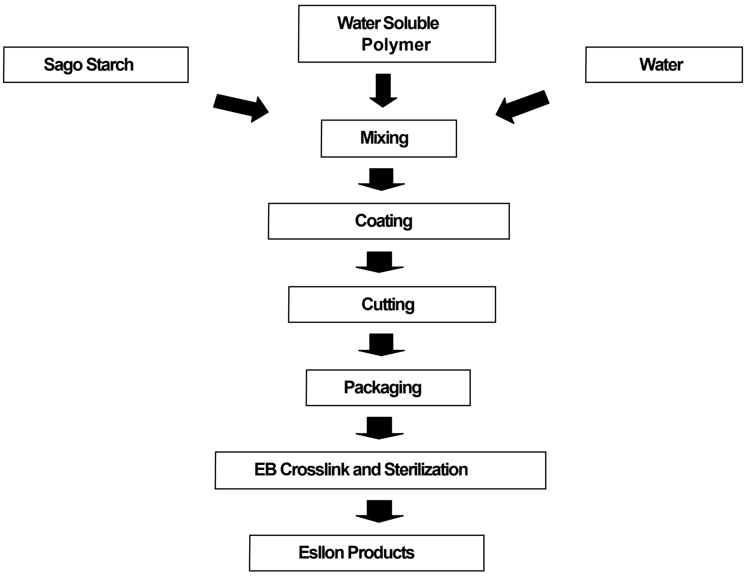

Fig. 2 Process flows for preparation of sago hydrogel facial mask.

Important Consideration

1) Mixing system to mix and heat the sago blend
2) Coating system with suitable substrate that will not absorb water or hydrogel
3) Efficient cutting machine to the facemask shape that will produce very 'clean' edges.
4) Packaging system that will not leak the moisture hence make the hydrogel dry. Packaging material must also suitable for electron beam irradiation.
5) Electron beam processing procedures and parameters

Fig. 3 Sago hydrogel facial mask.

Fig. 4 Electron beam processing of sago hydrogel facial mask.

3. Technology Transfer and Commercialization

3.1 Searching for potential partner

Sago hydrogel in product forms such as facial mask and sheets with commercial packaging have been exhibited at various events such as expo S&T since November 2002, innovation event, international & national conferences, seminars, show case for small and medium industry (SMI) and entrepreneurship program. The purpose is to introduce the product directly to the potential partner from industry that can take up further the product into developmental stage and pilot plant production prior to commercialization. A direct contact with an individual interested partner, entrepreneur and venture capital has also been carried out. Further efforts to match the potential partner with venture capital or government funding agency has been explored.

3.2 Process of transfer of intellectual property (IP)

The intellectual property of making sago hydrogel as facial mask and wound dressing have to be secured before the process of transfer of technology to the private company can be carried out. This is prerequisite for commercial technology transfer in order to protect the large capital input that the private company will invest in the manufacturing and marketing of such products. The technology of processing of sago hydrogel was file for patent by Nuclear Malaysia in July 2002. Subsequently, the licensing and technical agreements were signed between Nuclear Malaysia and the company, Rumbia Bio-Tech Sdn. Bhd. that took place on 3rd. September 2003.

3.3 Financial assistance

To introduce a new material for facial mask, it may need incubation period of few years for market acceptance and penetration. Market promotion would require a substantial amount of budget. At the same time, the company also need to invest in the pilot scale manufacturing line which include rental and modified space for GMP plant, purchasing of machinery and materials, hire new staff and logistic management from production to marketing To lighten the company financial burden, Nuclear Malaysia has provided a space close to the electron beam facility at a nominal rental charge for the setting up of a pilot manufacturing line. Nuclear Malaysia also assisted the company in preparing proposal and technical presentation to apply for loan from bank and grant from government funding agency, whereby the company has managed to secure financial backup for the capital investment and operation.

3.4 Pilot scale facility

Each component in the process flow as shown in Figure 2 would require efficient and suitable machines that can process large quantity of materials at reasonable speed. This is a challenge to scientists and entrepreneur who have no experience and knowledge on the pilot scale processing machine – where to buy, who is the manufacturer, guaranteed performance, machine durability, etc. The entrepreneurship skill of the entrepreneur himself is the driving force. The entrepreneur has to look around, visit other manufacturing facility that has similar processes, visit and talk to the manufacturer of the machine be it in Taiwan, Hong Kong, China, Korea, Japan or somewhere else. The cost of machine is also another factor in the selection of the machine for the manufacturing pilot plant line. In the case of sago hydrogel, the substrate materials for wet sago hydrogel and packaging materials are critical components that have undergone modifications for several times. This includes the cutting process and cutting machine for the facial mask. The quality control of the process and product is another important element in the pilot scale development stage to avoid contamination and re-contamination, after EB-sterilization. Consequently, a semi commercial scale good manufacturing practice (GMP) plant was established for the manufacturing of sago hydrogel facial mask in 2005.

3.5 Survey and product prospect

Survey on skin care product especially facial mask that already exist in the local market was carried out in term of form, type, material, price, demand and application. Visit to nearly 20 cosmetic companies existing in Malaysia was carried out for the purpose of promoting and briefing about sago hydrogel. During the visit, discussion with relevance company management director or personnel was held in order to have their opinion, comment and suggestion on future prospect of sago hydrogel facial mask in local as well as regional market. Comparison was made between sago hydrogel and existing products in local market in respect to the advantages of sago hydrogel for acne treatment or other skin disease, performance, user friendly and pricing. This was carried out by direct contact with end user such as individual, beauty salon, entrepreneur and marketing people on skin care product. The feed back from them are used to further improve the product performance and presentation in accordance to the market perception.

3.6 Marketing

Marketing process will determine the success of commercialization of product or technology to be delivered to end-users. Promoting sago hydrogel as facial mask is not easy since so many products already exist in the market in various type and form. The sago hydrogel facial mask should have unique features and better performance than other product available in the market. The company with the assistance of the Nuclear Malaysia technical staffs has made a lot of efforts through road show to explain and promote the products. Marketing through multi level marketing company is another approach that can help to reduce significantly financial burden in marketing directly the product to end-user.

4. Conclusion

Commercialization of sago hydrogel as facial mask could be considered as one of the successful story of the radiation processing of natural polymer. However, the process of bringing the product from laboratory to market is not an easy task. The commercialization of new product through entrepreneur requires tremendous energy and funding if compare through company that is already in the same business. Hence, it would require an entrepreneur that is resilient, has certain quality such as hard working, flexible, persistence etc. In addition, the continuous support and ‘follow through’ from laboratory to market, by the inventor and government agency are equally important for the success of the commercialization of the product or technology.

2. 1. 3 Semi-commercialization of PVP-Carrageenan Hydrogel

Lorna S. Relleve, Lucille V. Abad, Charito T. Aranilla, A. M. dela Rosa

Philippine Nuclear Research Institute

1. Introduction

The Philippine Nuclear Research Institute (PNRI) has developed the PVP-Carrageenan hydrogel wound dressing by radiation processing. The PVP-Carrageenan hydrogel has undergone clinical testing for burn and bedsores. It has already a pending patent application (No. 1-2000-02471) at the Philippine Patent Office. The techno-economic feasibility study has also been completed.

In order to commercialize this product, a project on semi-commercialization in partnership with the investor was proposed to Technology Incubation for Commercialization (TECHNICOM), a technology transfer program of the Department of Science and Technology (DOST). TECHNICOM was established in 2003 under the National Science and Technology Plan (2002-2020) as a strategic technology transfer program. The program aims to identify key technological breakthroughs especially those generated by R&D institutes. It can intervene through the following: technology assessment/commercial prototype development; business plan/feasibility study preparation; intellectual property rights protection; technology valuation negotiation and licensing; semi-commercial production assistance and training/consultancy services. High technology applications with commercial potentials are given priority.

Under semi-commercialization stage, government funds will be provided to match private sector investment in the commercial application of a particular technology innovation. This will lessen the risk of commercialization and ensure commitment from the investors. Commercial success in the shortest time is ensured since scientist can then work closely with the private sector at the production floor while testing the gaps in the technology.

2. PVP-Carrageenan Hydrogel for Burns and Bedsores

Several clinical trials have been conducted in major hospitals in Metro Manila (Philippine General Hospital, Veteran's Memorial Hospital, East Avenue Medical Center, United Doctors Medical Center and University of Santo Tomas Hospital). The PVP-Carrageenan hydrogel has been found effective and safe in debridement of ulcers with necrotic tissue and superior to the saline/gauze in treating bedsore/ulcers 1-2). The PVP-Carrageenan hydrogel has been on display at various exhibits. It has been also presented in various investor or business forum events in finding for potential partner. Figure 1 shows the PVP-carrageenan hydrogel in marketable form. Design of the packaging will be given by the interested company. The hydrogel dressing is available in two sizes.

Fig.1 PVP-Carrageenan hydrogel for burn/bedsore dressing in two available sizes.

3. Techno-Economic Feasibility Study/Business Plan

The techno-economic feasibility study showed economic viability of the project. In preparing for the market study, only burn patients of the Department of Health (DOH)-Philippine General Hospital (PGH) and retained hospitals were considered as an initial target market. According to the study, the ratio of burn patients to the total patient admissions for Philippine General Hospitals and all the government-retained hospitals is about 3%, 70% of which are first and second degree burns. The number of burn patients is estimated to increase by 3% annually according to the study of the Philippine Society for Burn Injuries. Table 1 gives the summary of patient admission of PGH and DOH retained hospitals and the projected demand of the hydrogel based from initial target market.

Table 1 Projected Number of Patient Admissions and Burn Patients in PGH and DOH-retained Hospitals and Projected Demand for Carrageenan-PVP Hydrogels.

Year	Projected patient admissions in PGH and DOH Retained Hospitals	Projected Number of Burn Patients	Projected Demand (pieces)*
2002	907,109	27,213	210,000
2003	934,322	28,030	216,000
2004	962,352	28,871	222,000
2005	991,222	29,737	229,000
2006	1,020,959	30,629	236,000

** The average stay of burn patients in hospitals is five weeks (35 days) and hydrogel is good for 3 days on burn patients. Thus, for every patient an average of 11 (35/3) hydrogels are used. (27,213 burn patients x 70% x 11 pieces = projected demand).*

Comparable products to Carrageenan PVP hydrogel which are available in the market include hydrocolloid dressings; medicated dressings, ointments/creams; and gauze. The main competitor product of the PVP-Carrageenan hydrogel is the hydrocolloid dressings, which are all imported. With the commercialization of this newly developed hydrogel dressing, price could be lower than its competitors making it more affordable to the poor sector of our country. The 3-year financial projection shows the viability and profitability of the product. Payback period for investment is less than a year or over ten months and return of investment is 117%, a profitable business.

4. Process of Technology Transfer

After presenting this product in different exhibits and forum, one company St. Raphael Lifeline Company (now known as Biotecos. Company) has signified interest in producing and marketing the hydrogel dressing but does not want to take the entire risk of commercialization. The company was informed about the project proposal on semi-commercialization to TECHNICOM and some activities are needed to be funded by them. The company has submitted a Letter of Intent indicating their willingness to commercialize the hydrogel dressing. The draft licensing agreement was also prepared. Both PNRI and Biotecos Company had negotiated on the terms and conditions of the licensing agreement. Signing of the licensing agreement will be made after semi-commercialization project.

4.1 Financial assistance from TECHNICOM

The PNRI has submitted a proposal to the TECHNICOM for semi-commercial production assistance in 2003. The submitted proposal was supported by clinical trials results, techno-economic feasibility study/business plan and Letter of Intent of the company. The proposal was approved for two phases. Phase I of the project involves the establishment of pilot plant in PNRI premises (YR 2004-2006). Phase II consists of the production of hydrogel and market acceptability study (YR 2007-2008). The budget approved for this project was PHP 1.4 million and PHP 3 million for Phase I and II, respectively. The Biotecos Company has also agreed to provide the amount of PHP 1.0 million as counterpart fund.

4.2 Activities of semi-commercialization (Phase I and II)

Phase I of the semi-commercialization was solely undertaken by PNRI. The pilot plant and equipment has been set up in the PNRI premises with a lot area of 60 sqm. The pilot plant will follow the process shown in Figure 2 in non-automated flow. The estimated capacity of the plant was determined in the initial trial production. The production of hydrogel was estimated to be 1,000 pieces for 8” x 8” or 4,000 pieces for 4” x 4” per day on 8 hours a day work.

Phase II could be undertaken by NRI and Biotecos Company as stated in the proposal.. Activities of PNRI and Biotecos Company for Phase II are summarized as follows;

Activities of PNRI

- Production of hydrogels
- QA/QC systems for the production of hydrogels
- Stability testing of hydrogels
- Protocol preparation and clinical test, if necessary

Activities of Biotecos Company

- Establishment of trial centers in two hospitals in Metro Manila
- Conduct clinical trials (if necessary)
- Application for BFAD health permit
- Market acceptability study

The company will carry out additional clinical trials if previous clinical studies are not enough. This will depend on the evaluation of Bureau of Food and Drug (BFAD). The company will design a study to determine whether the product will be acceptable to the market.

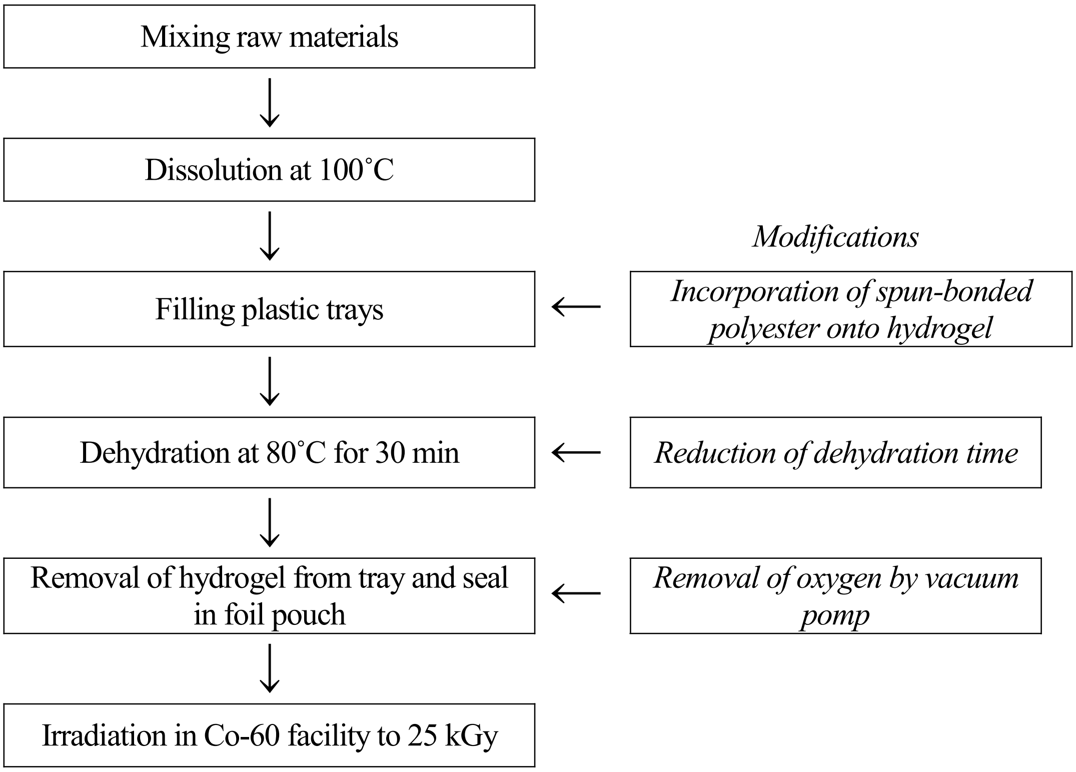

Fig. 2 Manufacturing process of PVP-Carrageenan hydrogel for burn/bedsore dressing.

5. Conclusion

Semi-commercialization is a stage that could fast-track commercialization of a product/process developed by R & D institutes. The TECHNICOM is an effective mechanism/program in initiating the transfer of technology and partnership with private sector. If successful, it is expected to be a model for other PNRI technology transfer activities.

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2. 1. 4 Radiation Processing of Cassava Starch Hydrogel

Suwanmala Phiriyatorn, Hemvichian Kasinee, Sonsuk Manit

Thailand Institute Of Nuclear Technology

Abstract

This paper consists of two topics on cassava starch (CS). The first paper deals with radiation-induced graft polymerization of 1-vinyl-2-pyrrolidinone (VP) onto CS. The results from PVP -grafted-starch were subsequently compared with those of PVP hydrogels and PVP-blended-starch hydrogels. It was found that the PVP-grafted-starch hydrogels, with gel fraction higher than 80%, could be prepared at the dose of 20 kGy, while PVP and PVP-blended-starch hydrogels require at least 30 kGy to obtain gels with more than 80% gel fraction. And at the same dose used for irradiation, the gel strength of the PVP-grafted-starch hydrogels is significantly higher than that of the PVP and PVP-blended-starch hydrogels. Radiation crosslinking of carboxymethyl CS is the second topic. CS was chemically modified by sodium monochloroacetate (SMCA) to yield carboxymethyl starch (CMS). The aqueous solution of CMS was irradiated and underwent radiation-induced crosslinking, resulting in a crosslinked CMS (XLCMS) hydrogel. The optimum condition for obtaining hydrogels with desirable properties is irradiation at low dose, 2 kGy. At higher doses, the gel fraction tends to diminish, due to the domination of degradation over crosslinking.

1. Introduction

1.1 Natural polymer

Natural polymers such as CS, chitin and chitosan are natural materials with high potential for a number of applications such as medical, environmental and agricultural applications. This is due to their unique characteristics such as biodegradability, biocompatibility and non-toxicity. Starch is a renewable natural polymer that can decompose easily in the environment and can be modified to various applications such as biomedical 1), agricultural 2) and pharmaceutical 3) applications. CS is produced abundantly in Thailand. Thailand is currently the world's largest exporter of CS, with an annual export of approximately 5~6 million tons. However, the production of CS in Thailand exceeds the export and consumption scale which cause too much surplus and unused cassava. This situation makes the CS low in cost. Native starch is a relatively low-valued commodity, but the value can be enhanced by means of chemical modification. Carboxymethyl starch is one of the most important starch derivatives 4~5), extensively used in many industrial applications ranging from food to medicine. With its biodegradability, biocompatibility and abundance, CS has become an attractive candidate for the development of biomedical materials.

1.2 Hydrogel

Wound dressing hydrogels have been successfully prepared by a mixture of polysaccharides and synthetic water soluble polymers 6~8). Agar, alginate, carrageenan and sago starch are examples of polysaccharides used to develop wound dressing hydrogels. This is mostly due to their biocompatibility, biodegradability and non-toxicity.

Radiation has been recognized as a highly suitable tool for the formation of hydrogels 9~12). Radiation processing offers a number of advantages, such as easy process control, capability to combine hydrogel formation and sterilization in one step, no needs for initiators or crosslinkers, which maybe harmful and difficult to remove. These qualities make irradiation the method of choice in the synthesis of hydrogels. When a polymer in aqueous solution is subjected to gamma irradiation, three main reactive species; hydrated electrons, hydroxyl radicals and hydrogen atoms, are formed 13). Hydroxyl radicals have been shown to be the main species responsible for reactivity transfer from water to the polymer chains. They abstract hydrogen atoms from macromolecules, therefore macroradicals are formed. The use of radiation has been introduced to many applications such as environmental, agricultural, food science, industrial and especially medical applications 14). This extensive utilization is due to the fact that radiation offers a number of unique benefits such as no requirements for additives or initiators, which can be harmful and very difficult to remove, environmental-friendliness compared to chemical processes and availability of simultaneous sterilization in one step. The last advantage is highly useful and appropriate for medical application. One of the materials extensively used for biomedical purposes is hydrogel.

Hydrogels are two-component systems in which one of the components is a hydrophilic polymer, and the other component is water. Hydrogels can absorb large amount of water and retain their original shape. Their water adsorption ability is due to the processes of hydration, which is related to chemical groups (such as –COOH, -OH, $CONH_2$, -CONH, $-SO_3H$), capillary effect, and differences in osmotic pressure. Hydrogels have a very low modulus of elasticity, and therefore cause minimal mechanical irritation. They usually show good biocompatibility in contact with blood, body fluids and tissues. They can absorb the exudates, and prevent the excessive loss of body fluids. In addition, they are chemically stable in a living environment, and permeable to low molecular weight metabolites, which are formed at the boundary between the living and non-living tissue. These properties make them suitable for biomedical applications such as wound dressing, controlled drug delivery system, dental materials, and implants 7, 11, 13). Hydrogels can be classified as homopolymer hydrogels, copolymer hydrogels, multipolymer hydrogels or interpenetrating polymeric hydrogels. Homopolymer hydrogels are crosslinked network of one type of hydrophilic monomer unit, while copolymer hydrogels are prepared from the crosslinking of two comonomer units, one of which must be hydrophilic. Multipolymer hydrogels are formed by the crosslinking of more than three monomers, Interpenetrating polymeric hydrogels are formed by first swelling a network in a monomer after that reacting the latter to form a second interpenetrating network structure.

PVP has excellent transparency and biocompatibility. It has been used widely for biomedical applications 8, 16~17). Hydrogels, which consist of natural polymers or their composites with synthetic polymers, produced by irradiation technique have been under an attention of researchers due to their biodegradability and availability at low cost. The combination of natural and synthetic polymers can give the optimal properties for wound dressing.

The purpose of this research is to convert natural polymers into useful products potentially applicable for medical applications.

2. Cassava Starch Hydrogel by Radiation Graft Polymerization

2.2. Experimental

2.2.1 Materials

Cassava starch (Siam Quality Starch, Thailand), PVP of M.W. average 44,000 (BDH Laboratory Supplies, England), and VP of purity 99% (Aldrich, USA) were used without further purification for the preparation of hydrogels. In a gelatinization container, 10g of starch was mixed with 190 ml of distilled water. The mixture was continuously stirred using a mechanical stirrer. The gelatinization was done under nitrogen purge. The mixture was gradually heated from ambient temperature to 80˚C and held at this temperature for 1 hr. The mixture was left to cool down to room temperature to yield the gelatinized starch.

2.2.2 Preparation of Hydrogels

PVP hydrogels was prepared as follows; 20g of PVP were dissolved in 180 ml of distilled water. The mixture was then equally transferred into eight of 25x150 mm screw-capped glass tubes. The tubes were purged with nitrogen for about 2 min before they were sealed with caps. These eight tubes were vertically put in a rack and evenly positioned in a 60-Co γ source (Gammacell 220 Excel from MDS Nordian), with a dose rate of 0.27 kGy/min. The samples were irradiated at various doses from 10 to 100 kGy. After irradiation, the obtained hydrogels were thoroughly washed with water to dispose of non-gel water-soluble fraction and dried to constant weight at 50˚C.

PVP-blended-Starch hydrogels was prepared as follows; the gelatinized starch was mixed with PVP solution in distilled water, with the final concentration of starch and PVP at 2.5% and 5%, respectively. The mixture was continuously stirred to form a homogeneous blend. The mixture was then transferred into screw-capped glass tubes, exposed to γ radiation at various doses. After irradiation, the obtained hydrogels were washed well with water and dried at 50˚C until the weight was constant.

PVP- grafted-starch hydrogels was prepared as follows; the gelatinized starch was mixed with 50ml of 1-vinyl-2-pyrrolidinone (VP). The two-component solution was continuously stirred for 1 hr to form a homogeneous mixture. The gel-like mixture was transferred into the glass tubes and purged with nitrogen gas for 5 minutes. The tubes were tightly closed with caps, and then irradiated under γ-ray radiation at various doses. After irradiation, the obtained hydrogels were washed with water to dispose of non-gel water-soluble fraction, and dried at 50˚C until constant weight was reached. At a fixed dose rate of 0.27 kGy/min, various quantities of total dose of γ-ray irradiated to the mixture of the gelatinized CS and 1-vinyl-2-pyrrolidone were investigated. The dried samples were characterized with FTIR, TGA and DSC. In addition, equilibrium degree of swelling, gel fraction, and gel strength were determined.

2.2.3 Gel Strength, Equilibrium Degree of Swelling, Gel Fraction and Grafting Efficiency

To determine the gel strength, the hydrogels were prepared in the same manners as previously described, except that 25 x 55 mm screw-capped glass tubes were used instead. The gel strength of the hydrogel samples were determined using the compressive test of the Universal Testing Machines from Lloyd Instruments (LR 5K Series.) The maximum deformation was set at 75% of the sample's thickness. The test speed used was 10 mm/min. The load at the maximum deformation was reported in Newton.

The gel samples were immersed directly in distilled water for 72 h at ambient temperature, to reach the equilibrium state of swelling. The weight of the swollen gel (Ws) was then measured. The swollen gels were later dried at 50˚C until the weight of the dried gels (Wd) remained constant. Equilibrium Degree of Swelling (EDS) was determined from the following equation:

$$EDS = Ws / Wd \times 100$$

The gel samples were wrapped into a 200-mesh sieve and autoclaved at 121˚C for 2 h to remove the soluble (sol) fraction. The samples were then taken out of the autoclave and dried to constant weight at 50˚C to gravimetrically determine the insoluble (gel) fraction using the following equation:

$$\text{Gel Fraction} = \text{Wd}/\text{Wi} \times 100$$

where Wd is the weight of dried gel after extraction and Wi is the initial weight of gel before extraction.

The grafting efficiency can be calculated as follows:

$$\text{Grafting Efficiency} = (\text{Wd} - \text{Wcs})/\text{Wi} \times 100$$

where Wd is the weight of dried gel after extraction, Wi is the initial weight of gel before extraction, and Wcs is the weight of initial CS used for gelatinization.

2.2.4 FTIR Analysis and Thermal Analysis

Infrared spectra were taken from a Fourier transform infrared spectrometer (Bruker Tensor 27). For powder samples, the samples were pressed into KBr pellets and analyzed using transmission mode, with 16 co-added scans and a resolution of 4 cm^{-1}. For hydrogel samples, the samples were shaped into films and characterized using Attenuated Total Reflectance (ATR) technique, with 64 co-added scans and a resolution of 4 cm^{-1}.

A differential scanning calorimeter (DSC822e) and a thermal gravimetric analyzer (TGA/SDTA851e) from Mettler Toledo were used to characterize the thermal properties of the samples. All experiments were done under nitrogen purge; with a flow rate of 60 ml/min. A heating rate of 10˚C/min was used for all DSC and TGA experiments.

3. Results and Discussion

3.1 Evidence of grafting

3.1.1 FTIR analysis

FTIR analysis was used to provide evidences for grafting reaction of PVP onto starch. The FTIR spectra of the original starch, the original PVP, and the PVP-grafted-Starch hydrogel are taken and comparatively shown in Figure 1, while the structures of starch and PVP are illustrated in Figure 2. Additionally, a detailed numerical listing of some key functional groups of starch, PVP, and PVP-grafted-Starch hydrogel, along with their IR absorption frequencies, are summarized in Table 1.

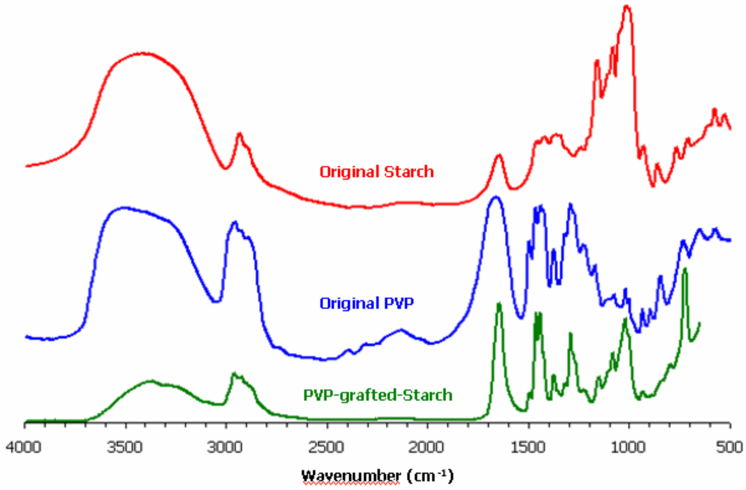

Fig. 1 FTIR Spectral of original starch, original PVP, and PVP-grafted-Starch Hydrogel.

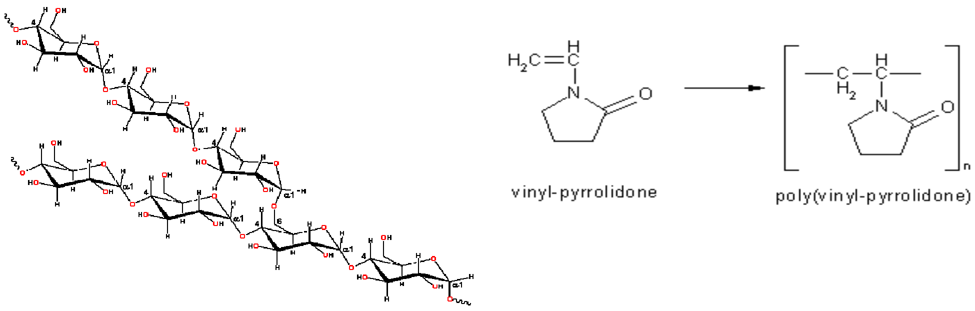

Fig. 2 Chemical structures of starch (left) and PVP (right).

From Figure 1 and Table 1, it is obvious that the FTIR spectrum of PVP-g-Starch hydrogel contains major characteristic peaks seen in the spectrum of original starch, especially the frequency range of 1200~1000 cm^{-1}, which is a unique region of alcohol compound. For a comparison, the FTIR spectrum of PVP is also shown in Figure 1, with unique region being the frequency range of 1700~1300 cm^{-1}, identifying the presence of amide compound. This region is also present in the spectrum of PVP-g-Starch hydrogel, confirming the grafting of PVP onto starch.

Table 1 List of some key functional groups with their IR absorption frequencies.

Original Starch		Original PVP		PVP-grafted-Starch Hydrogel	
Frequency	Assignment	Frequency	Assignment	Frequency	Assignment
3600~3200	O-H Stretch	3600~3200	O-H from Humidity	3600~3200	O-H Stretch
2923	C-H Stretch in Aliphatic -CH_2-	2945	C-H Stretch in Aliphatic -CH_2-	2947	C-H Stretch in Aliphatic -CH_2-
		1658	C=O in Amide	1643	C=O in Amide
1639	O-H Bending			1639	O-H Bending
1452	CH_2 Scissors Vibration in Aliphatic -CH_2-	1460	CH_2 Scissors Vibration in Aliphatic -CH_2-	1461	CH_2 Scissors Vibration in Aliphatic -CH_2-
		1421	C-N Stretch in Amide	1423	C-N Stretch in Amide
1153	C-O-C Stretch in Aliphatic Ether			1145	C-O-C Stretch in Aliphatic Ether
1078	C-O Stretch in Alcohol			1080	C-O Stretch in Alcohol
1010	C-O Stretch in Cyclic Alcohol			1014	C-O Stretch in Cyclic Alcohol
		727	-CH_2- Rocking in Hydrocarbon	725	-CH_2- Rocking in Hydrocarbon

3.1.2 Thermal analysis

From Figure 3, the melting peaks of the original starch and the original PVP show up at approximately 100°C and 165°C, respectively. The melting peak of the PVP hydrogel can also be seen at about 165°C, but appears much broader than that of the original PVP. As for the PVP-blended-starch hydrogel and the PVP-grafted-starch hydrogel, the melting peaks show up between those of the original starch and the original PVP, approximately at 145°C and 130°C, respectively, thus confirming both the blending and grafting reactions.

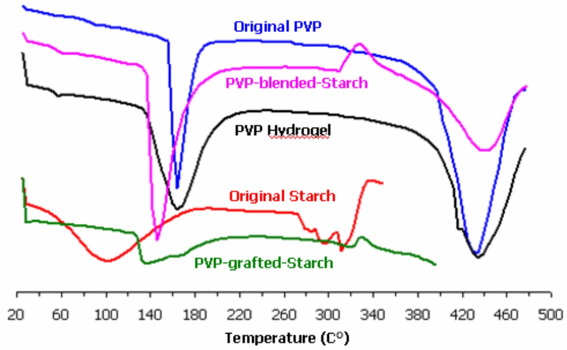

Fig. 3 DSC thermograms of original starch, original PVP, PVP hydrogel, PVP-blended-Starch Hydrogel and PVP-grafted-Starch Hydrogel.

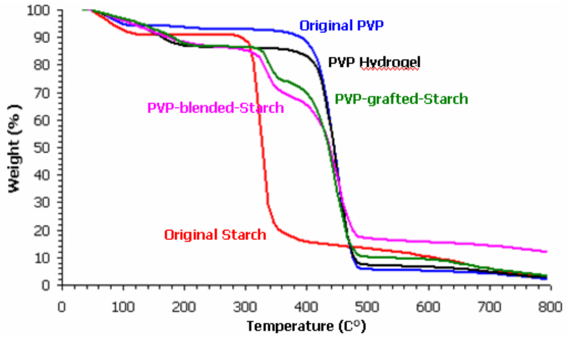

Fig. 4 TGA thermograms of original starch, original PVP, PVP hydrogel, PVP-blended-Starch Hydrogel and PVP-grafted-Starch Hydrogel.

TGA results of these five samples are presented in Figure 4. The original starch shows a one-stage weight loss process, centered at about 300˚C. The original PVP and the PVP hydrogel also show a one-stage weight loss process, with a maximum rate of weight loss located at about 450˚C. On the other hand, the PVP-blended-starch and PVP-grafted-starch hydrogels demonstrate a two-stage weight loss process, with the first one centered at roughly 350˚C and a second one centered at around 450˚C. These two processes clearly demonstrate the presence of both starch and PVP in the chemical structure of these two hydrogels, hence again proving radiation-induced crosslinking of the PVP-blended-starch and PVP-grafted-starch hydrogels.

3.2. Physical Properties of PVP, PVP-blended-starch and PVP-grafted-starch hydrogels

3.2.1 Gel strength

The effect of the total dose on the gel strength is presented in Figure 5. For all three series of hydrogels, the gel strength increases with dose increment. However, it is obvious that the gel strength of PVP-grafted-Starch hydrogels increases faster and more significantly with dose, compared with those of PVP and PVP-blended-Starch hydrogels. With this excellent gel strength, PVP-g-Starch hydrogel can be used as a material for wound dressing. At high dose, the gel strength decreases slightly, possibly due to the domination of degradation over crosslinking.

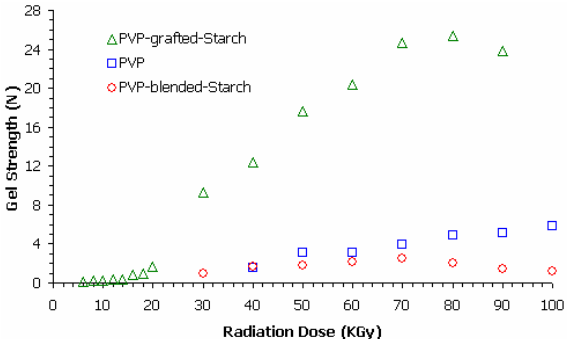

Fig. 5 Gel strength of PVP, blended-Starch and grafted-Starch hydrogels.

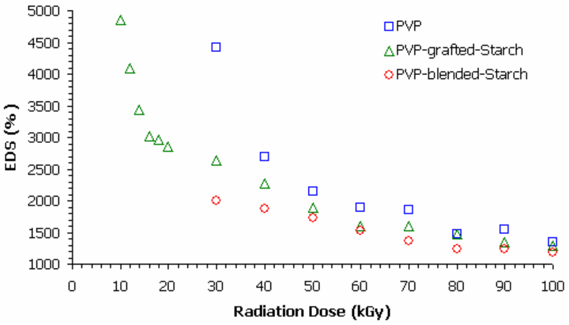

Fig. 6 EDS of PVP, blended-Starch and grafted-Starch hydrogels.

Radiation-induced grafting polymerization not only results in PVP-grafted-Starch hydrogels with higher gel strength, but also makes hydrogel formation possible at low dose. The formation of PVP-grafted-Starch hydrogels can be achieved at low dose, while the minimum dose to form PVP and PVP-blended-Starch hydrogels is at least 30 kGy.

3.2.2 Swelling behavior

The swelling behavior of the hydrogels as a function of dose is presented in Figure 6. The EDS of all three hydrogel series decreased with increasing dose. This can be explained from the fact that the crosslinking density of the hydrogels three-dimensional (3D) network increases with radiation dose, resulting in a smaller amount of water that can be absorbed.

3.2.3 Gel Fraction

Figure 7 shows the gelation behavior of all three series of hydrogels that were synthesized by γ-ray irradiation. It is evident that the minimum dose required to obtain the hydrogels with gel fraction over 80% is 30 kGy for the PVP-blended-Starch and pure PVP hydrogels, whereas lower dose is enough to form the PVP-grafted-Starch hydrogel.

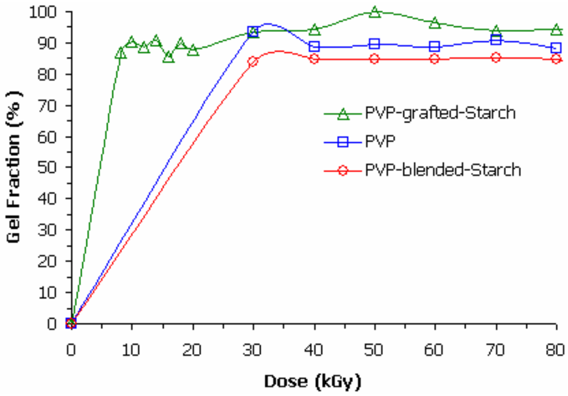

Fig.7 Gel Strength of PVP, blended-Starch and grafted-Starch hydrogels.

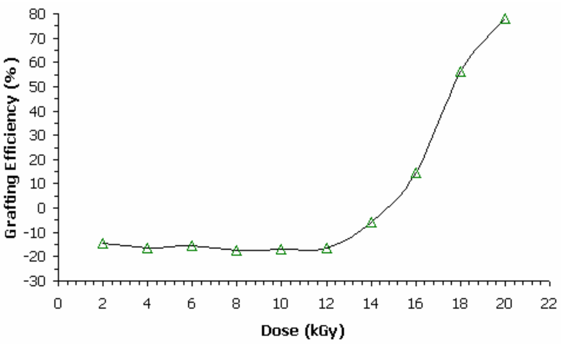

Fig. 8 Grafting efficiency of PVP onto starch prepared by radiation-induced grafting polymerization, as a function of dose.

The grafting efficiency is shown in Figure 8. It can be seen that at low dose, the grafting efficiency is negative. With increasing dose, grafting efficiency begins to rise and finally turn into positive value above 16 kGy. This is because during the irradiation process, the energy from γ-ray radiation is transferred to the irradiated material, resulting in a variety of modifications that change the chemical and molecular structure of the material. These modifications include crosslinking, degradation, grafting, crystal lattice modification, and polymerization (curing) of monomers and oligomers. Generally, when a polymer is irradiated, crosslinking and degradation take place simultaneously. Nevertheless, the ratio of their rates depends on a number of factors, including the chemical structure of the polymer, its physical state, and the irradiation state. Polymers are generally divided into those that predominantly crosslink and those that predominantly degrade. PVP is easily crosslinked in its homogeneous mixture with water, while starch easily decomposes upon irradiation. In this case, during low dose irradiation, the decomposition of starch and grafting takes place concomitantly. However, the grafting reaction in a short period of time at low dose is not enough to take over the starch degradation. But at higher dose, enough reaction time results in the prevailing of the grafting reaction over the degradation of starch, hence resulting in the formation of the hydrogels.

3.3 Conclusion

A series of PVP-grafted-Starch hydrogels were successfully prepared from radiation-induced crosslinking. FTIR and thermal analyses by DSC and TGA verified the grafting reaction. To elucidate the efficiency of grafting technique, two additional series of PVP-based hydrogels were synthesized; pure PVP hydrogels and PVP-blended-Starch hydrogels. The physical properties of these three series of hydrogels were characterized and compared. For the swelling behavior, the equilibrium degree of swelling of all three series of hydrogels considerably decreases with increasing dose. On the other hand, the irradiation dose has a less intense effect on gel content. The gel fraction of all the hydrogels was in the range above 80% and hardly varied with dose. The formation of the PVP-grafted-starch hydrogels is possible at low dose, i.e. 10 or 20 kGy, while the optimum dose to form the PVP and PVP-blended-starch hydrogels is at least 30 kGy. The gel strength of the PVP-grafted-starch hydrogels significantly improves with dose, and is much higher than that of the PVP and PVP-blended-starch hydrogels, at the same dose.

3. Hydrogel by Radiation Crosslinking of Carboxymethyl Cassava Starch

3.1 Experimental

Cassava starch and 99.9% ethanol were mixed and stirred in a flask for 30 min, then 50% NaOH solution was gradually dropped into the mixture, and stirring continued for another 20 min. SMCA was added to the solution at various concentrations. The mixture was heated to 45-50˚C and continuously stirred at this temperature for 2 hr. The synthesized CMS samples were filtered, washed thoroughly with water, and finally dried at 50˚C. The degree of substitution (DS) was determined by back titration method [18)]. The dried CMS samples were mixed with deionized water to the desired concentration. The CMS aqueous solution was irradiated in a Gammacell 220. The crosslinked CMS (XLCMS) were filtered, washed with water, and dried in an oven at 50˚C. The swelling ratio of the obtained hydrogels was identified by immersing the gels into distilled water for 72 hours. The gel fraction was determined by autoclaving the gels at 121˚C for 2 hours. The thermal properties of the hydrogels were characterized using differential scanning calorimeter (DSC) and thermal gravimetric analyzer, TGA.

3.2 Results and discussion

For the carboxymethylation process, the DS of CMS increased with increasing concentration of SMCA (Figure 9).

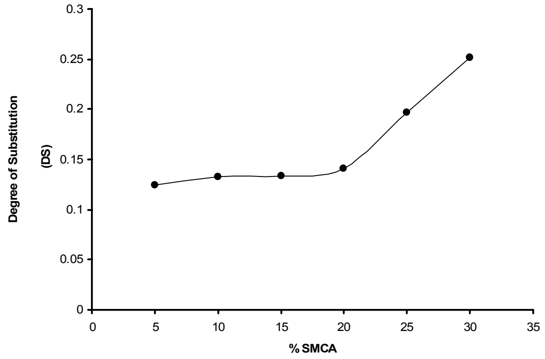

Fig. 9 Effect of % SMCA on degree of substitution (DS).

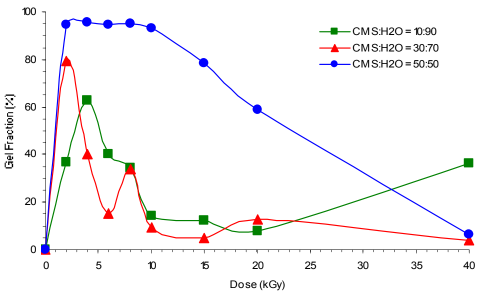

Fig. 10 Effect of concentration of CMS (DS 0.14) and dose on gel fraction.

Figure 10 displays the gel fraction of the XLCMS hydrogels, as a function of dose and concentration of CMS (DS 0.14). It can be seen from this Figure that at high concentration solution (30, 50%), gel fraction reached 80% at a low dose of 2 kGy and it trends to decrease with increasing dose. This indicates that at higher dose, the degradation of CMS simply dominates the crosslinking reaction. Therefore, irradiation in 50% solution at low dose is effective for crosslinking of CMS.

In Figure 11, the gel fraction of XLCMS hydrogels is shown as a function of %SMCA and dose. There is no noticeable relationship between the gel fraction and % SMCA. Nonetheless, the gel fraction seems to decrease with dose probably due to the degradation of CMS.

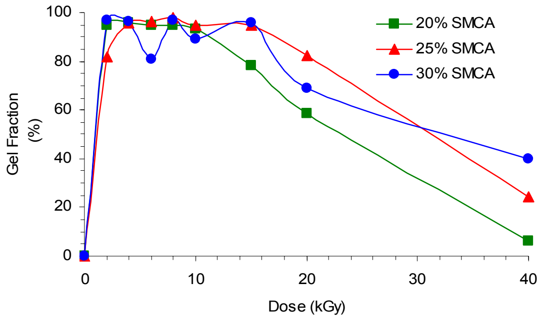

Fig. 11 Effect of %SMCA and dose on gel fraction.

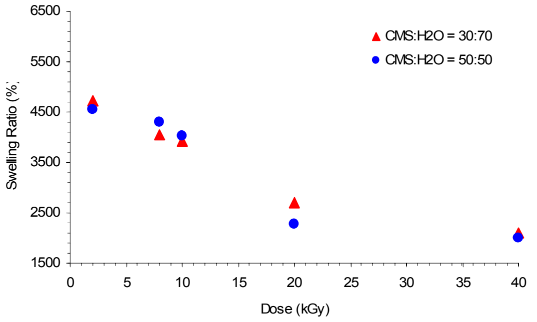

Fig. 12 Effect of concentration of CMS (DS 0.14), and dose on swelling ratio.

The swelling ratio of the XLCMS hydrogels as a function of concentration of CMS (30, 50%, 0.14 DS) and dose is presented in Figure 12. The swelling ratio in deionized water decreases with increasing dose as well as with increasing concentration of CMS. This is probably due to the increase of crosslinking density with irradiation dose.

DSC thermograms of CS, CMS and XLCMS are presented in Figure 13. It can be seen that the melting peak of these three samples shift toward the right, i.e. higher temperature, indicating the differences in thermal properties which come from chemical distinctions.

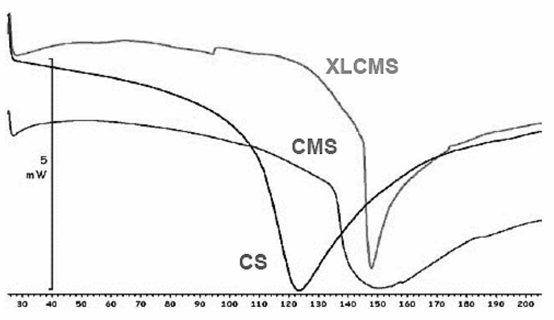

Fig. 13 DSC thermograms of XLCS, CMS, and CS.

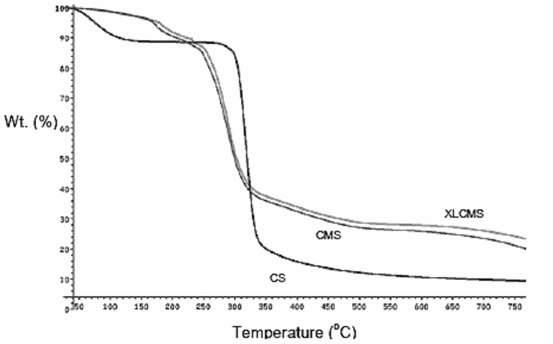

Fig. 14 TGA thermograms of XLCS, CMS, and CS.

TGA thermograms of CS, CMS and XLCMS are shown in Figure 14. The thermogram of starch displayed a two-stage weight loss process. The first process started very early and slowly continued until 160˚C, indicating the evaporation of approximately 12% moisture content in starch. The second weight loss process began at about 270˚C and reached its maximum rate of weight loss at roughly 320°C. The amount of char left at 800°C is nearly 10%. Compared with CS, CMS and XLCMS illustrated slightly different thermograms, with the first process of weight loss shifting to higher temperature (about 160°C) and the second one shifting towards lower temperature (roughly 240°C). A major difference took place at approximately 330°C, where CS continued to degrade with high rate of weight loss, but CMS and XLCMS did so with a gradual rate, leaving around 19% and 21% char yield, respectively. This clearly demonstrates that CMS and XLCMS have different chemical structures, compared with CS, and also better thermal stability.

3.4 Conclusion

Crosslinked carboxymethyl CS hydrogel was successfully synthesized by radiation-induced crosslinking at low dose of 2 kGy. Irradiation in paste-like condition (50% CMS) is effective for crosslinking of carboxymethyl CS.

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2. 1. 5 R&D on Utilization of Indigenous Materials for Hydrogel Wound Dressing

Md. Emdadul Haque, Nirmal Chandra Dafader, Ruhul Amin Khan

Institute of Nuclear Science and Technology, Bangladesh Atomic Energy Commission

Abstract

Utilization of indigenous materials for the preparation of hydrogel wound dressing is highlighted in this report. Hydrogels were prepared by two different formulations using PVP and PVA separately. Considering the price of the main two raw materials PVA was chosen for the next course of development. To reduce the cost of raw materials further flour was added to the PVA formulation. Ingredients concentrations for preparing good quality hydrogel were optimized. PVA containing both carrageenan and flour produces hydrogel with good properties. PVA containing 0.75% of both carrageenan and flour produces hydrogel of desirable properties. Seminar and demonstration about the usefulness of hydrogel for wound dressing were arranged at a city hospital.

1. Introduction

At the early stage hydrogels were prepared based on synthetic polymers which include poly(vinyl pyrrolidone) (PVP), poly(vinyl alcohol) (PVA), poly(hydroxyalkylmethacrylate), poly(acrylamide), poly(ethylene oxide) (PEO) etc. The natural polymers are also drawn attention of the researchers to contribute in the particular field. Derivatives of polysaccharides such as carboxymethyl (CM) starch, CM-cellulose, CM-chitosan are being used to prepare hydrogels by radiation processing[1)]. Development of hydrogels by blending water soluble synthetic polymers with the natural ones shows improved quality and better biodegradable property. Kappa-carrageenan with PVP is used to improve gel strength, swelling ratio and water absorption properties of the hydrogel[2,3)]. The applications of hydrogels from polysaccharides in medical and cosmetic field as coolant have been foreseen[4)]. J. Shin et al reported the preparation of radiation processed gelatin hydrogels for tissue scaffold materials[5)]. Hydrogels of sago starch blended with water soluble polymers shows good properties for wound dressing and it was patented in Malaysia[6)]. Hydrogels with poly(vinyl alcohol) and silk fibroin and PVP grafted starch have been prepared by Sonsuk[7,8)] and found to have comparable properties with the PVP hydrogels. Hydrogels with excellent properties were obtained using PVA with wheat powder and K-carrageenan[9)]. In this report both PVP and PVA have been used separately and properties of the prepared gels have been evaluated.

2. Experimental

2.1 Materials and methods

PVA from BDH, England and PVP (k-90, medical grade) from Fluka Ag, Switzerland were procured and used as received. agar (medical grade) was obtained from Difco Laboratories, USA and κ-carrageenan κC) from Shemberg Corp., Philippines. Food grade flour was purchased from the local market. PVA/PVP was mixed well with flour/carrageenan/agar in hot water and autoclaved at 121°C. The aqueous mixture was cast in pet tray and irradiated for 27 kGy in sealed condition.

2.2 Determination of gel content

A small piece of hydrogel was dried to constant weight in an oven at 60°C. The dried hydrogel was immerged in distilled water to remove soluble part for 24 hours. The insoluble part was taken out from the distilled water and again dried to constant weight. The gel content was calculated using the following relation.

$$\text{Gel Content (\%)} = (G_d/G_0) \times 100$$

where G_d and G_0 are the weight of the extracted dry gel and initial weight of dried gel respectively.

2.3 Determination of water absorption rate

The water absorption rate was determined by soaking the dried gel in distilled water and it was taken out at different time intervals. The excess water on the surface of the swollen gel was removed by soft tissue and weighed. Absorption rate was calculated by using the following relation.

$$\text{Absorption Rate (\%)} = (G_t - G_d)/G_d \times 100$$

where G_t is the weight of the swollen gel at time t.

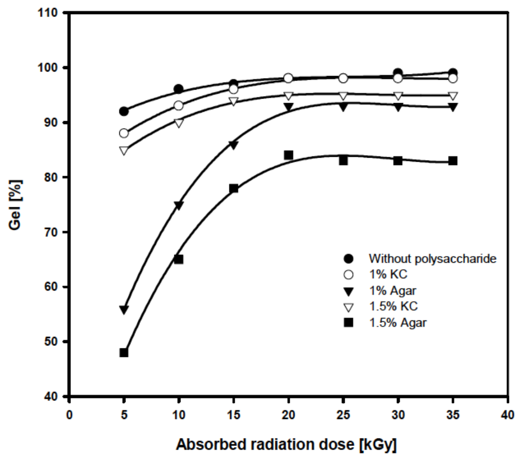
2.4 Observation of microorganism (Bacteria, Fungi) effect on hydrogel

Observation of microorganism effect on hydrogel was carried out by standard plate count method. Nutrient agar and potato dextrose agar were used for bacteria and fungal count respectively. Weighed slice hydrogel were dissolved in physiological saline. Then 0.1 ml suspension was spread onto the solidified media and 0.1 ml suspension was poured in sterile petri dishes and media within 45-50°C and mixed well swirling the plate. The plates were then incubated at 37 and 30°C for bacteria and fungus, respectively. The plates were checked for visible growth every day for 21 days. No visible growth on 21st day was found.

3. Results and Discussion

3.1 Gel content of PVP hydrogel with various polysaccharide concentrations

Figure 1 shows the plot of gel content in hydrogel against the absorbed radiation dose for various concentrations of polysaccharides (agar and kappa carrageenan, κC). It is found that gel formation developed with the increased radiation dose and get saturation at the doses between 20 and 25 kGy. The gel fraction of the hydrogel with no added polysaccharide is highest at all radiation doses. The gel content in the hydrogels varies according to the additives. The hydrogel containing κC possesses higher gel than that of the hydrogel with agar. The concentration of the polysaccharides has also effect on the gel content in the hydrogel. Gel content decreases with the increased concentration of a particular polysaccharide. It is noticeable that κC is a better additive between the two in gel formation for hydrogel preparation with the aid of radiation.



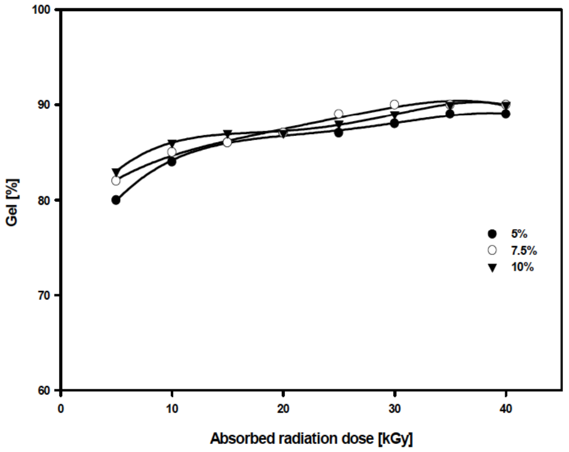


Fig. 1 Gel versus radiation dose for PVP with varying polysaccharide concentration.

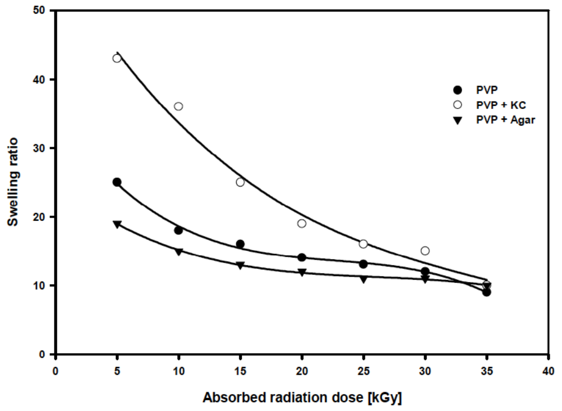
Fig. 2 Gel versus radiation dose of PVA hydrogel.

3.2. Gel versus radiation dose of PVA hydrogel

Figure 2 shows the gel formation trend of the hydrogel prepared with various concentrations of PVA at various radiation doses. In this case about 25-30 kGy radiation dose was found to be optimum for maximum gel formation. It depends on the concentration of the polymer but not so significant. 7.5% of PVA seems a good concentration to have gel at the optimum dose.

3.3 Water swelling pattern of PVP hydrogel

Figure 3 shows the water swelling behavior of the PVP hydrogel with and without added polysaccharides. It is found that the water absorption property changes with the addition of polysaccharides. Water swelling decreases with the increase of absorbed radiation dose because the gel is increased. Maximum swelling occurs with the hydrogel having κC.



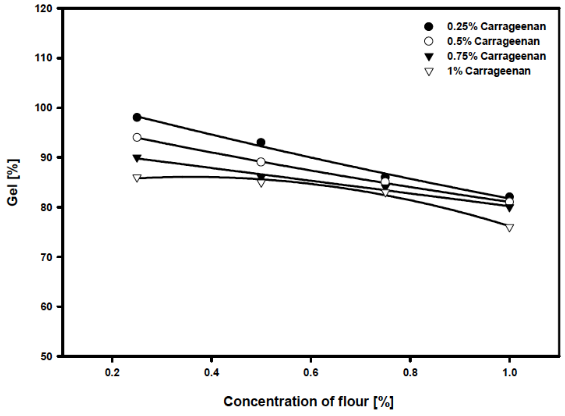


Fig. 3 Water swelling of PVP hydrogel versus radiation dose with and without polysaccharide.

Fig. 4 Gel fraction of PVA hydrogel with various concentrations of flour against carrageenan content.

3.4 Gel Fraction of PVA hydrogel prepared with flour and carrageenan

Incorporation of carrageenan and flour into PVA/water system produces a good quality hydrogel. The hydrogel possesses high elasticity with good mechanical strength and good transparency. The optimum concentration of both carrageenan and flour is 0.75%. Figure 4 shows the gel fraction of the hydrogel with various concentrations of flour as a function of carrageenan contents. It is found that the gel decreases with the increase of flour concentration and it is also true for the concentration of carrageenan. Similar findings were obtained for PVP hydrogels.

3.5 Water absorption of PVP hydrogel

Figure 5 shows the water absorption curve for PVP hydrogel with and without added κC corresponding to the time of absorption. It is found that water absorption in the hydrogel increases with elapsed time and it becomes saturated in about 24 hours. The water absorption of the hydrogel with κC is much higher than that of the PVP hydrogel alone. The increased water absorbance in case of κC -hydrogel is due to the ionic nature of the κC which contains $-OSO_3^-$ group.

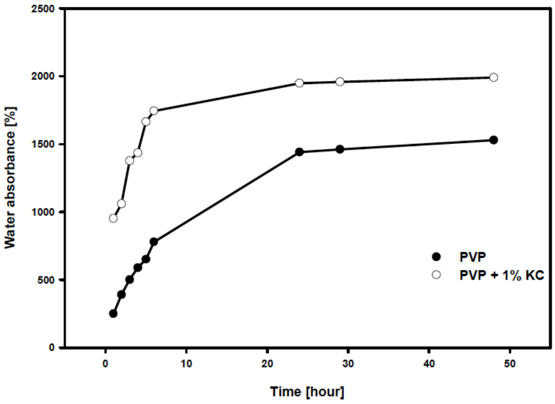


Fig. 5 Water absorption of PVP hydrogel at various lengths of time.

3.6 Sterility test

Analysis of micro-organism of the hydrogel prepared from PVA, flour and carrageenan shows that non-irradiated sample contains bacteria (2.2 x 10^2 cfu) only whereas irradiated samples are free from bacteria and fungi [9].

4. Demonstration

The prepared hydrogel samples were demonstrated at Govt. Medical College Hospital in Dhaka, Bangladesh (Fig.6).

Hydrogel sample *Strength test* *Demonstration for dressing*

Fig. 6 Demonstration of hydrogel.

5. Conclusion

Medically applicable hydrogels were prepared in a small scale. Addition of indigenous materials in the formulation of PVA hydrogel shows good results. Further works for practical application are in progress.

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2.2 Super Water Absorbent

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2. 2. 1 Radiation Processing of Natural Polymers for Industrial and Agricultural Applications

El-Sayed A. Hegazy, H. AbdEl-Rehim, D. A. Diaa, A. El-Barbary

National Center for Radiation Research and Technology, Atomic Energy Authority, Egypt

Abstract

Radiation induced degradation technology is a new and promising application of ionizing radiation to develop viscose, pulp, paper, food preservation, pharmaceutical production, and natural bioactive agents industries. Controlling the degree of degradation, uniform molecular weight distribution, saving achieved in the chemicals (used in conventional methods) on a cost basis, and environmentally friendly process are the beneficial effects of using radiation technology in these industries. However, for some development countries such technology is not economic. Therefore, a great effort should be done to reduce the cost required for such technologies. One of the principle factors for reducing the cost is achieving the degradation at low irradiation doses. The addition of some additives such as potassium per-sulfate (KPS), ammonium per-sulfate (APS), or H_2O_2 to natural polymers (carboxymethylcellulose (CMC), chitosan, carrageenan and Na-alginate) during irradiation process accelerates their degradation. The highest degradation rate of polysaccharides obtained when APS was used. The end product of irradiated CMC, chitosan, carrageenan and Na-alginate may be used as food additive or benefited in agricultural purposes. On the other hand, radiation crosslinking of PAAm or PNIPAAm is affected by the presence of natural polymer like CMC-Na and carrageenan due to their degradability which could be controlled according to its concentration in the bulk medium and irradiation dose. Accordingly, the gel content, thermo-sensitivity (LCST) and swelling properties of PNIPAAm based natural polymers could be controlled. The swelling of the prepared copolymer hydrogels was investigated for its possible use in personal care articles particularly diapers or as carriers for drug delivery systems. The prepared crosslinked copolymers possessed high and fast swelling properties in simulated urine media and the swelling ratios of CMC-Na /PAAm gels in urine are acceptable for diaper application.

1. Introduction

When organic materials are irradiated by ionizing radiation, they are divided into two types, degradation (chain scission) and chain link (crosslinking). Interest in radiation degradation chemistry of natural and synthetic polymers has increased tremendously as the potential was recognized for using radiation to improve industrial process such as pulping, viscose, cosmetics and food preservation and new natural active agents. Possibilities for using radiation in degradation include; Natural polysaccharides with high molecular weight like alginate and chitosan, which are found in seaweed and crustaceans and are widely utilized in food, pharmaceutical and bioengineering industries. A new class of biologically active compounds of polymer type, as well as the technology for overall protection of food products, has been developed. Recently, oligosaccharides derived from the depolymerization of polysaccharides by enzyme reaction were shown to have novel features such as the enhancement of antibiosis, promotion of germination and root elongation of plants. Radiation-induced depolymerization caused by chain scission was successfully used for such purposes and has been tested and implemented in the industry. Moreover, new food protection technology has been proposed, using active polymer coatings and packages (prepared by radiation method) with improved barrier and bactericidal properties.

Degradation is a very important reaction in the chemistry of high-molecular-weight compounds. It is used for determining the structure of polymeric compounds, and obtaining valuable low molecular weight substances from natural polymers. Sometimes degradation is used to lower the molecular weight of polymers partially to facilitate fabrication. The splitting of polymeric macromolecules to form free radicals is employed for synthesizing modified polymers. At the same time polymer degradation may often be considered as an undesirable side reaction occurring during the chemical transformation, fabrication and usage of polymers.

Polysaccharides and their derivatives exposed to ionizing radiation had been long recognized as degradable type of polymers 1, 2). First event observed during the irradiation of polysaccharides leads to breakdown of the ordered system of intermolecular as well as intramolecular hydrogen bonds. Consequently, the rigidity of chains is influenced by intramolecular hydrogen bonding and the degree of crystallinity of the material decreases. Polysaccharides irradiated in solid state and in diluted aqueous solutions suffer scission of acetal linkages in main chains. Radiation chemistry of cellulose, and its derivatives, has long been investigated with special attention. Random cleavage of glycoside bonds in the main chain, initialized by radicals placed on macromolecules was found to be a leading reaction 3, 4).

In this respect, the present work is dealing with studying the effect of ionizing radiations on the crosslinking and degradation of some natural polymers such as CMC-Na and starch. Trials were made t control and reduce the irradiation dose required for the CMC-Na degradation by the addition of some additives and controlling the irradiation conditions. The possibility to crosslink CMC-Na/PAAm and starch/PAAm blends using electron beam irradiation to obtain good adsorbent materials of unique properties for possible practical uses was also investigated.

This research project is dealing with controlling of degradation in radiation processing of natural polymers used for agricultural and industrial purposes. This report will cover all the entire period of the project (the work done during the first two years and during the last third year). In the following, the work done during the first two years will be presented.

2. Effect of Ionizing Radiations on Crosslinking and Degradation of Natural Polymers

2.1 Radiation effects on cellulose

Cellulose exposed to high-energy radiation in dry state undergoes ionization, then most of kicked out electrons are thermalized and eventually recombined with their parent ions. As a result, excited fragments of the polymer are formed. They decompose with cleavage of chemical links, mostly splitting of carbon-bonded hydrogen. This leads to the formation of free radicals on polymer chains and hydrogen atoms. The localization of the energy initiates degradation and dehydrogenation reactions. Several studies revealed that in the case of cellulose derivatives, as CMC, Nitrocellulose Chitosan and Alginate significant part of the free radicals are generated at the substituted side chains. Thus, these free radicals were reported to be responsible for such reactions as grafting or intermolecular crosslinking [5, 6)].

In this sense; radiation effect on CMC, using high energy radiation, was investigated under different conditions. The irradiation process of CMC was taken place in a solid state or in a water-soluble form of different concentrations. The effect of some additive, such as KCl and H_2O_2, on the degradation process during irradiation was also discussed. To elucidate the effect of irradiation on CMC; an aqueous solutions of different concentrations of CMC were exposed to electron beam irradiation. It was found that, the irradiation underwent degradation at high and low concentrations, however, the crosslinking of these polymer occurs when the polymer irradiated at concentrations ranged between (40 ~ 70 wt / wt %) as shown in Figure (1).

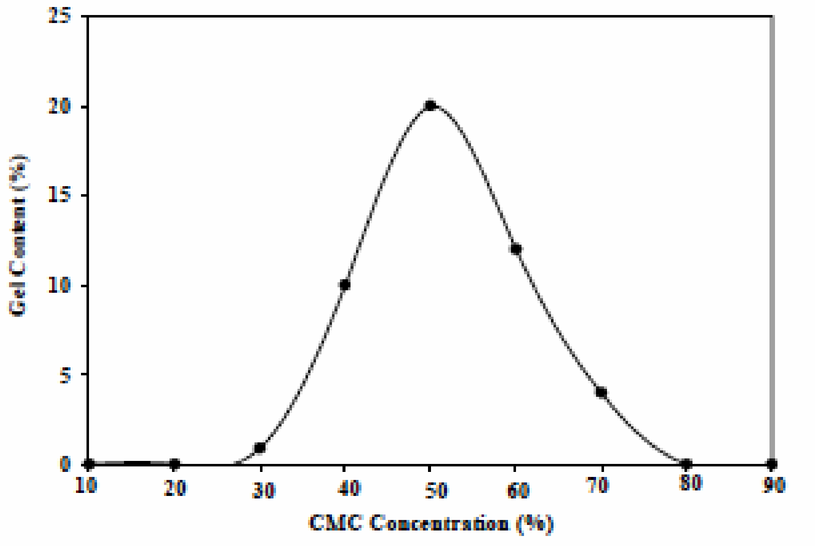

Fig. 1 Effect of different CMC concentrations on its gel content at 20 kGy using EB irradiation in air atmosphere.

It can be assumed that, water contributes in the crosslinking process of CMC in two ways. First, it enhances the mobility of the rigid molecules of CMC, allowing the diffusion of macro radicals to close the distance between each others and consequently allow their recombination. Second, it induces an increase of radical concentration such as, hydrogen atoms and hydroxyl radicals, which resulted from water radiolysis. These radicals can create CMC macro radicals by abstracting H-atom from the polymer chain. Hence, the presence of water enhances the yield of macro radicals; crosslinking of CMC was achieved from a direct effect of irradiation when radiation interacts directly with polymer chains and from an indirect effect when it interacts with the products of water radiolysis.

2.2 Radiation degradation of CMC in solid state

Dry CMC was irradiated at different doses (Figure 2). It can be seen that there is an extreme reduction in intrinsic viscosity at the early doses and thereafter, a gradual decrease is observed with increasing the dose. The viscosity sharply decreased from 17 to 2 when CMC was irradiated at 20 kGy. Thereafter, as the irradiation dose increased, the intrinsic viscosity gradually decreased. Meanwhile, as shown in Figure 3, the addition of 10% water enhanced the degradation process at 20 kGy. The intrinsic viscosity of dry CMC is higher than that of moistened CMC at low irradiation doses. However, at 50 kGy irradiation, the intrinsic viscosity of moistened CMC is higher than that of dry CMC. In the presence of water, beside the CMC chain scission, the CMC have the ability to crosslink at high doses. Generally CMC degrade by scission of the glycoside bond.

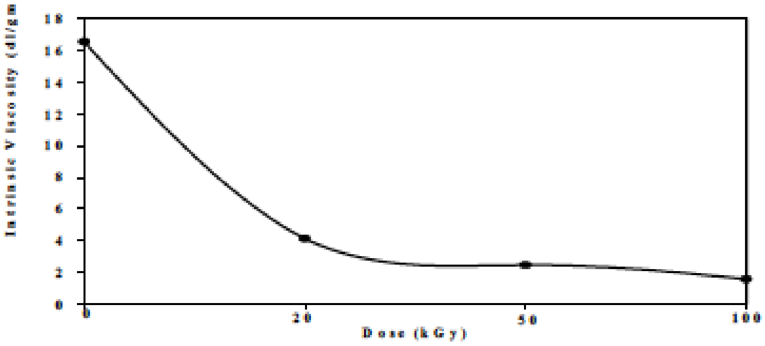

Fig. 2 Effect of irradiation dose on intrinsic viscosity of dry CMC-Na; in 0.01M NaCl, measured in 0.01M NaCl.

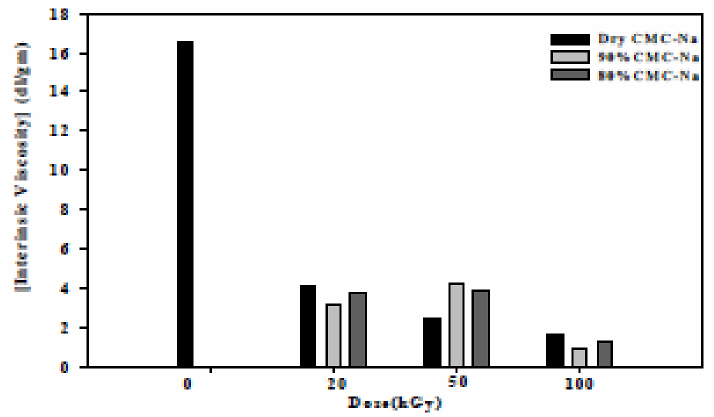

Fig. 3 Effect of irradiation dose on degradation processes of different aqueous CMC-Na concentrations in terms of intrinsic viscosity, measured in 0.01M NaCl.

The effects of moistened CMC-Na concentration and salt additive on the intrinsic viscosity at

20 kGy irradiation dose are shown in Figure 4. It was found that the intrinsic viscosity decreases as the water content increases compared with that irradiated in dry form. However, in the presence of 1% KCl, the intrinsic viscosity is higher than that of moistened CMC, it enhances the crosslinking process and controlling the degradation effects during radiation processing.

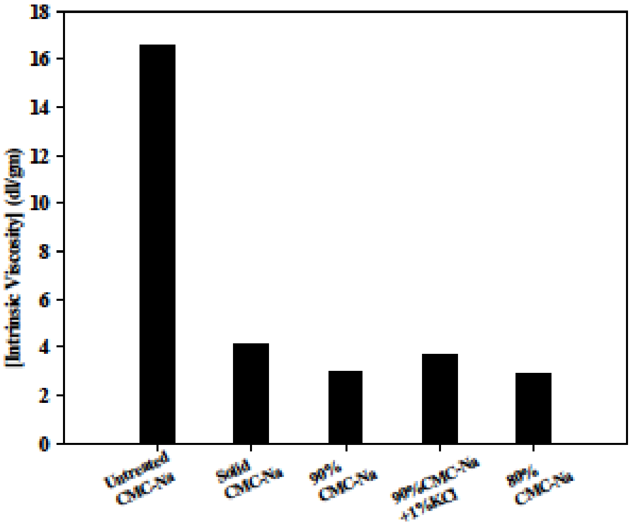

Fig. 4 Effect of different CMC-Na concentrations on the intrinsic viscosity; measured in 0.01M NaCl and irradiated at 20 kGy.

2.3 Thermo gravimetric analysis (TGA)

The occurrence of chain scission is clearly demonstrated by TGA. If the polymer undergoes degradation, its weight will decrease.

Thermo-gravimetric TG curves of irradiated and un-irradiated CMC-Na is investigated and shown in Figure 5. It is clear that the % weight loss of un-irradiated and irradiated 50% CMC-Na appeared at 300 and 280 ˚C, respectively, indicating that the irradiated CMC-Na decomposed at lower temperature than that the un-irradiated one by 20 ˚C which corresponds to the reduction of its molecular weight. The same behavior was observed when the samples of CMC-Na were irradiated in the dry and moistened form.

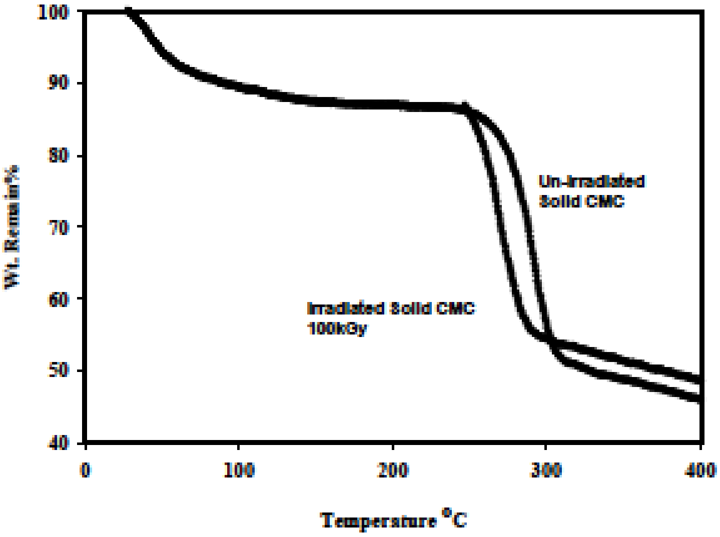

Fig. 5 TGA Thermal Diagram of un-irradiated and irradiated CMC-Na at 100 kGy.

The thermal stability of dried irradiated CMC-Na is higher than that of moistened one.

2.4 FTIR studies on the radiation degradation of CMC at different doses

FTIR was performed to follow up the effect of different irradiation doses on structural changes in the CMC-Na. Figure 6 shows that the intensity of the carboxylate groups at 1625 cm-1 decreases with increasing the irradiation dose. Also, the aliphatic stretch band at 2890 cm-1 and C-O band at 1065 cm-1 decrease as the irradiation dose increases. This means that the cleavage not only occurred in the main chain of CMC-Na but also in carboxymethylated groups on the cellulose ring.

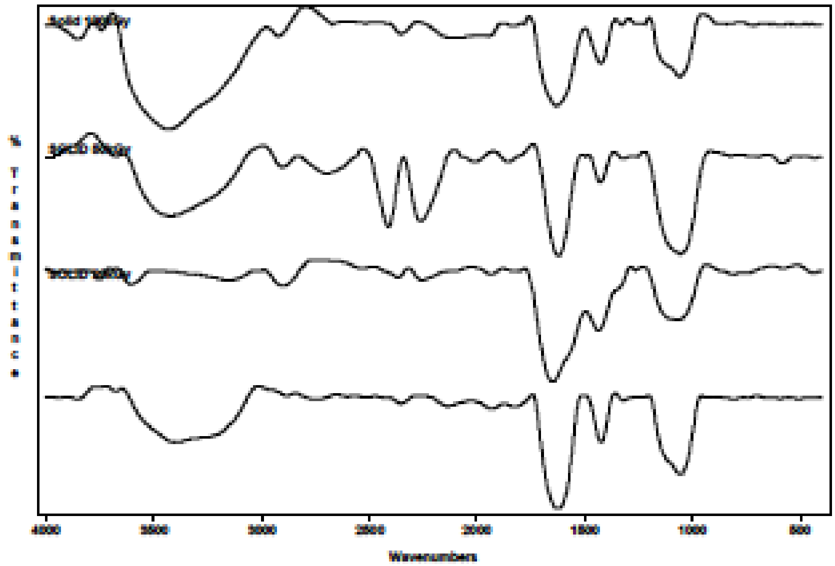

Fig. 6 FTIR spectra of solid CMC-Na irradiated at different doses.

2.5 Effect of radiation on the thermal parameters of CMC-Na

The capability of gamma irradiation on the CMC-Na to cause changes in some of its measurable physical and chemical properties can be detected by thermal analysis. To determine the morphological and structural changes in the polymers, the change in thermal parameters, such as melting temperature (Tm) and heat of fusion (ΔH) of irradiated CMC-Na at different doses under various conditions, were investigated using DSC as shown in Figure 7 and Table 1. From the DSC thermal diagrams, it can be seen that there is a significant change in the (Tm) of the original CMC-Na exposed to gamma irradiation at different doses. A decrease in (Tm) was observed with increasing the exposure dose t certain limit. Thereafter, the increase in radiation dose leads to an increase in (Tm). The same behavior was observed for heat of fusion (ΔH). The apparent decrease in (Tm) and (ΔH) of CMC-Na irradiated with low doses indicated that the irradiation caused structural changes in the CMC-Na chains and consequently, in the crystallinity. However, the apparent increases in the (Tm) and (ΔH) of CMC-Na irradiated with high doses can be attributed to the increase in its crystallinity. The degradation by high dose gamma irradiation results in fragments have a capability to reorient again in crystal form, therefore, there is no significant change in (ΔH) of un-irradiated and high dose irradiated CMC-Na.

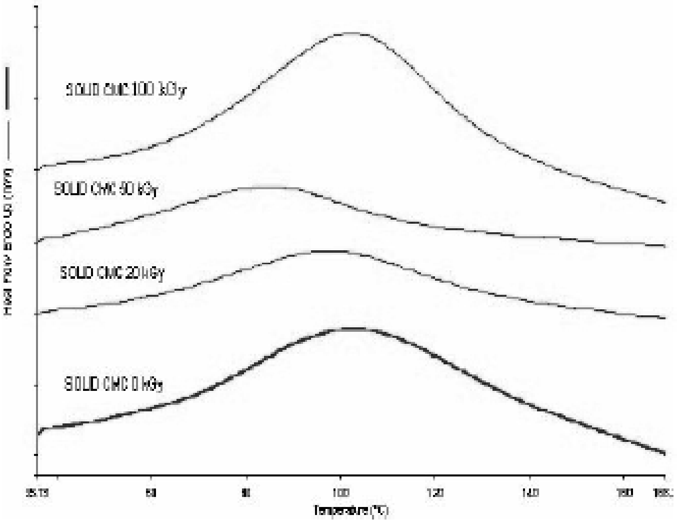

Fig. 7 DSC diagram of solid CMC under the effect of different irradiation doses.

Table 1 Effect of irradiation dose on melting temperature and heat of fusion for solid CMC.

Dose (kGy)	Melting temperature (˚C)	Heat of fusion (J/G)
0	102.5	359
20	91.03	214.9
50	85.6	217.7
100	102.6	442.3

Change in Tm and ΔHm of CMC-Na irradiated at same dose under different conditions was investigated as shown in Figure 8 and Table 2. It was observed that (Tm) and (ΔHm) changed depending on irradiation condition, in solid or wet state and in presence of additives such as KCl. The Tm is remarkably decreased for 80% CMC-Na and in presence of KCl compared to the solid CMC-Na.

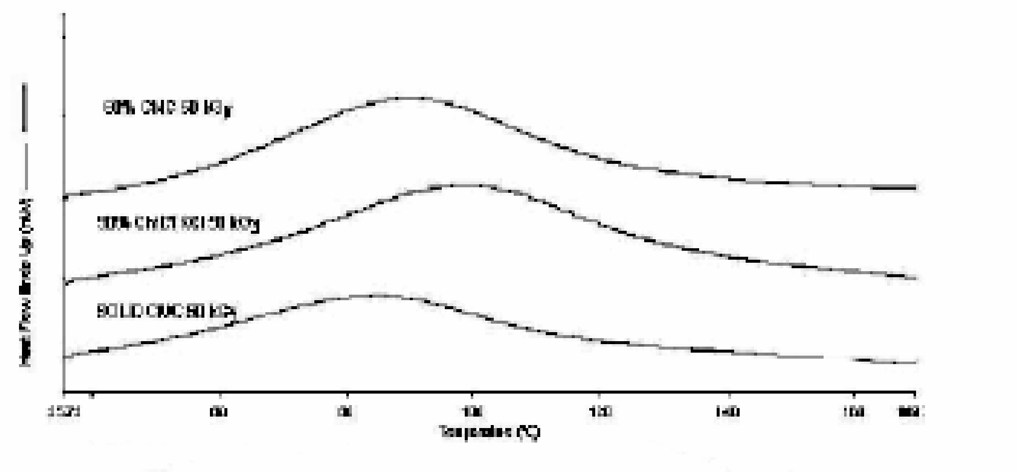

Fig. 8 DSC diagram of different CMC concentration; irradiated at 50 kGy.

Table 2 Effect of concentration on melting temperature and heat of fusion for CMC-Na at 100 kGy.

Sample	Melting temperature (˚C)	Heat of fusion (J/G)
Solid CMC	102.3	442.3
90% CMC +1% KCl	92.0	424.9
80% CMC	90.0	329.6

2.6 Synergistic effect of radiation and oxidizing agents on degradation of natural products

Studying the effect of hydrogen peroxide and/or gamma irradiation on the degradation process of Na-alginate was investigated and shown in Figure 9. It was found that the molecular weight of the polymer decreases by using gamma radiation or H_2O_2. However, combining both gamma radiation and H_2O_2 accelerates the degradation rate of alginate and reduces the dose required to degrading the alginate.

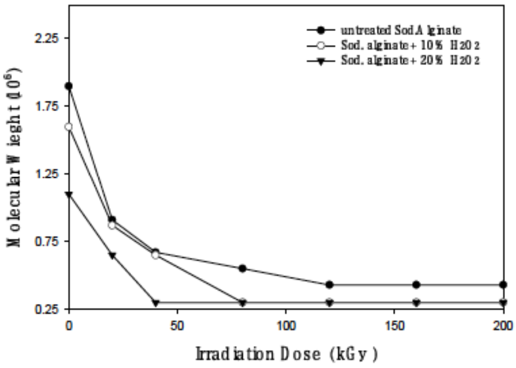

Fig. 9 Effect of H_2O_2 % and different irradiation dose on molecular weight of Na- alginate.

The dose required to reduce the molecular weight of Na-alginate from 1.9 x 10^6 to about 3 ~ 4 x 10^5 is 120 kGy. Meanwhile, the higher the H_2O_2 concentration the more pronounced the degradation of Na- alginate. Similar behavior is observed for Chitosan and CMC-Na as shown in Figs. 10 and 11, respectively.

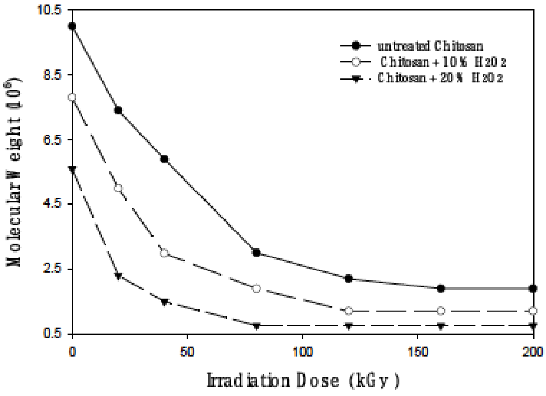

Fig. 10 Effect of dose on molecular weight of chitosan (high molecular weight) in H_2O_2.

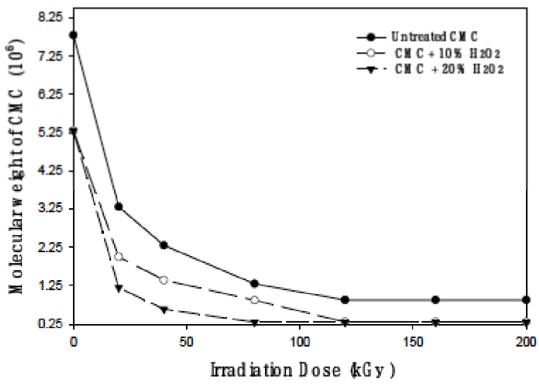

Fig. 11 Effect of dose on change in molecular weight of CMC in H_2O_2.

2.7 Application of degraded Na-alginate incorporated with PAAm in agriculture

Degraded Na-alginate could be used as additives during radiation crosslinking of PAAm for the use as soil conditioner in agriculture purposes. The growth and other responses of bean plant cultivated in the soil that treated with PAAm and PAAm/Na-alginate copolymer were investigated. The test field results showed that the mixing of small quantities of PAAm or PAAm/Na-alginate copolymer with sandy soil results in increasing its ability to water retention. The growth of the bean plant cultivated in the soil treated with PAAm/Na- alginate is better than that one in PAAm alone (Photo 1).

Photo 1 Bean plant cultivated in soil after 9 weeks.
(A) Untreated (control), (B) Treated with PAAm and (C) treated with PAAm/Na-alginate.

The most significant difference between the PAAm and PAAm- Na-alginate copolymer is that the latter is partially undergoing radiolytic and microbial degradation to produce oligo-alginate, which acts as plant growth promoter. The increase in bean plant performance by using PAAm/Na-alginate copolymer suggested its possible use in agriculture uses as a soil conditioner providing the plant with water as well as oligo-alginate growth promoter. Therefore, it could be concluded that the efficiency of PAAm as soil conditioner increases by the addition of Na-alginate.

2.8 Use of controlled degraded CMC incorporated with PAAm in diaper industry

The radiation crosslinking of PAAm is affected by the presence of CMC-Na due to the degradability of the latter one which could be controlled according to its concentration in the bulk medium and irradiation dose. Accordingly, the gel content and swelling properties of PAAm-Na-CMC could be controlled. Figure 12 shows that the degree of swelling increases with dose and showing a maximum swelling at 30 kGy and thereafter it deceases at higher dose (40 kGy). This is due to the degradation processes at relatively medium doses up to 30 kGy and the partial crosslinking may occur at 40 kGy. So, this is a matter of degradation/ crosslinking ratio depending on the dose and concentration of CMC-Na in the mixture.

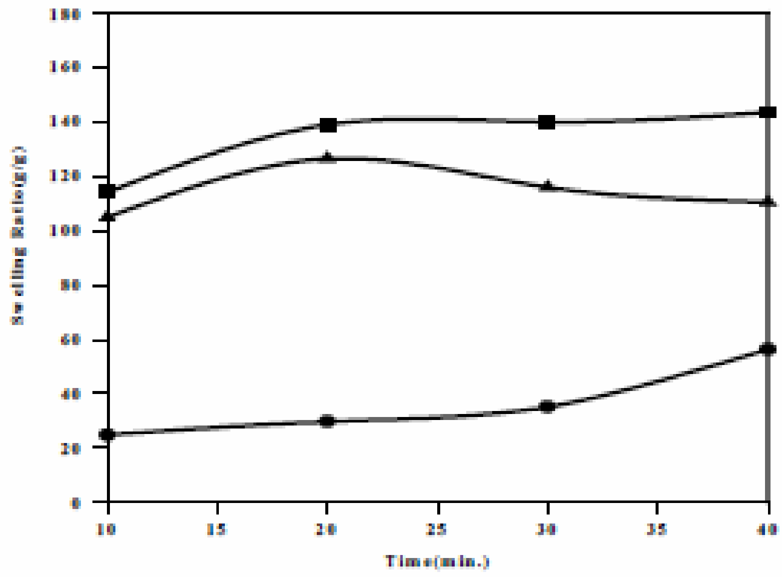

Fig. 12 Swelling ratio for CMC-Na in distilled water, irradiation dose; (■) 30 kGy, (▼) 40 kGy and (●) 20 kGy.

The swelling of the prepared hydrogel was investigated for its possible use in personal care articles particularly diapers. Thus, its degree of swelling was measured in simulating urine solution, and compared with commercial super-porous hydrogels based on acrylate polymers, Figure 13. It is clear that there is a slight difference between the swelling of the prepared CMC-Na/PAAm hydrogel and the commercialized one in the simulated urine solution. The prepared crosslinked copolymers possess high and fast swelling properties in simulated urine media. An acceptable swelling capacity for super-absorbent is approximately 20 ~ 40 g of urine per gram of hydrogel. Therefore, the swelling ratios of CMC-Na /PAAm gels in urine are acceptable for diaper application.

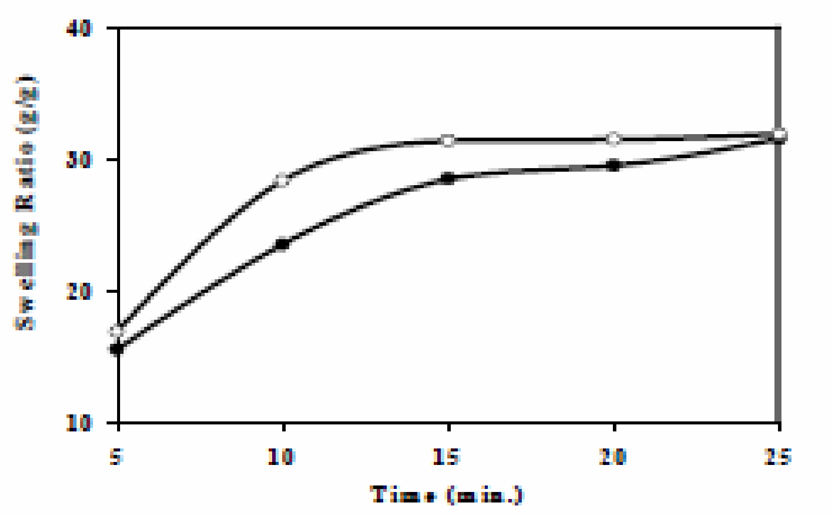

Fig. 13 Swelling ratio of (●) CMC-Na /PAAm super-absorbent hydrogel, (o) commercial diaper; in simulated urine solution.

3. Effect of Irradiation and Salt Addition on Degradation Process of Natural Polymers

Radiation can induce degradation on natural polymers like chitosan, CMC, etc. in their liquid form (concentration of chitosan should be less than 5%) at dose ranged from 40 ~ 200 kGy. In spite of the dose required is relatively low; the degradation process is not economic. On the other hand, the dose required for degrading of solid polysaccharides ranged from 200 ~ 500 kGy. In fact, from the economic point of view these doses are not accepted; the cost is high. Therefore, trails have been made to reduce the cost of degradation process of solid polysaccharides by using some additives during irradiation processes by reducing the dose of irradiation.

3.1. Degradation of molecular weight of natural polymers by radiation and additives

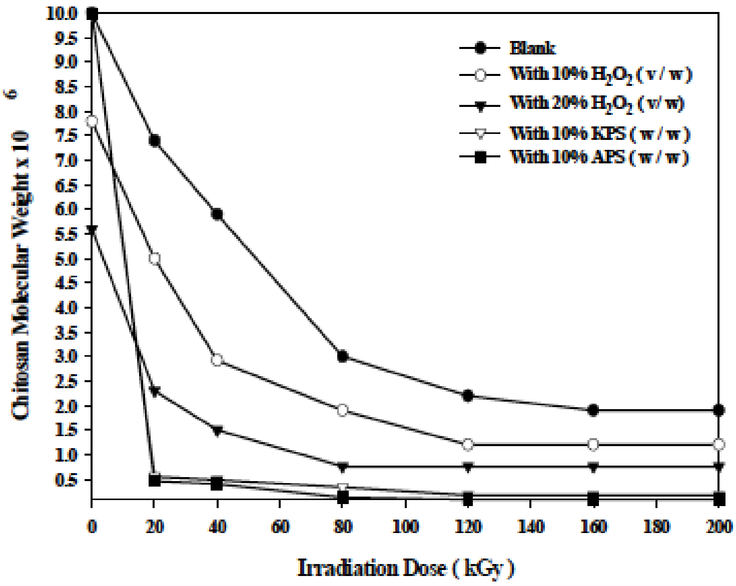

Fig. 14 Effect of irradiation dose on degradation of chitosan in presence and absence of different additives.

Chitosan in a solid form (pure) and that one mixed with different additives (w/w); 10 % H_2O_2 and 10 % potassium per-sulfate KPS or 10 % ammonium per-sulfate APS that soluble in 1 ml water were subjected to gamma irradiation at different doses that ranged from 20 up to 200 kGy. The molecular weights of irradiated chitosan, Na-alginate and CMC were determined using Mark-Houwnik equation by using the viscometeric method in 0.3 M Acetic acid and 0.2 M sod. acetate as a solvent. Figures 14, 15 and 16 show the effect of different irradiation doses on the Mw weights of pure chitosan Na-alginate and those mixed with different additives, respectively. It is observed that the addition of additives to the chitosan during the irradiation process accelerates the degradation of chitosan. Meanwhile, as the irradiation dose increases the degradation process of chitosan increases. The degradation rate of chitosan depends on the type of additives used. The highest degradation rate of chitosan is obtained when APS is used and the lower one in pure chitosan. Using 40 kGy irradiation dose reduces the Mw of chitosan from 1×10^7 to 5.9×10^6. The irradiation of chitosan at 40 kGy in the presence of APS is enough to reduce the Mw of chitosan from 1×10^7 to 4×10^5. Results also showed that the behavior of Na-alginate and CMC degradation is similar to that obtained for chitosan (Figures 15 and 16, respectively). Therefore, the presence of such additives accelerates the degradation processes of such natural polymers resulting in reducing the irradiation dose, which is of economical value to reduce the cost.

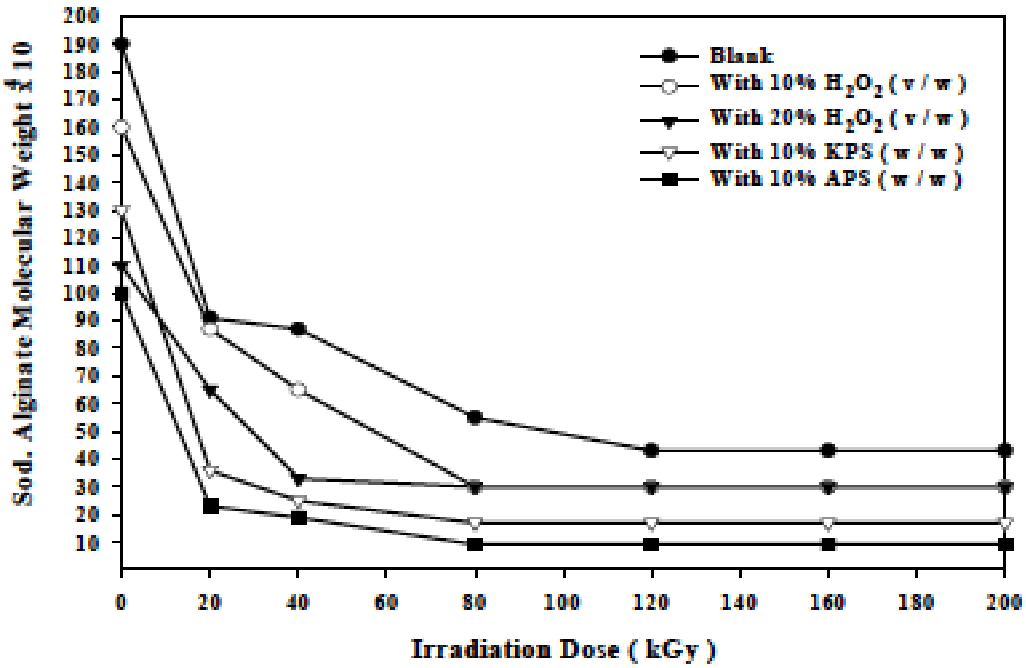

Fig. 15 Effect of irradiation dose on degradation of Na-Alginate in the presence and absence of different additives.

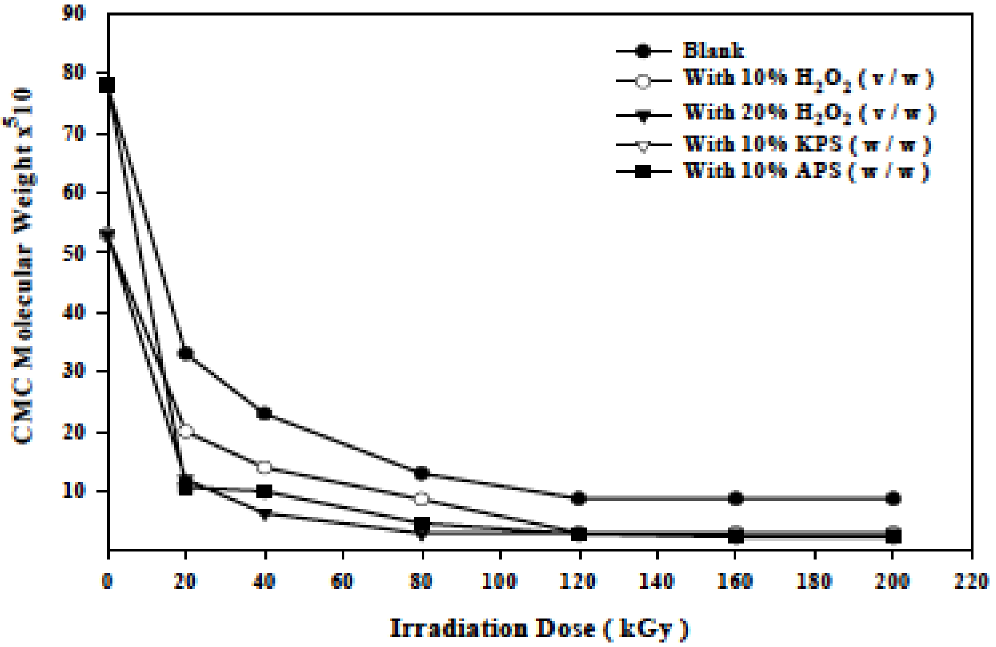

Fig. 16 Effect of irradiation dose on degradation of CMC in the presence and absence of different additives.

3.2. Comparison of radiation degradation with thermal degradation

From the economic point of view, the degradation of chitosan and Na-Alginate in the presence of H_2O_2 or APS as a function of time using thermal heating at 70 ˚C, or gamma irradiation was investigated as shown in Figures 17 and 18, respectively. It is clear that the presence of additives accelerates the rate of degradation for both polymers by heating or by gamma irradiation as well. However, the rate of degradation for both polymers during irradiation, at a given additives, is higher than that for thermal degradation at 70 ˚C. This means that there is a synergistic effect on the degradation rate of such natural polymers when gamma irradiation is used in the presence of APS or H_2O_2.

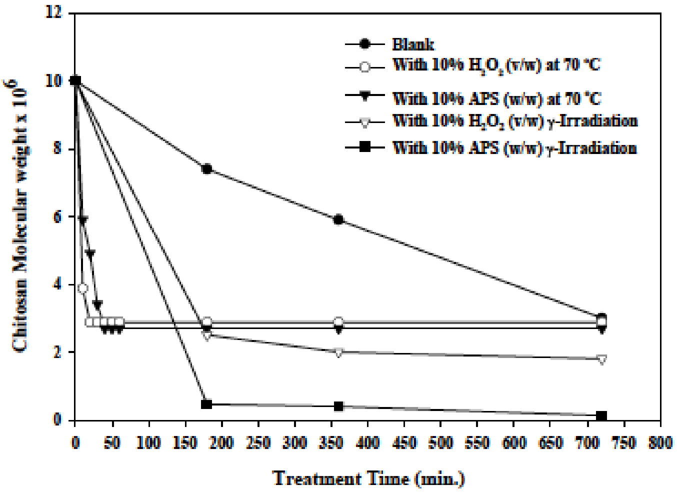

Fig. 17 Effect of treatment time on degradation of chitosan in the presence and absence of additives using gamma irradiation (dose rate 0.66 kGy/h) or thermal heating at 70 ˚C. Blank (Chitosan treated by radiation).

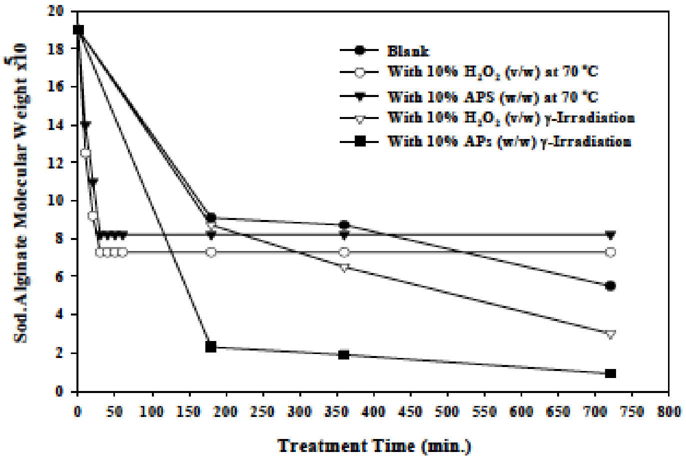

Fig. 18 Effect of treatment time on degradation of Na-Alginate in the presence and absence of additives using gamma irradiation (dose rate 0.66 kGy/h) or thermal heating at 70 ˚C. Blank (Na-Alginate treated by radiation).

3.3. Applications of degraded natural polymers as plant growth promoter

Degraded Na-alginate and chitosan could be used in agriculture purposes as a growth promoter for plants. The growth and other responses of zea maze plant that treated with irradiated

Na-alginate or chitosan of different Mw were investigated. The test field results (Photo 2) showed that the treatment of the zea plant with the irradiated Na-alginate at doses 120, 160, and 200 kGy in the presence of APS results in increasing in plant growth. Meanwhile, the results of the test field (Photo 3) showed that the treatment of the zea plant with irradiated chitosan at similar doses and additive enhances not only the plant growth but also the productivity. The increase in plant performance by using degraded alginate or chitosan suggested its possible use in agriculture purposes as growth promoter.

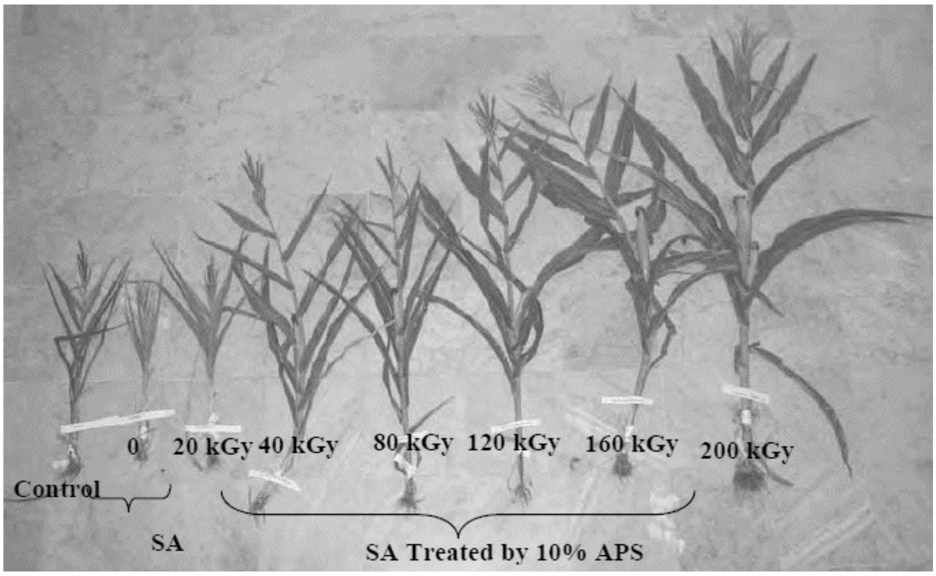

Photo 2 Effect of irradiation dose and APS(10%) on the growth and other responses of zea maze plant that treated with irradiated Na-alginate of different Mw.

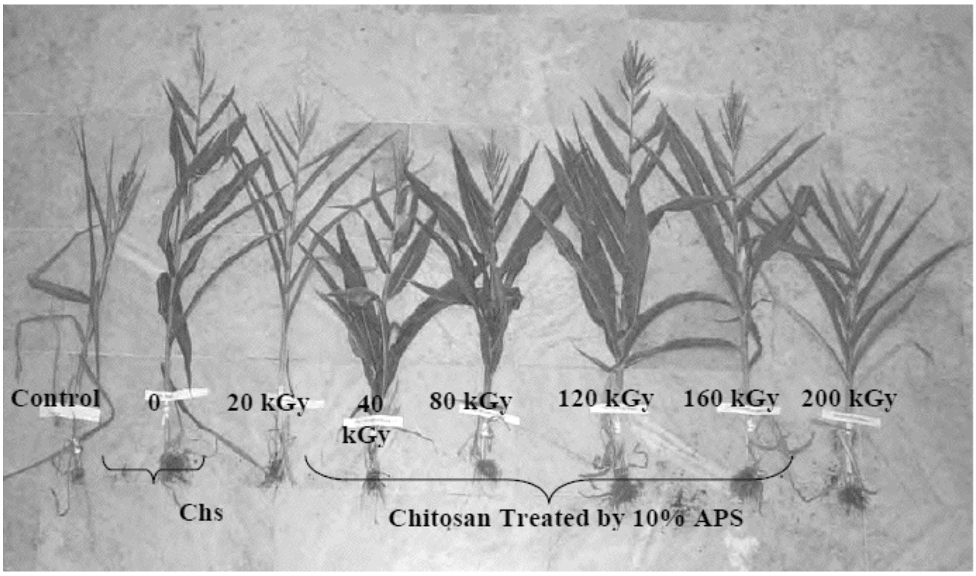

Photo 3 Effect of irradiation dose and APS(10%) on the growth and other responses of zea maze plant that treated with irradiated chitosan of different Mw.

3.4 Modification of LCST of PNIPAAm based natural polymers

LCST of PNIPAAm (thermo responsive polymer) is around 32 ˚C. To modify the LCST of the PNIPAAm, the hydrophilic / hydrophobic balance between PNIPAAm chains, it is necessary t change its characteristic properties mixing with different polymers of different properties. In this connection, NIPAAm monomer was mixed with different types of natural polymers such as polysaccharides. Thereafter, the mixtures exposed to ionizing radiation at different doses to obtain copolymer with different molecular weights by controlling the degradation of natural polymers. In this regards, the following investigations and applicability of the obtained copolymers are presented.

3.4.1 Effect of irradiation dose and natural polymer on gel content of PNIPAAm

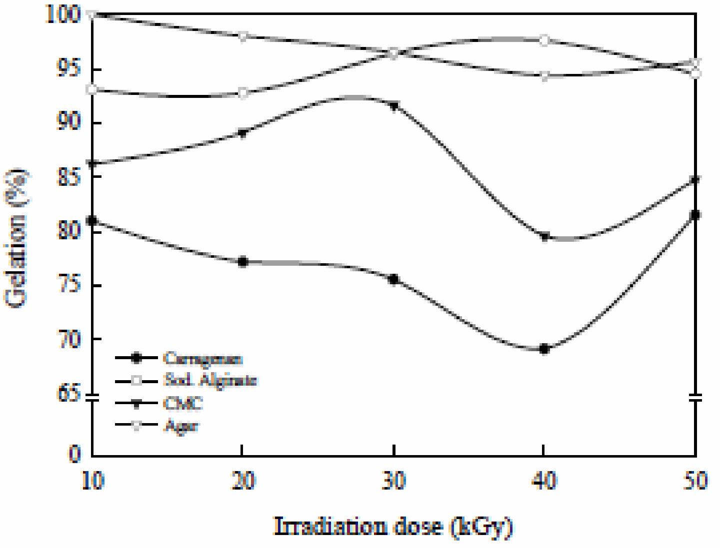

Fig. 19 Effect of irradiation dose on the gelation percent of NIPAAm in the presence of different natural polymers.

Figure 19 shows the effect of irradiation dose on the gelation of PNIPAAm copolymer hydrogel based on natural polymeric materials like carrageenan, Na-alginate, CMC and agar-agar. It is obvious that the gelation of NIPAAm-natural copolymer that prepared by γ-radiation are completely dependent on the nature of the natural polymer. The gelation percent decreases with increasing the dose in the presence of carrageenan and agar. Meanwhile, it increases for Na-alginate and CMC to reach its maximum at 30 kGy. Results showed that agar and Na-alginate are able to form hydrogels of higher gel content than that one containing carrageenan or CMC polymer chains in their structures. The higher gelation of Na-alginate and agar based hydrogel may due to the high binding tendency and excellent gelling ability of alginate and agar, respectively. However, the low gelation of CMC and carrageenan copolymers could be attributed to the higher rate of radiation degradation than the rate of crosslinking. Generally, by exposing the natural polymers to the ionizing radiation, the degradation and crosslinking simultaneously may take place. Crosslinking or degradation of the natural polymer is directly dependent on the rate difference of degradation and crosslinking which is completely dependent on the characteristic properties of the natural polymer. On the other hand, the presence of vinyl monomer such as NIPAAm in such irradiated mixture enhances the formation of crosslinked network structure. From these results it is concluded that the gel content can be controlled by the degradation of natural polymer. As a consequence, the swelling behavior of the NIPAAm/CMC and NIPAAm/carrageenan copolymers could be affected by irradiation dose due to the resulted degradation content.

3.4.2. Effect of natural on the equilibrium swelling of PNIPAAm/natural polymer hydrogels

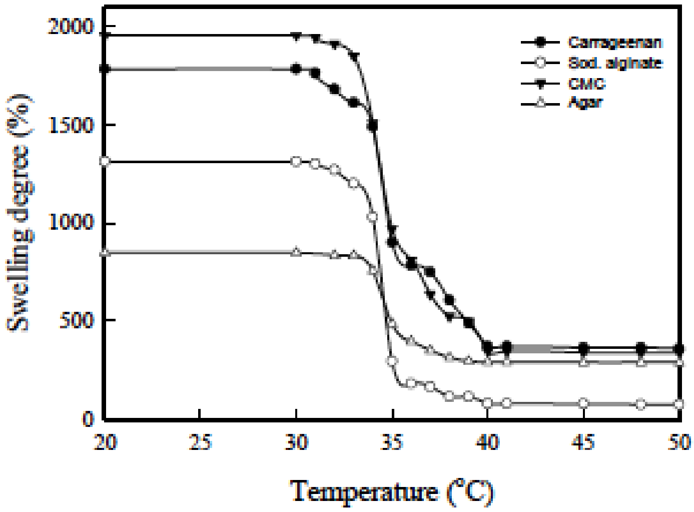

Fig. 20 Temperature dependent swelling behavior of PNIPAAm containing different natural polymeric materials.

Temperature sensitivity of NIPAAm -natural polymer hydrogels was investigated by determining the swelling behavior of the prepared hydrogels as a function of temperature as shown in Figure 20. It can be seen that the prepared PNIPAAm/natural polymer hydrogels possess discontinuous phase transitions. The position and width of such phase transition are dependent on the nature of the natural polymer. The PNIPAAm hydrogel containing CMC- or Carrageenan showed the highest phase transition whereas NIPAAm/ agar showed the lowest phase transition. From these results, it can be seen an inverse relation between the temperature sensitivity and the gelation degree of the prepared copolymer, i.e. CMC and Carrageenan which possessed the lowest gelation degrees showed the highest phase transition. Meanwhile, agar and Na-alginate PNIPAAm copolymers which possessed higher gelation showed lower phase transition. Such interesting observation may confirm and reveal the importance of the crosslinking density on the degree of phase transition. The low gelation of carrageenan or CMC/PNIPAAm hydrogel would produce a network structure of low crosslinking density which is of large for spaces swelling and do not retard the de-swelling process resulted from the collapse of PNIPAAm moieties. Whereas, the gelling and binding properties of agar and Na-alginate, respectively would increase the crosslinking density which reduces the free spaces available for swelling. In addition such properties would retard the chain relaxation which also restricts the collapse of NIPAAm moieties.

Figure 21 shows also the equilibrium swelling of PNIPAAm/natural polymers based copolymers in water at temperatures lower and higher than LCST of NIPAAm, respectively (25 and 45 °C). It is clear that the swelling behavior is very dependent on the nature of added natural polymer in which the higher swelling percent is obtained for PNIPAAm/ Carrageenan or CMC copolymers at 25 ˚C. Below the LCST of PNIPAAm (at 25 ˚C), the prepared copolymer possess as super absorption material. However, above its LCST, the swelling percent very significantly decreased. The obvious difference in the equilibrium swelling at 25 and 45˚C is attributed to the swelling/deswelling behavior of such temperature sensitive hydrogel and inter/intra-molecular hydrogen bonding exchange that takes place by rising the temperature to exceed the LCST of PNIPAAm.

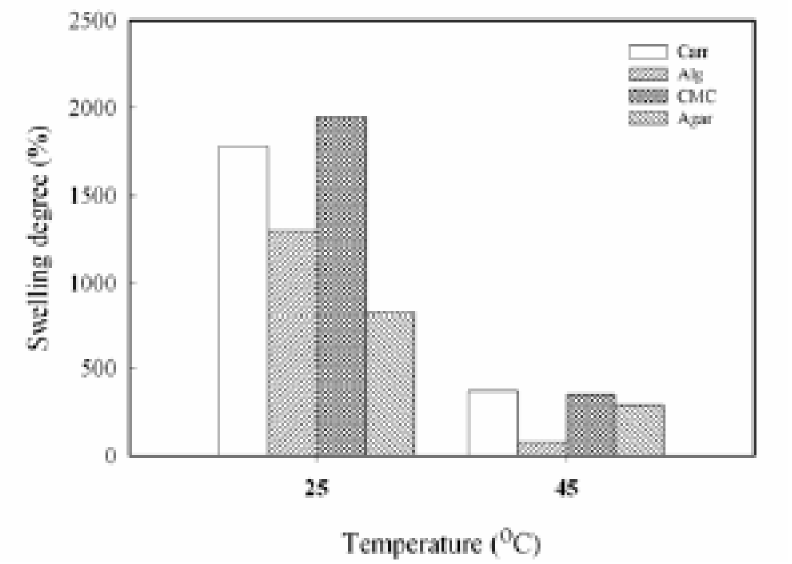

Fig. 21 The equilibrium swelling of PNIPAAm/natural polymers 25 and 45°C.

3.4.3 Effect of irradiation dose on the LCST of NIPAAm/natural polymer hydrogels

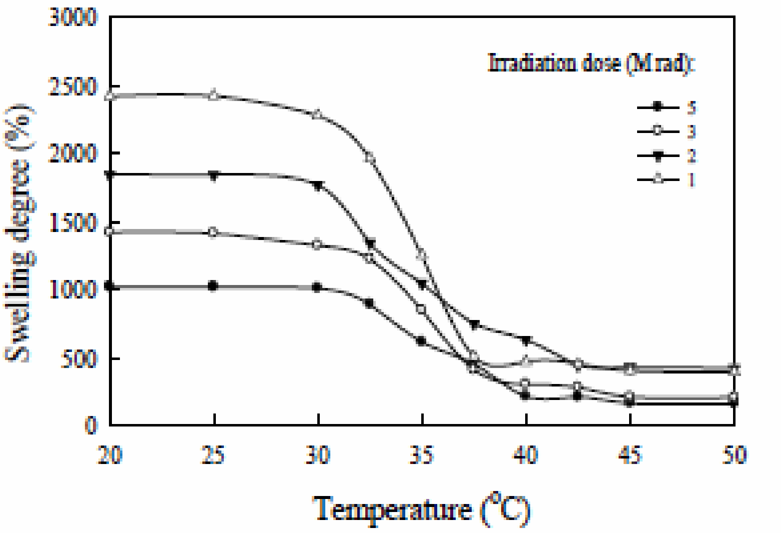

Fig. 22 Effect of temperature on the swelling percent for PNIPAAm/natural polymer hydrogels prepared at different irradiation doses.

To Confirm the relation between LCST and crosslinking density, the effect of irradiation dose on the temperature sensitivity of PNIPAAm/carrageenan hydrogel was investigated (Figure 22). It shows clearly a direct relation between crosslinking density and the degree of phase transition expressed as a function of swelling degree. The PNIPAAm/carrageenan hydrogel prepared at low irradiation doses showed higher phase transition. Whereas, the prepared one at high doses showed lower phase transition character leads to the reduction in the swelling degree.

3.5. Application of PNIPAAm grafted with natural polymers

The prepared thermo-sensitive based natural polymer hydrogels may be used as pH-stimuli responsive for drug delivery systems. Therefore, a trial was made to evaluate its possibility for the use in such purposes for drug delivery under control release depending on the type of based natural polymer. Figure 23 shows the time dependent cumulative release of ketoprofen from PNIPAAm based natural polymer formulations at buffer solutions of pH 1 and pH 7. It can be seen that at pH 1, almost 5% of ketoprofen was released within 3h. On the other hand, as soon as the PNIPAAm based natural polymer formulations moved to the dissolution medium of pH 7, immediate release of ketoprofen began. The rate of its release from PNIPAAm-agar hydrogel is much higher than that from other PNIPAAm based natural hydrogels. In general such based natural polymers hydrogels showed pronounced pH-stimuli responsive and the content of released drug is very dependent on the type of natural polymer in the PNIPAAm hydrogel. Such characteristic properties may make them acceptable for drug delivery systems under control release to specific sites such as colon without side effect on the stomach.

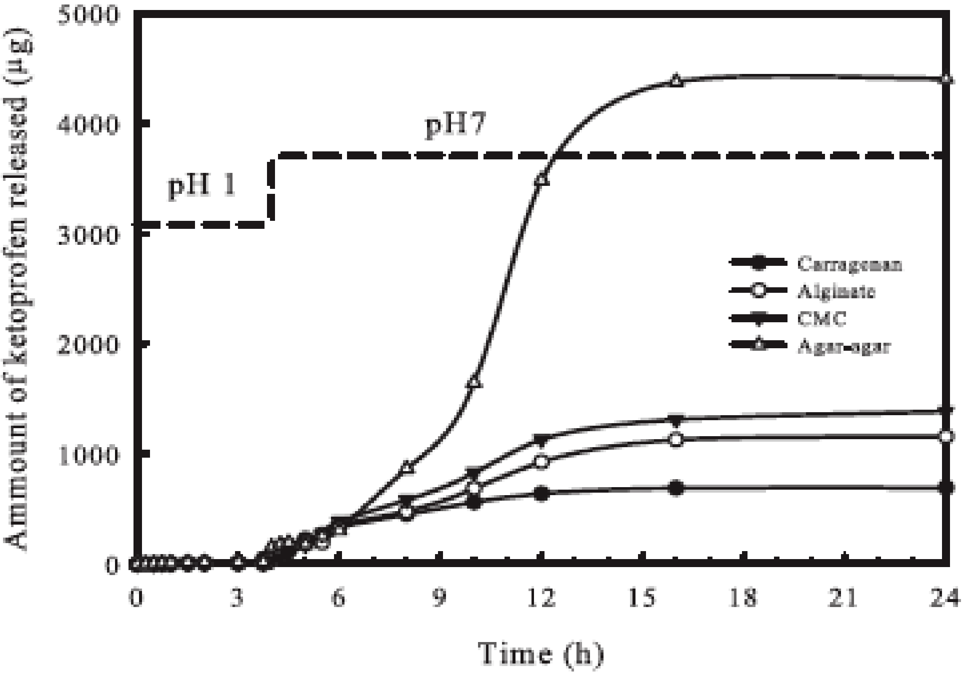

Fig. 23 Effect of natural polymer on the release of ketoprofen from its corresponding copolymer with PNIPAAm at different interval times and pH.

4. Conclusion

It can be concluded that radiation is a very effective tool for controlling the degradation and crosslinking of natural occurring polymers and the synthesis of relative economic, environmentally friendly super-absorbent hydrogels, which may potentially be used in personal care products industry and in agricultural purposes. One of the principle factors for reducing the cost is achieving the degradation at low irradiation doses. This not only reduces the cost of radiation but also improve the quality of the end use products. The end product of irradiated natural products such as carboxymethyl cellulose, chitosan and Na-alginate may be used as food additive or benefited in agricultural purposes. The dose required for degrading the solid polysaccharides is ranged from 200-500 kGy. From economic point of view these doses are not accepted, it was significantly reduced by the addition of APS, KPS and H_2O_2. The addition of such additives t chitosan or

Na-alginate during irradiation process accelerates their degradation. The highest degradation rate of polysaccharides obtained when the Ammonium per-sulfate was used. There is a synergistic effect on the degradation rate of polysaccharides when irradiation was carried out in the presence of additives like APS or H_2O_2. Radiation crosslinking of PAAm or PNIPAAm is affected by the presence of natural polymer like CMC-Na and carrageenan due to the degradability of the latter ones which could be controlled according to its concentration in the bulk medium and irradiation dose. Accordingly, the gel content, thermo-sensitivity (LCST) and swelling properties of polymer based natural polymers could be controlled. The swelling of the prepared hydrogel was investigated for its possible use in personal care articles particularly diapers or as carriers for drug delivery systems. The prepared crosslinked copolymers possessed high and fast swelling properties in simulated urine media and the swelling ratios of CMC-Na /PAAm gels in urine are acceptable for diaper application. Degraded Na-alginate and chitosan could be used as growth promoter for plants in agriculture purposes. The growth and other responses of Zea maze and bean plants that treated with irradiated Na-alginate or chitosan of different Mw's were investigated. The test field results showed that the treatment of the zea plant with irradiated Na-alginate or chitosan, enhanced the plant growth and increases its productivity.

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2. 2. 2 Super Water Absorbent by Radiation Graft Polymerization of Acrylic Monomers onto Cassava Starch

Doan Binh

Research and Development Center for Radiation Technology, Vietnam Atomic Energy Commission

1. Introduction

Water superabsorbent gel has been applying in personal care, agriculture, medical supplies and water purification. In agricultural application 1), the gel will help to control soil erosion, limit loss of nutrients and silt for plants, decrease irrigation frequency, improve infiltration, and increase water retention in prolonged arid soil and droughts. The gel absorbs many times its weight in available water. The gel from poly(acrylamide) was developed in the 60's to grow plants in the deserts 2). The other gel from poly(acrylic acid) was used to absorb rapidly in baby diapers, sanitary napkins. These polymers are commonly produced from natural gas, which have recently been introduced as a soil conditioner with great success 3). Prior to these polymers, peat moss, agro-waste (sugar-cane waste, coffee-shell, etc.), activated kaolin were the alternative soil additives to hold water (20 times its weight), but poly(acrylamide) absorbs 400 times its weight and polyacrylate is capable of absorbing greater amounts of liquid than poly(acrylamide) 4, 5). In addition, starch and cellulose are biodegradable naturally occurring polymers, which are not capable of holding a great amount of water, but their modification by graft polymerization or crosslinking through radiation or chemical initiation techniques, they become the potential superabsorbent polymers. Radiation initiation of chemical reactions has been widely known for making novel materials because the degree of polymerization, grafting and crosslinking process can easily be controlled 6). Recently, it was shown that the starch and cellulose derivatives such as carboxymethyl starch, carboxymethyl starch can be synthesized by radiation-induced crosslinking at high concentrations. Their utilization in agriculture seems to be appropriately evaluated 7). In this article, the graft polymerization and crosslinking of acrylic acid onto cassava starch and field trial of its product (GAM-Sorb S) are reported.

2. Preparation of Super Water Absorbent

Cassava starch was supplied by Bidofood Co. Ltd., Vietnam. Acrylic acid (AAc) was provided by Merck, Germany. Used KOH and methanol were analytical grades from China. The α-amylase enzyme (3,000 IU) was from Vietnam. 10 grams of cassava starch was gelatinized with 120 ml of 10 (%) KOH at room temperature for 45 minutes. The mixture was cooled at room temperature. A weighed quantity of acrylic acid monomer was added into the gelatinized starch during stirring at 60 rpm for 30 min. The starch-monomer mixture was poured into polyethylene packages and sealed tightly. The above mixture was gamma-irradiated in the presence of oxygen in Gamma irradiator (SV-ST Co-60/B type, made by Hungary) in VINAGAMMA at absorbed doses of 4.5, 11, 15 kGy for a dose rate of 1.6 kGy/hr.

3. Characterization of Super Water Absorbent

The graft product was cut into small chips, dried in a vacuum oven at 60 ˚C for 20 h, ground in the granular form of 300 mesh average size. To removal of homopolymer, poly(acrylic acid, PAAc) 5 grams of ground product was extracted in a Soxhlet extractor with methanol for 24 h. The extracted samples was dried in a vacuum oven at 60 ˚C for 24 h and weighed to analyzed the amounts of the grafted copolymer. Graft copolymer percentage (% G) and Homopolymer percentage (% H) were calculated according to the following equations.

$$\text{Homopolymer percentage (\% H)} = (m_1\text{-}m_2) \times 100)/ms$$

$$\text{Graft copolymer percentage (\% G)} = (m_2\text{-}m_s) \times 100)/ms$$

where m_1: dry weight of irradiated sample (g); m_2: dry weight of extracted sample, (g); m_s: Initial dry weight of starch (g).

Effects of adsorbed dose and AAc-to-starch ratio on grafting ratio were shown in Figure 1. Figure 2 shows the effects of adsorbed dose and AAc-to-starch ratio on formation of homopolymer.

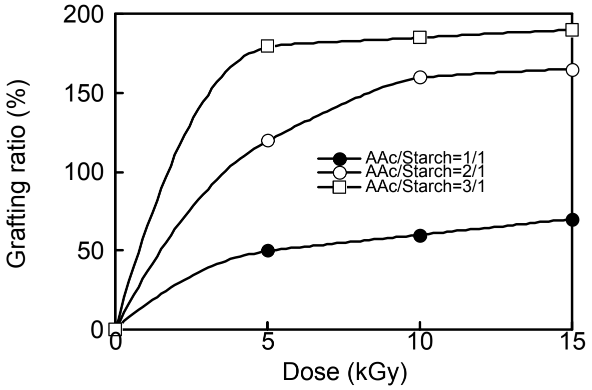


Fig.1 Relationship between absorbed doses, AAc-to-starch ratio and graft copolymer percentage.

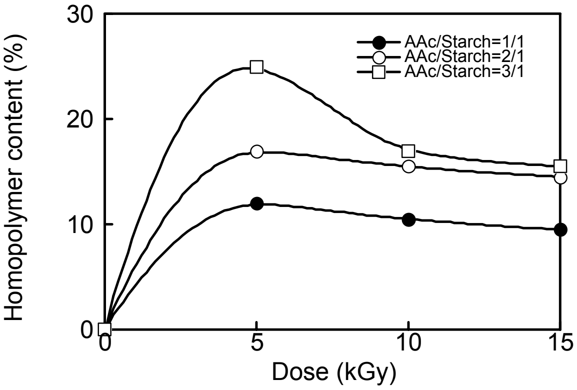


Fig.2 Relationship between absorbed doses, AAc-to-starch ratio and homopolymer percentage.

To measure the Swelling ratio, 0.5 gram of the dry gel sample was immersed in deionized water for 48 h at room temperature. The swollen gel was filtered through a stainless steel net and then weighed. The swelling ratio was determined as follows;

$$\text{Swelling ratio} = (w_2\text{-}w_1)/w_1$$

where w_1: weight of swollen gel (g), w_2: initial weight of dry insoluble part of sample after extracted by distilled water (g).

Effect of AAc-to-starch ration and swelling time on swelling time ratio in deionized water was shown in Figure 3.

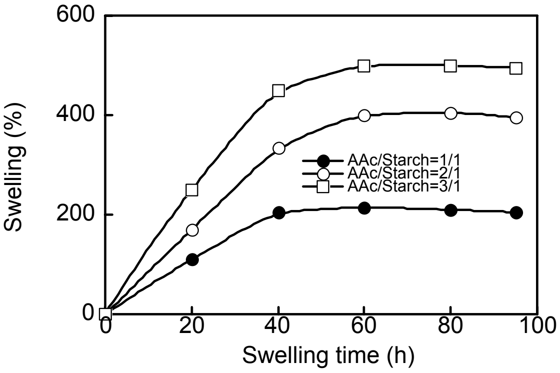


Fig.3 Effect of AAc-to-starch ratio and swelling time on the swelling ratio in deionized water.

To measure the percentage of dehydration, 20 grams of maximum swollen gel was put in a petri-disk, observed the loss of water and then weighed the part of residual gel in certain time duration at room temperature. The dehydration ratio was calculated as follows:

$$\text{Dehydration percentage} = (m_0 - m_1)/m_0 \times 100$$

where m_0: the initial weight of maximum swollen gel (g), m_1: the weight of residual gel after water evaporated (g).

The water dehydration percentage versus time (AAc-to-starch ratio of 1:1, 5 kGy) was shown in Figure 4.

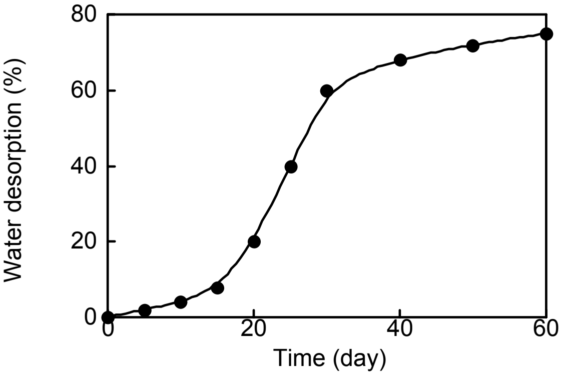


Fig. 4 Dehydration percentage of gel versus time at room temperature.

To analyze the structural of the graft sample, the homopolymer extracted graft was mixed with KBr and pressed to a disk, then measured by FTIR by a Brucker-IFS8 instrument. The FTIR spectrum of starch, starch-g-PAAc (1:1), starch-g-PAAc (1:2), starch-g-PAAc (1:3) and PAAc show that the IR spectra of starch gives the characteristic absorption peaks at 2927 cm^{-1}, 1157, 1080, 1017 cm-1 for the O-H, C-H and C-O stretching, respectively. The IR spectra of starch-g-AAc copolymer gives all the absorption peaks of cassava starch and PAAc, especially appears the additional peaks at 1711 cm^{-1} attributed to –COOH group in the acrylic acid grafted onto starch.

The residue of acrylic acid monomer in graft sample was determined as follows; graft samples in the wet and dry form were immersed with methanol and shaken slightly 48 h, analyzed by HPLC instrument, Shimadzu, Japan. Table 1 shows that the content of residual acrylic acid monomer in both wet and dry graft copolymerization samples is low and be allowed to use according to IPCS [8)].

Table 1. Analysis of residual AAc monomer in the graft sample (5 kGy).

Components	Residual AAc monomer (ppm)	
	Wet state	Dry state
AAc/starch=1/1	34	3.8
AAc/starch=2/1	45	5.1
AAc/starch=3/1	85	7.0

4. Evaluation of Super Water Absorbent

The enzymatic biodegradability test was carried out as follows; 5 mg of dry sample was put in a capped test-tube, which contained 4 ml of an available acetate buffer solution at a pH being 4,6; 1 ml of 2% α-amylase enzyme solution and 1 ml of 0.1% $CaCl_2$ solution. Sample-solution containing test tubes were shaken slightly in a thermostat at 45 ˚C. At given intervals, residual degraded samples were taken out, washed by distilled water for some times, dried in vacuum oven at 60 ˚C for 24 h and then weighed. The rate of enzymatic degradation of graft sample is shown in Table 2.

Table 2 Evaluation of weight loss of graft sample by α-amylase enzyme, 5 kGy.

No.	Time (h)	Loss of weight (%)
1	24	35.8 ± 0.7
2	48	40.1 ± 1.9
3	72	52.2 ± 0.6
4	96	78.0 ± 2.2

The biodegradable method in soil was performed a s follows; 5 grams of dry sample was wrapped by stainless steel net, fixed in the ground at 3 cm depth in the greenhouse at 25 ~ 28 ˚C. At given intervals, the samples were dug from the soil, removed the sticky matters by washing, dried and weighed. The rate of biodegradation of graft sample in soil is shown in Table 3.

Table 3 Observation of weight loss of graft sample in soil (AAc/starch in 2:1, 5 kGy).

No.	Time (month)	Loss of weight (%)
1	1	35.4 ±1.1
2	3	46.2 ± 1.8
3	6	82.1 ± 2.3
4	9	85.5 ± 2.5

The toxic heavy metals such as Hg, Pb, Cd, As were analyzed according to Vietnamese standard by AAS method. Table 4 shows the analytical results of heavy metals.

Table 4 Analysis of heavy metals (AAc/starch in 2:1, 5 kGy).

No.	Metal	Results and detective threshold (mg/kg)
1	Hg (Mercury)	No-detective (MLOD=0.01)
2	Pb (Lead)	No-detective (MLOD=0.05)
3	Cd (Cadmium)	No-detective (MLOD=0.5)
4	As (Arsenic)	0.04 mg/kg

The acute toxicity of graft sample was evaluated according to Vietnamese pharmacopoeia III by using rats by oral exposure. Table 5 shows the evaluated results of acute toxicity test on rats.

Table 5 Acute toxicity on rats through oral exposure (AAc/starch in 2:1, 5 kGy).

No.	Dose of oral route, five rats/oral dose	Observation
1	0.005 g/ml (swelling of 200 times), each rat administered 0.5 ml is equivalent in oral dose of 0.125g/kg of rat weight	No-observed-adverse-effect level
2	0.01 g/ml (swelling of 100 times), each rat administered 0.5 ml is equivalent in oral dose of 0.25g/kg of rat weight	No-observed-adverse-effect level
3	0.02 g/ml (swelling of 50 times), each rat administered 0.5 ml is equivalent in oral dose of 0.5g/kg of rat weight	No-observed-adverse-effect level
4	Higher oral dose of 0.5g/kg of rat weight	Rats can not be administered due to highly concentrated gel

5. Field tests of Super Water Absorbent (GAM-Sorb S, a product of starch-g-AAc)

5.1 Cabbage vegetable

5.1.1 Trial conditions

- Soil type: Rich soil
- Trial place: Hocmon District, Hochiminh city
- Trial quantity: 01
- Test period: March-May, 2005
- Fertilizing method: once for basal fertilizing before planted

5.1.2Trial formulation (kg/ha)

- Substrate (only soil without GAM-Sorb S gel): 120 N + 60 P_2O_5 + 60 K_2O + 5 tons of compost (control test)
- Substrate + 30 kg gel/ha
- Substrate + 40 kg gel/ha

5.1.3Trial results

Formulations	Increasing yield compared to the control (%)
1. Substrate (control)	-
2.Substrate + 30 kg gel	10.3
3. Substrate + 40 kg gel	15.4

5.2 Corn tree

5.2.1 Trial conditions

- Soil type: Rich soil
- Trial place: Duchoa district, Longan Province
- Trial quantity: 01
- Variety: LVN-10
- Test period: November 2005- May 2006
- Fertilizing method: once for basal fertilizing before planted

5.2.2 Trial formulation (kg/ha)

- Substrate (only soil without GAM-Sorb S gel): 140 N + 90 P_2O_5 + 120 K_2O (control test)
- Substrate + 30 kg gel/ha
- Substrate + 40 kg gel/ha

5.2.3 Trial results

Formulations	Increasing yield compared to the control (%)
1.Substrate (control)	-
2.Substrate +30 kg gel	18.8
3.Substrate +40 kg gel	28.8

5.3 Peanut tree

5.3.1 Trial conditions

- Soil type: Rich soil
- Trial place: Trangbang district, Tayninh Province
- Trial quantity: 01
- Variety: Ly
- Test period: winter-spring crop of 2005-2006
- Fertilizing method: once for basal fertilizing before planted

5.3.2 Trial formulation (kg/ha)

- Substrate (only soil without GAM-Sorb S gel): 50 N + 60 P_2O_5 + 90 K_2O + 3 tons of Humix compost (control test)
- Substrate + 30 kg gel/ha
- Substrate + 40 kg gel/ha

5.3.3 Trial results

Formulations	Increasing yield compared to the control (%)
1.Substrate (control)	-
2.Substrate +30 kg gel	16.3
3.Substrate +40 kg gel	21.1

5.4 Cotton tree

5.4.1 Trial conditions

- Soil type: Basalt soil
- Trial place: Trangbang district, Tayninh Province
- Trial quantity: 01
- Variety: VN 02-2
- Planting densities: 4,500 trees/ha
- Test period: Winter-Spring crop of 2005-2006
- Fertilizing method: once for basal fertilizing in combination with compost before planted

5.4.2 Trial formulation (kg/ha)

- Substrate (only soil without GAM-Sorb S gel): 150 N + 75 P_2O_5 + 90 K_2O + 800 kg of earth-worm feces (control test)
- Substrate + 20 kg gel/ha
- Substrate + 30 kg gel/ha
- Substrate + 40 kg gel/ha

5.4.3 Trial results

Formulations	Increasing yield compared to the control (%)
1.Substrate (control)	-
2.Substrate +20 kg gel	9.3
3.Substrate +25 kg gel	24.1
4.Substrate +30 kg gel	31.1

5.5 Coffee tree

5.5.1 Trial conditions

- Soil type: Basalt soil
- Trial place: Đăknong district, Dăklăk Province
- Trial quantity: 01
- Variety: Robusta, 10 years old
- Planting densities: 1,000 trees/ha
- Test period: December 2004- December 2005
- Fertilizing method: once for fertilizing combination at the end of raining season

5.5.2 Trial formulation (kg/ha)

- Substrate (only soil without GAM-Sorb S gel: 250 N + 125 P_2O_5 + 250 K_2O (control test)
- Substrate + 40 kg gel/ha
- Substrate + 60 kg gel/ha

5.5.3 Trial results

Formulations	Increasing yield compared to the control (%)
1.Substrate (control)	-
2.Substrate +40 kg gel	17.3
3.Substrate +60 kg gel	23.8

5.6 Green dragon tree

5.6.1 Trial conditions

- Soil type: fertile soil
- Trial place: Binhthuan Province
- Trial quantity: 01
- Planting densities: 1,200-1,500 trees/ha
- Test period: 2005-2006
- Fertilizing method: once for fertilizing combination at the end of raining season

5.6.2 Trial formulation (kg/ha)

- Substrate (only soil without GAM-Sorb S gel): 800 kg of compost (control test)
- Substrate + 30 kg gel/ha
- Substrate + 50 kg gel/ha

5.6.3 Trial results

Formulations	Increasing yield compared to the control (%)
1.Substrate (control)	-
2.Substrate +30 kg gel	16.3
3.Substrate +50 kg gel	24.8

5.7 Grape tree

5.7.1 Trial conditions

- Soil type: Sandy soil
- Trial place: Ninhthuan Province
- Trial quantity: 01
- Planting densities: 2,000 trees/ha
- Test period: 2005-2006
- Fertilizing method: once for fertilizing combination at the end of raining season

5.7.2 Trial formulation (kg/ha)

- Substrate (only soil without GAM-Sorb S gel): 2 tons of compost (control test)
- Substrate + 30 kg gel/ha
- Substrate + 50 kg gel/ha

5.7.3 Trial results

Formulations	Increasing yield compared to the control (%)
1.Substrate (control)	-
2.Substrate +30 kg gel	18.5
3.Substrate +50 kg gel	29.8

5.8 Sugar-cane

5.8.1 Trial conditions

- Soil type: Impoverished soil
- Trial place: Tayninh Province
- Trial quantity: 01
- Planting densities: 3.000 trees/ha
- Test period: 2006-2007
- Fertilizing method: once for basal fertilizing at the end of raining season

5.8.2 Trial formulation (kg/ha)

- Substrate (only soil without GAM-Sorb S gel): 50 N + 60 P_2O_5 + 90 K_2O + 3 tons of compost (control test)
- Substrate + 40 kg gel/ha
- Substrate + 60 kg gel/ha

5.8.3 Trial results

Formulations	Increasing yield compared to the control (%)
1.Substrate (control)	-
2.Substrate +40 kg gel	10.5
3.Substrate +60 kg gel	19.8

5.9 Cassava

5.9.1 Trial conditions

- Soil type: basalt soil
- Trial place: Binhduong Province
- Trial quantity: 01
- Planting densities: 4,000 trees/ha
- Test period: 2006-2007
- Fertilizing method: once for basal fertilizing

5.9.2 Trial formulation (kg/ha)

- Substrate (only soil without GAM-Sorb S gel): 50 N + 60 P_2O_5 + 90 K_2O + 3 tons of compost (control test)
- Substrate + 30 kg gel/ha
- Substrate + 50 kg gel/ha

5.9.3 Trial results

Formulations	Increasing yield compared to the control (%)
1.Substrate (control)	-
2.Substrate +40 kg gel	13.5
3.Substrate +60 kg gel	22.8

5.10 Lily flowering plant (Asiatic hybrid flower)

5.10.1 Trial conditions

- Soil type: basalt soil
- Trial place: Dalat city, Lamdong Province
- Trial quantity: 01
- The genus: Lilium, herbaceous flowering plant growing from bulb.
- Planting densities: 45,000 trees/ha
- Test period: in early 2007
- Fertilizing method: once for basal fertilizing

5.10.2 Trial formulation (kg/ha)

- Substrate (only soil without GAM-Sorb S gel): 50 N + 60 P_2O_5 + 90 K_2O (control test)
- Substrate + 25 kg gel/ha
- Substrate + 40 kg gel/ha

5.10.3 Trial results

Formulations	Height of harvested plants (cm)	Blooming time
1.Substrate (control)	80-90	90 days
2.Substrate +25 kg gel	90-100	Earlier than 6 days
3.Substrate +50 kg gel	90-100	Earlier than 10 days

5.11 Reference of field trials of commercialized super water absorbent gel

5.11.1 Tomato

5.11.1.1 Trial conditions

Trial place: Florida, USA
Trial quantity: 01
Trial polymer: Poly(acrylamide)
Test period: Spring 2000

5.11.1.2 Trial formulation (kg/ha)

Substrate (only soil without gel): (control test)

Substrate + 60-70 kg gel/ha

5.11.1.3 Trial results

5% increase in productivity/ ha

5.11.2 Potato

5.11.2.1 Trial conditions

Trial place: San Juan district, Ica, Peru and Matt Heimrich Farm, Crowley County, Colorado

Trial quantity: 01

Trial polymer: Poly(acrylamide) (Horta-Sorb)

Test period: March 1995

5.11.2.2 Trial formulation (kg/ha)

Substrate (only soil without gel): 240 N + 80 P_2O_5 + 80 K_2O (control test)

Substrate + 120 kg gel/ha proportion of the mixture: 1,000 g mixture containing 600 g of gel (60%) and 400 g of ammonium nitrate (40%))

5.11.2.3 Trial results

18 (%) increase in productivity/ ha

5.11.3 Pepper

5.11.3.1 Trial conditions

Trial place: Florida, USA

Trial quantity: 01

Trial polymer: Poly(acrylamide) (watersorb)

Test period: Spring 2000

5.11.3.2 Trial formulation (kg/ha)

Substrate (only soil without gel): (control test)

Substrate + 60-70 kg gel/ha

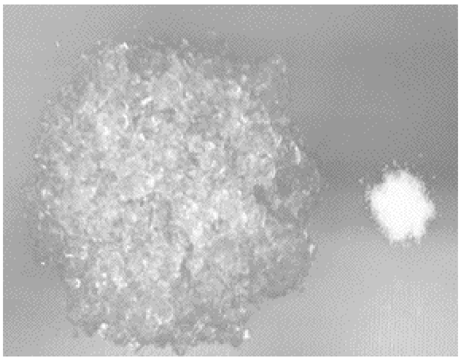
5.11.3.3 Trial results

24 (%) increase in productivity/ ha

Reference

1) http://www.horticulturalalliance.com
2) http://www.watersorb.com
3) http://www.ingentaconnect.com
4) Report on results of field test of Gam-Sorb S gel for conditioning the soil. Institute for the Southern Agricultural Science and Techniques, Hochiminh City, Vietnam, March 2006

6. Photographs Taken for Field Tests of GAM-Sorb S



The swelling observation of GAM-Sorb S Right: Before swelling, Light: After swelling

GAM-Sorb S Product.

Field trial of GAM-SORB S product

1. Grape

2. Cotton

3. Dragon

4. Cassava

Lily flowering plant

Field test of Gam-Sorb S gel on Lily flower in Dalat, Vietnam, July-Sept., 2007

With GAM-Sorb gel *Without GAM-Sorb gel*

1 week

1 week

4 weeks

4 weeks

9 weeks

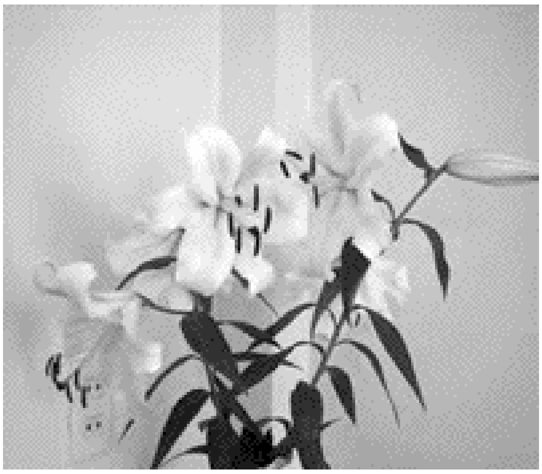
9 weeks

12 weeks

12 weeks

Roots after 12 weeks

Roots after 12 weeks



Blooming

Blooming

7. Conclusion

1). Starch-g-PAAc product can absorb a large amount of water of 200-500 times in their weight depending on starch-to-AAc ratio (1/1, 1/2, 1/3) at an absorbed dose of 4.5 kGy for a dose rate of 1.6 kGy/h.

2). The product is a biodegradable one through study test of α-amylase enzyme and soil-buried sample. 70-85 (%) weight loss of above experimental samples is very potential for promising agricultural applications in the near future (soil conditioner).

3). The field tests of some plants with use of the gel were shown that their productivities had increased 10-30 (%) if compared to plants without use of the gel for different soil sorts.

4). The Ministry of Agriculture and Rural Development allows producing GAM-Sorb S product as a soil conditioner in Vietnam according to the decision no. of 1247 QĐ/BNN-KHCN dated 28 April 2006 9).

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2. 2. 3 Effective Utilization of Agro-Waste by Application of CMC Dry-Gel

Fumio Yoshii

Japan Atomic Energy Agency

1. Introduction

Radiation crosslinking, graft polymerization and degradation are useful technologies to improve polymer materials. Processability of radial tires and heat resistance of wire/cable is improved by crosslinking technology. Polysaccharides such as starch/cellulose of natural polymers and their derivatives are typical degradable polymers. Molecular weight of polysaccharides was remarkably reduced at lower dose, 50 kGy. To expand application field of polysaccharides, it is essential to obtain crosslinking structure. It was found that polysaccharide derivatives such as carboxymethyl cellulose (CMC) and carboxymethyl chitosan undergo crosslinking at past-like condition and form hydrogels1,2). Concentration of past-like condition to induce crosslinking should be more than 10%. High molecular weight (Mw) and high degree of substitution (DS) is preferable for crosslinking of polysaccharide derivatives. In this paper, treatment of agro waste and improvement of Japanese traditional paper by addition of CMC dry gel is reported.

2. Production of CMC Dry Gel

CMC was irradiated at past-like condition in concentration range 20 - 30% for crosslinking. After that, irradiated CMC was dried (CMC dry gel) to be applied as a water absorbent. CMC gel often degrades during drying at high temperatures such as shown in Figure 1. According to these data, gel fraction decreased remarkably for CMC with DS 0.88 and 0.95. Thus, it is confirmed that 60 - 70℃ is better to get CMC dry gel. Furthermore, crosslinking behavior of CMC at past-like condition was investigated. High dose is not favorable to lead lower water absorption for high crosslinking density. Irradiation at low dose, 5 kGy for CMC paste, was adopted. CMC paste was irradiated at concentration 20% to obtain high water absorption after drying.

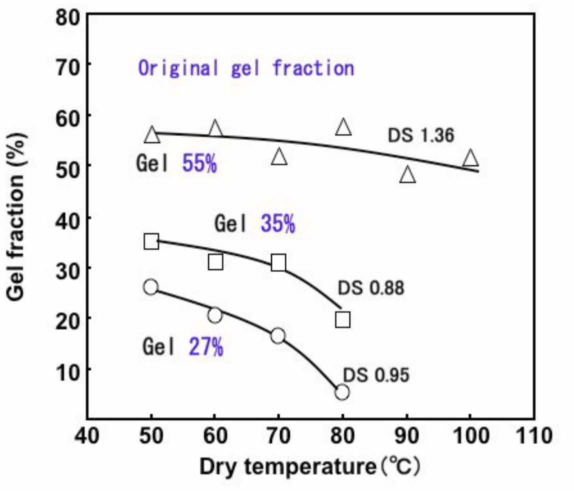


Fig. 1 Effect of dry temperature on gel fraction.

Large scale irradiation of CMC paste was carried out for treatment of agro waste, improvement of Japanese traditional paper and other applications. 750 kg of 20% CMC paste in one bath was irradiated at 5 kGy. After irradiation 150 kg of CMC dry gel was obtained. 1g of dry gel absorbed 300g pure water and 50 - 60g of artificial urine. Figure 2 shows the swelling behavior of CMC gel. CMC dry gel adsorbed water in Petri dish.

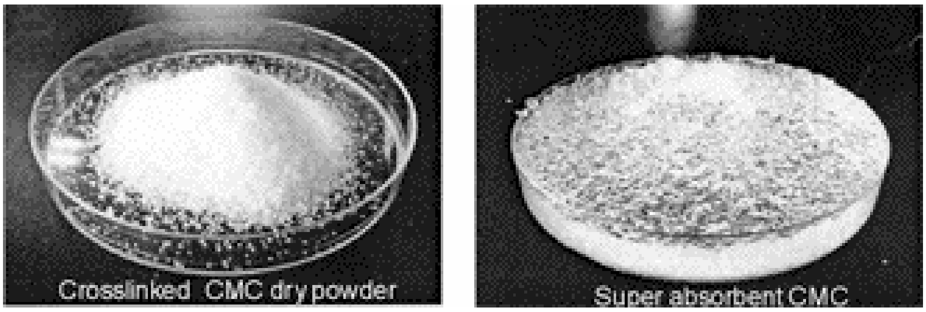


Fig. 2 Swelling behavior of CMC gel.

3. Agro Waste Treatment by CMC Dry Gel

In Japan, release of excrement and urine from domestic animals, such as cattle and pigs to the river and penetration into underground water was prohibited since November 2004. In this law, it is desired to convert immediately excrement and urine into organic fertilizer by fermentation. However, excrement and urine from cattle contain 85% to 90% water, so that it is difficult to carry out fermentation smoothly. Thus, present method consists of mixing sawdust in amount 1.0 ~ 1.5 (volume ratio) with the excrement and urine to reduce 65 ~ 70% water content and enhancing fermentation. Addition of 0.2% CMC dry gel to the process can reduce consumption of sawdust to 1/7 in comparison with the present method. This novel technology gives following advantages: 1) reduction of saw dusts, small storage area for saw dust, [3)] decrease in heavy work, reduction of odor diffusion in environment3).

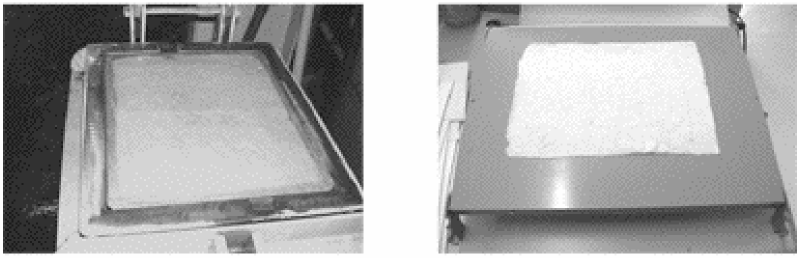
Japanese liquor, Shochu (alcohol content, 25%) is produced by fermentation of rice and sweet potatoes. After production of Shochu, a lot of Shochu residues are formed. These residues, which contain 90% of water, are thrown away in the deep sea but throwing of Shochu residues in the sea will be soon prohibited. Thus, it is desired to find new technology for reuse of Shochu residue. It was found that CMC dry gel and comcob added to Shochu residues easy removed of water during drying and convert it to animal feed [3)].

4. Improvement of Japanese Traditional Paper

Japanese traditional paper (Washi) is well applied with toughness properties in fold screen and book paper but it is necessary to lead high function for increase the application field. CMC micro gel prepared by mixing with warm water was added to original Washi fluid (Figure 3a). The mixture was poured in cast plate (Figure 3b) and dried to get paper (Figure 3c). From measurements of physical properties of obtained paper, it was confirmed that addition of CMC micro gel is effective for improvement of strength and has lower shrinkage by changing the environment from dry to water.

Mixture of original paper and CMC micro gel (a)

Casting of the mixture

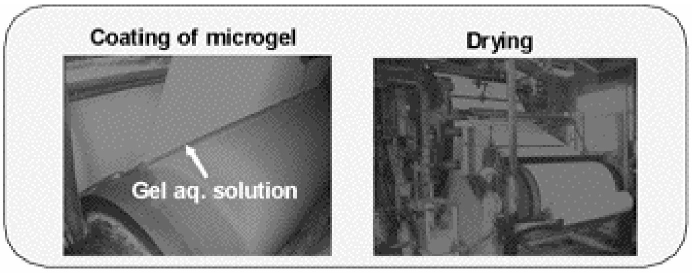


(b)

Drying (c)

Fig. 3 Modification of Japanese traditional paper by addition of CMC dry gel.

According to these experiments, CMC micro gel was dispersed in the Washi by practical instrument (Figure 4). Physical properties of paper after drying are shown in Table in Figure 4. Strength of paper increased from 2.91kg to 10.5kg for length and from 3.06 kg to 4.6 kg for width, respectively. Elongation of Washi with added gel immersed in water was retarded from 1.3% to 1.1%. It is apparent that change in shrinkage of Washi is smaller by addition of CMC micro gel.



Coating of microgel

Drying

Length immersed in water

Gel conc.	Length(%)	Width(%)
0%	1.3	1.3
1%	1.1	1.1
2%	1.1	1.1
3%	1.0	1.1

Tensile properties

紙質試験表		Gel 0%	Gel 2%
Strength (kg)	Length	2.91	10.5
	Width	3.06	4.6
Elongation (%)	Length	1.6	1.9
	Width	1.9	2.4
Burst strength (g)		1.5	2.7

Fig. 4 Production of Washi with addition of gel and its properties.

5. Regulations for New Material Production in Japan

CMC of water soluble polymer is well used in medical, food and industry fields. But in Japan, there is “Law Concerning the Examination and Regulation of Manufacture, etc of Chemical Substances” to prevent environment contamination by chemical substances. CMC dry gel had new covalent bond by radiation crosslinking and properties changed from water soluble to insoluble, so that it was evaluated that CMC dry gel is new material for government. It is obligated to clear this law by production of new materials in amount above one ton. Now we are going to carry out various long terms tests such as 6 months examinations using animals and fish by cooperation of two companies.

References

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2.3 Plant Growth Promoter

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2. 3. 1 Commercial Application of Radiation Degraded Alginate

Le Quang Luan

Center for Nuclear Techniques, Vietnam Atomic Energy Commission

Abstract

For commercial any product in agriculture, it must be carried out in several steps. The basic research should be done at fist. The interesting results on irradiated alginate and chitosan were obtained. In particular, alginate with Mw *ca.* 9.04 x 10^5 was irradiated at 75 kGy (Mw ~ 1.43 x 10^4Da) had the highest positive influence for growing of flower plants, namely limonium, lisianthus and chrysanthemum. The product of chitosan with 80 % degree of deacetylation and Mw approx. 4.8 $\times 10^4$ irradiated at 100 kGy (Mw ~ 1.6×10^4 Da) showed the strongest growth promotion effect on the mentioned plants *in vitro*. The survival ratios of the transferred plantlets treated with irradiated alginate were almost the same as the control value in the green house condition, while the treatment of irradiated chitosan improved the survival ratio and growth of transferred plantlets acclimatized from 10 to 30 days in a greenhouse condition. Based on above results, a plant growth promotion product prepared from irradiated alginate namely T&D. To get the certificate for commercialization, the toxicity tests and trial field tests must be done to satisfy the Department of Plant Protection, Ministry of Agriculture and Rural Development.

1. Introduction

Oligoalginate, a degraded product of alginate was found to have several novel features, which can be useful in agricultural field. It was reported that this oligosaccharide had successfully acted as plant growth promoter, phytoalexin induction trigger as well as it enhanced the activity of enzymes toward plants [1~5)]. Adachi, et al. [1)] reported that the addition of oligoalginate into the growth medium had strong effect in increasing leaf weight (114%) and tuber weight (324%) of Japanese radish. Yonemoto, et al. [2)] showed that oligoalginate with Mw ca. 1.8 x 103 had a strong effect on shoot elongation of rice, grains and tobacco. Germination rate of barley and growth rate of its root was positively affected by a supplement of 800 mg/l oligoalginate [3)]. Degraded chitosan has been reported to have various novel biological effects [4 ~ 8)]. Oligochitosan can cause an accumulation of antibiotic phytoalexins to prevent infection of fungal diseases [9 ~ 14)] as well as stimulation of plant growth, induction of the root system and strengthening stem of plants.

Recently much attention has been paid to apply the radiation processing technology for obtaining degraded natural polysaccharides due to several superiority of this method over conventional enzymatic degradation process. Main advantages include: degradation reaction can be carried out at room temperature, after processing the degraded alginate can be used without purification, simplicity of controlling the whole process and above all the large scale application.

The above points suggest the possibility of the application of irradiated polysaccharides in agriculture as plant growth promoter and plant protector.

2. Methods

2.1 Preparation of irradiated alginate and chitosan

Alginate and chitosan were kept overnight in water and 2.5 % solution of acetic acid, respectively at room temperature for swelling and then stirred for 5 hours to obtain the solution [15)]. The solutions were then irradiated by γ-rays from a Co-60 source at the doses up to 200 kGy for degradation.

2.1.1 In vitro plant growth test

Flower plants used in the present experiments are limonium (*Limonium latifolium*), lisianthus (*Eustoma grandiflorum*) and Chrysanthemum (*Chrysanthemum morifolium*). To investigate the effect of irradiation dose for alginate on the growth of plantlet, 20 plant shoots were cultured in a vessel containing MS medium, supplemented with irradiated alginate and irradiated chitosan.

2.1.2 Plantlet culture

To investigate the effect of dose, the plant shoots were cultured in a vessel containing half strength of MS medium modified as described previously 18[)] and supplemented with 50 mg/L chitosan irradiated at different doses. Samples were incubated for 15 days for chrysanthemum and 20 days for limonium and lisianthus.

2.2.3 Transfer to soil

A hundred of plantlets with good developed roots were removed and washed gently with tap water. The plantlets were then transferred to pots containing a mixture of soil and fertilizer and cultivated for 30 days in a greenhouse.

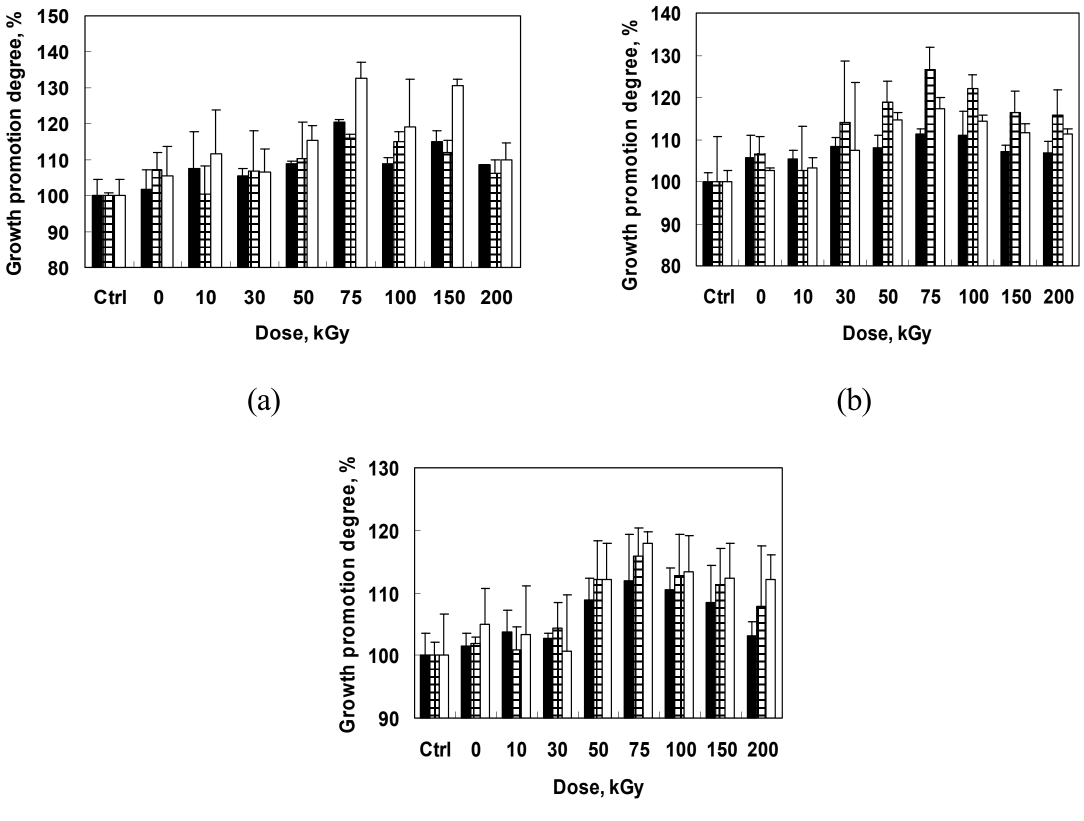
3. Results and Discussion

3.1 Basic researches

3.1.1 Plant growth promotion effect of the irradiation alginate

Nowadays, ornamental flowers such as chrysanthemum, lisianthus, limonium, etc. are of special interests to horticulturists because of their popularity and commercial importance. Tissue culture technique has been used as a useful method for *in vitro* propagation to obtain the high quality young plants for plantation of for example mentioned above flowers. The technique requires a suitable medium, supplementation of phytohormones, conditions of culture, etc. but the gain is worth of it. In addition, oligosaccharides have been reported to have biological effect on growth of plants, particularly on morphogenetic process [16)], root and shoot elongation, promotion of antibiotic enzymes induction and enhancement of enzyme activity [3,16~21)]. Mw or degree of the polymerization (DP) of polysaccharides is the key point for its biological activity [15,18)]. This experiment was carried out to investigate the most appropriate irradiation dose required for degradation of alginate to obtain a suitable Mw, which can be effective for plant *in vitro* propagation.

Previous studies revealed that oligoalginate had high positive effects on the increase of root length of barley seedling (2.4 mm/h) [4], tuber mass of Japanese radish (324%) [2] and dried mass of rice (20%) [15]. In plantlet culture, the induction and development of root are important processes to obtain plantlets of good quality. The irradiated alginate has the ability to affect these two steps of plant development. The comparison of the growth promotion effect on chrysanthemum is presented in Figures 1(a) ~ (c). The treatment by alginate irradiated at 75 ~ 150 kGy increases shoot height (9.0 ~ 20.5%), root length (11.6 ~ 12.1%) and fresh biomass (19.0 ~ 32.6%) of plants. On the other hand, the treatment of plants by alginate irradiated at doses below 75 kGy or above 200 kGy gave unstable results and no significant difference was observed compared with the untreated control. The growth promotion effects of irradiated alginate on lisianthus and limonium are shown in Figures 1(b) and (c).



(a)

(b)

(c)

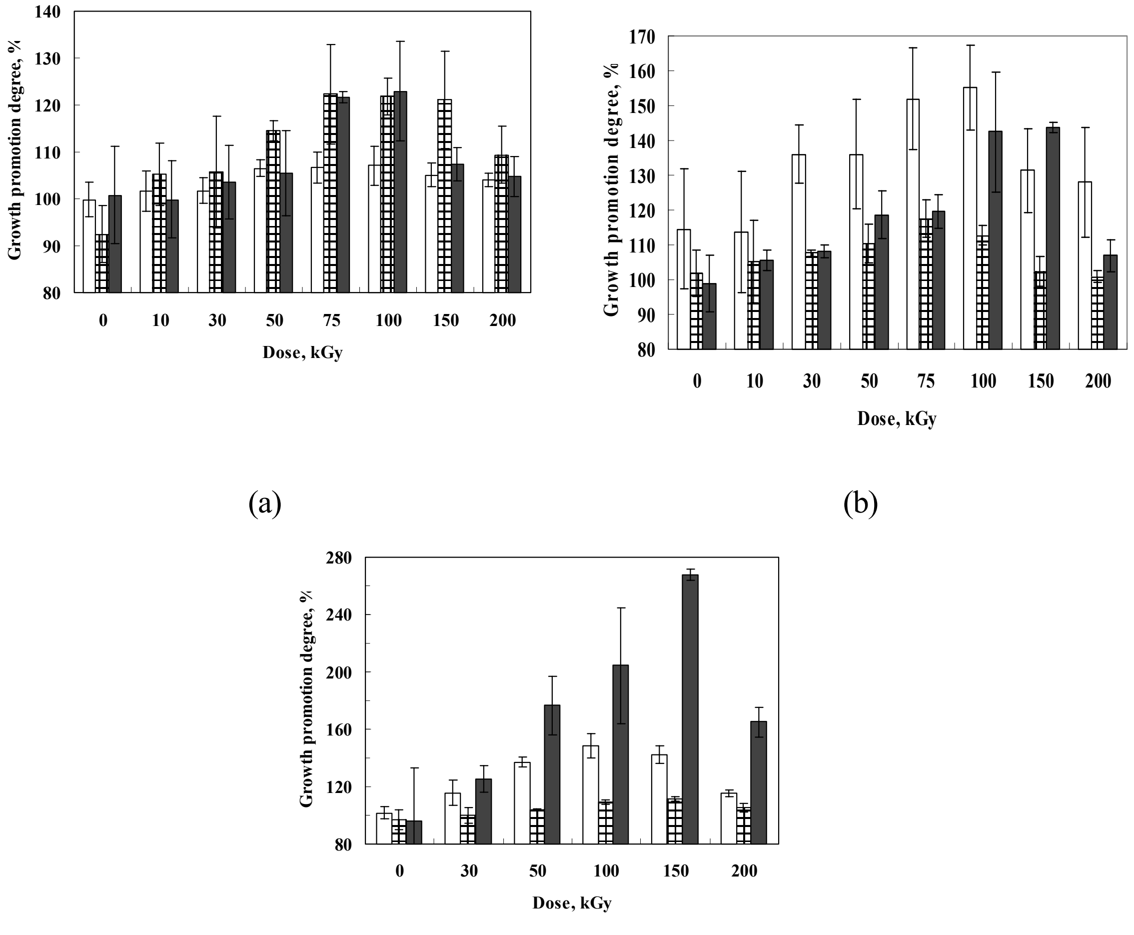
Fig. 1 Effect of irradiation dose for alginate degradation on the growth of flower plants. (a) chrysanthemum (b) lisianthus; (c) limonium. Dark bar: shoot height; hatched bar: root length; open bar: fresh biomass.

Major increase in shoot height, root length and fresh biomass were observed in beds supplemented with alginate irradiated at 50 ~ 200 kGy for lisianthus and 50 ~ 150 kGy for limonium.

Alginate irradiated at doses below 50 kGy showed no significant effect on any of the development process for both the plants. Thus, the alginate irradiated at 75 kGy, *i.e.* with Mw ~ 1.43×10^4 (DP ~ 76) displays the highest growth promotion effect in tissue culture condition for all varieties that were tested. Although the mechanism of the influence of irradiated alginate on the growth promotion of plant is still unclear, it was proved apparently that oligoalginate has some physiological abilities on plants such as: enhancement of enzyme activity (alcohol-dehydrogenase, lactate-dehydrogenase, 5'–phosphodiesterase and chitinase) and increase of net photosynthesis process [4~7].

3.1.2 Plant growth promotion effect of irradiated chitosan

The results in Figure 2a indicated that the chitosan irradiated from 50 to 150 kGy showed a remarkable increase of the shoot height (14.6 ~ 22.3 %) and fresh biomass (5.0 ~ 7.1 %) of chrysanthemum compared to that of untreated control.



(a) (b)

(c)

Fig. 2 Effect of irradiation dose for chitosan degradation on the growth of plantlets. (a) chrysanthemum; (b) lisianthus & (c) limonium. Dark bar: root length; hatched bar: shoot height; open bar: fresh biomass.

Even so, the growth effect on root length (21.6-23 %) was only observed at the doses of 75 and 100 kGy. On the other hand, the growth effect was not significant in treatments with unirradiated chitosan or chitosan irradiated at the doses below 30 kGy, while treatments with chitosan irradiated at the doses ranging from 75 ~ 100 kGy showed a more positive effect. The supplementation of irradiated chitosan also increased the shoot height, root length and fresh biomass of lisianthus by 10.4 ~ 17.5 %, 18.6 ~ 43.6 % and 36.0 ~ 55.2 %, respectively (see Figure 2b). As exhibited in Figure 2c, treatments with chitosan irradiated at doses ranging from 50 to 150 kGy showed a significant effect on the elongation of root length (76.9 ~ 167.9 %), shoot height (9.0 ~ 11.4 %) and increase of fresh biomass (37.2 ~ 48.3 %) of limonium compared to that of untreated control. In the test of strawberry, the results in Figure 2d showed that it was clear to ascertain the optimum dose at 100 kGy. Chitosan irradiated at this dose showed the strongest effect on the increase of fresh biomass (26.1 %), shoot height (20.6 %) and root length (19.5 %).

Similar to oligoalginate, irradiated chitosan showed a strong effect on the increase of dry weight and root length of rice and barley as well as wet bio-mass of orchid in tissue culture. But the growth promotion effect was reported to depend on irradiation dose for degradation of chitosan [7,21,22)]. In the present experiment, effect of irradiated chitosan on the growth of shoot cluster and plantlet was tested to determine the appropriate irradiation dose for degradation of chitosan to get product that can be used for plant tissue culture. The products obtained from chitosan irradiated at 75 ~ 100 kGy showed a significant enhancement of the growth promotion of mentioned plants. Irradiated chitosan (100 kGy) with Mw approx. 1.6×10^4 Da was the most optimal for growth promotion of all tested plants, suggesting that the product containing much oligochitosan with suitable molecular weight for the growth of plants.

3.1.3 Survival test of plantlets treated with irradiated alginate and chitosan

In plant cell, oligosaccharides were considered to be signaling chemicals to induce phytoalexins that protect plants from fungal infection 17,18). Furthermore, irradiated alginate exhibited not only a remarkable growth promotion effect but also a protection effect for plants 15). After acclimatizing for 30 days in a green house, the plantlets with irradiated alginate exhibited a similar survival rate as those of untreated control, but a better growth was observed for supplemented plantlets (Table 1). These results suggest that the plantlets treated with irradiated alginate showed a better response to environmental influence during acclimatization in a green house.

On the other hands, the results in Table 1 also showed that after acclimatizing for 30 days in a green house, the survival rates of transferred plantlets treated with irradiated chitosan were increased compared to those of untreated control, while irradiated alginate did not show a significant effect. In addition, a better growth was also observed for plantlets treated with irradiated chitosan. These results suggested that the treatment of irradiated chitosan increase not only phytoalexin enzyme (chitinase) but might induced some elicitor that helped the treated plantlets to respond better to environmental influences during the acclimatization in a green house condition. As a result, irradiated chitosan can be applied for plant in vitro propagation to produce high quality plants.

Table 1 Survival ratio of flower plantlets treated with irradiated alginate after 30 days acclimatizing in green house.

Dose (kGy)	Average number of survival plants per 100 transferred plantlets					
	Treatment of irradiated alginate			Treatment of irradiated chitosan		
	Chrys	Lisianthus	Limonium	Chrys	Lisianthus	Limonium
Control*	84.3a	81.4a	87.1a	78.0a	55.0a	77.0a
0	79.9a	75.1a	84.0a	-	-	-
10	84.6a	76.8a	92.1a	-	-	-
30	75.7a	77.1a	92.6a	-	-	-
50	87.0a	83.8a	92.5a	92.0b	57.6a	86.0b
75	89.7a	86.0a	91.9a	-	-	-
100	89.9a	86.3a	91.9a	90.3b	76.5c	87.0c
150	81.8a	85.2a	92.5a	92.0b	61.9b	83.1b
200	78.6a	80.2a	91.6a	89.0b	61.4b	82.8b

** without supplement of irradiated alginate or chitosan; mean followed by the same letter within a column were not significantly different as determined by LSD at 5 % probability level.*

After getting good results from the basic research, the irradiated alginate with optimum size of Mw for plant growth effect was prepared as a plant growth promotion product namely T&D. This product was used for the next steps in order to get the certificate for commercialization.

3.2 Field test

T&D product we used for testes in larger scale on the field. Plants namely rice, coriander, carrot and tea were used for test in a scale of 500 - 1000m^2 for each plant and the final results are listed below:

- The treatments of T&D product (40 ppm) on rice and coriander reached the highest increase of fresh biomass in 75.5 and 40.2%, respectively.
- On carrot, the results indicated that in the range of from 20 to 200 ppm of oligoalginate, the treatment at 60ppm reached the highest increase of bio-matter (52.6%) and root yield (59.5%).
- On tea, the results indicated that in the range of from 25 to 200 ppm of T&D, the treatment at 100ppm attained the highest increase of bud density (22.1%), bud weight (4.5%) and bud yield (19.4%).
- The T&D product also shows a significant growth - promotion effect on chrysanthemum in the concentrations ranging from 20 to 200ppm. Of seven treatments, the treatment of 80 ppm T&D increased the shoot height (25.9%), leaf number (13.7%), flower diameter (10.4%) and shoot weight (48.4%).

Thus, the product of irradiated alginate namely T&D showed a strong effect on the increase of the yield of all tested plants. These results again confirmed the growth promotion effect of irradiated alginate product for plant.

3.3 Toxicity test

The toxicity test is one of an important documents submitted to Department of Plant Protection, Ministry of Agriculture. To get the certificates of toxicity, the product of irradiated product (T&D) was sent to Vacine Institute for testing the toxicity on mice.

3.4 Application of the trial certificate for field test

The results collected from step 1&2 were used for preparation of the technical documents. The application form including technical documents, toxicity certificates and one litter of product were submitted to Department of Plant Protection, Ministry of Agriculture.

3.5 Get the permeation certificate for commercial

The submitted product of T&D was tested in several Plant Protection Agencies in many Provinces located in the North and South of Vietnam by Department of Plant Protection. After getting good growth promotion effects in 2 crops (about one year), the Department of Plant Protection, Ministry of Agriculture and Rural Development issued the certificate for production and commercialization in whole of Vietnam.

4. Conclusions

- Irradiated alginate with Mw ~ 1.4×10^4 and irradiated chitosan with Mw ~ 1.6×10^4 Da showed a positive effect on the growth of plant *in vitro*.
- The irradiated alginate enhanced the fresh biomass and yield of plants namely rice, coriander, carrot, tea and chrysanthemum.
- The plant growth promoter product namely T&D has been accepted for commercialization in whole of Vietnam.

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2. 3. 2 Development of Radiation Degraded Chitosan as Plant Growth Promoter and its Economic Evaluation

Gatot Trimulyadi Rekso

Centre for Research and Development of Isotopes and Radiation Technology
National Nuclear Energy Agency, Indonesia

Abstract

The development and field test of radiation degraded chitosan as plant growth promoter combine with waste from chitin process was carried out. The plant used for field test was red chili, potato and carrot. The fertilizer used was from chitin process and irradiated chitosan using as growth promoter. The field test data using irradiated chitosan combine with chitin waste shows higher the crops of the harvest compare with common fertilizer used. Based on these experiments, economic analysis of radiation degraded chitosan as plant growth promoter was carried out. The result shows that by using of oligo chitosan give more profit almost twice compare using common fertilizer and ROI, B/C shows a better value that mean have a better prospect for cultivation of chili plant. The BEP value of using oligo chitosan was Rp.2.154 and by using common fertilizer was`Rp.2.014.

1. Development and Field Test of Radiation Degraded Chitosan as Plant Growth Promoter

1.1 Introduction

Chitosan is a linier polysaccharide derived from chitin, a mayor component of the shell of the crustacean organisms and the second most abundant biopolymer in nature next to cellulose. In the last year chitosan has proved to be valuable product for using in different application such as seed coating, chelating and growth promoters etc. Chitosan reported to have various biological functions, antimicrobial activity, and growth inhibitor of some pathogens.

Radiation processing can modify the molecules weight, hydrophilic and mechanical properties of chitosan resulting in enhanced properties. Radiation processing also provides a simple and fast method for degradation of chitosan for a specific application. Radiation degraded chitosan has documented physiological effect on plants and soil organisms, including plants growth enhancement, and antimicrobial ability. This paper focuses on the field test of waste from chitin process combine with an irradiated chitosan as growth promoters for red chili, potato and carrot plants

1.2 Material and Exprimental

1.2.1 Preparation of chitin and fertilizer from waste of chitin process

Chitin extracted from prawn shell (*Penaeus monodon*), it was got from Muara Karang, North Jakarta. To deproteinization of the shell, aqueous of 1 N sodium hydroxide was used to remove protein from a known weight of a particular fraction. The deproteinized shell was then demineralized by means of 1.0 N hydrochloric acid in order to remove inorganic salt. The liquid waste from deproteinization and the mineralization were collected and mix with ratio 1:1 stirred slowly for 1 hr and keep in room temperature for 24 hr. Finally screen with stainless steel screening of 100 #.

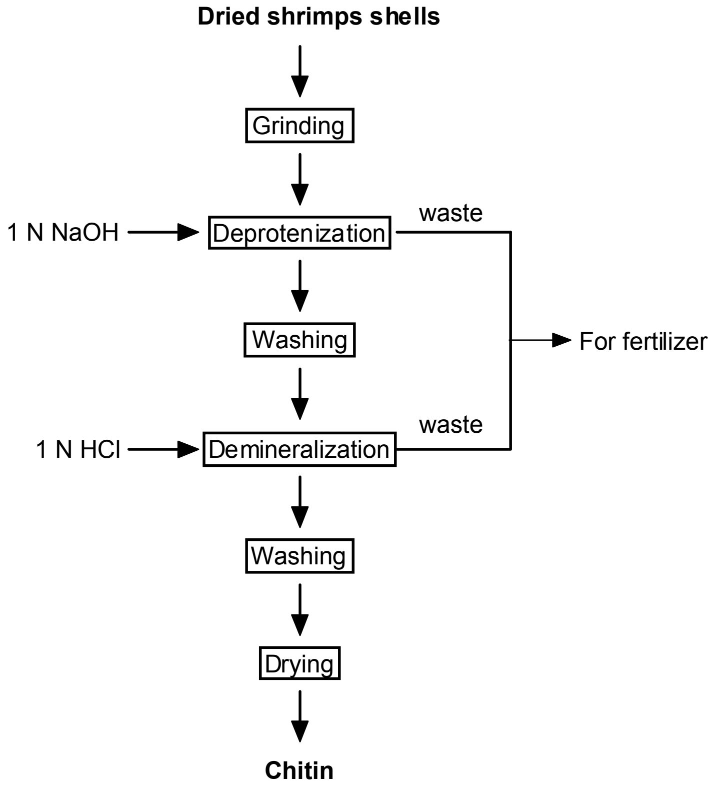

Fig. 1 Flow diagram of the isolation of chitin.

1.2.2 Preparation of chitosan

Chitosan can be obtained by treating chitin with 50 % sodium hydroxide with liquid solid ratio of 20:1 at 100 °C for 300 minutes.

1.2.3 Irradiation of chitosan

The irradiation of chitosan was carried out in a Co-60 gamma irradiation source. The conditions of chitosan for irradiation were solid state. The irradiation dose used was 75 kGy with a dose rate of 5.1 kGy/hr.

1.2.4 The effect of irradiated chitosan on the growth of the plant

The field-test was done in Cisarua village 1100 m osl with soil pH of 5.8. Three series field test for each plants (chili, potato and carrot) were done, the experiment was carried out in farmer plants. Every field test the area were 0.2 ~ 0.25 Ha, plot using chitosan and chitin waste and another using common used by the farmer. The irradiated chitosan were dissolved in water and 300 mL of water that contains concentration of 50 ppm chitosan was sprayed to plant three times a week for each plant. Fertilizer used were the waste from chitin process 300 mL each plant, two times every a week for 2 ~ 3 month.

1.3 Results and Discussion

1.3.1 Chemical content on waste from chitin process as fertilizer

In the preparation of chitin there are two-step the deproteinization and demineralization every step with ratio of solid and liquid of 1:10. The liquid waste get from every process are as follows for 1 kg shrimp shell as raw material, the waste from the deproteinization is 6 L and 8 L for demineralization. The fertilizer is made by mixture of the waste with ratio of 1:1, and for application must be mix with water with ratio of 1:50, and spray it to the plant every 3 day for a 2 ~ 3 month.
The laboratory test of chemical content in the waste as follows:

Table 1 Chemical analysis of liquid waste from chitin process compare with Indonesian National Standard (SNI) for liquid fertilizer.

No	Parameter	Results	Unit	Technique Analysis	Standard - SNI No 19-0429-1989
1	C- Organics	5.12	%	Wet Oxidation	≥ 4.5
2	N- Element		%	Kjeldahl, Titrimetry	≥ 0.5
	- N- organic	0.63			
	- $N\text{-}NH_4$	0.081			
	- $N\text{-}NO_3$	0.054			
3	Suspended solid	0.8	%	Screening	≤ 2,0
				AOAC 973.03.2000	
4	Heavy metal ions		ppm	AAS	
	-As	0		AOAC 986.15,2000	≤ 10 ppm
	- Hg	0		AOAC 971.21,2000	≤ 1.0 ppm
	- Pb	0.86		AOAC 999.10,2000	≤ 50 ppm
	- Cd	0.13		AOAC 957.02.2000	≤ 10 ppm
5	pH	7.5		pH meter	4.0 ~ 8.0
6	Total of			Spectrometry	
	P_2O_5	4.57	%	AOAC 958.01,2000	
	K_2O	4.62		AOAC 983.02.2000	≤ 5.0
7	Pathogen microbe			Most Probable Number	≤ 5.0
	- *E. Coli*	0	cell/g	(MPN)	List
	- *Salmonella sp*	0			List
8	Micro elements (%)		ppm	AAS	Unit (%)
	- Zn	1.34		AOAC 975.02,2000	≤ 0.2500
	- Cu	11.32		AOAC 975.01,2000	≤0.2500
	- Mn	2.09		AOAC 972.03,2000	≤ 0.2500
	- Co	3.43		EWW 311 B,1988	≤ 0.0005
	- B	6.12		AOAC 982.01,2000	≤ 0.1250
	- Mo	5.71		EWW 3111 D,1998	≤ 0.0010
	- Fe	30.5		AOAC 980.01,2000	≤ 0.0400

AAS: Atomic Absorption Spectrophotometer
AOAC: Analysis of analytical Chemist
EWW: Examination of water and wastewater

1.3.2 Preparation of chitosan

The conversion of chitin to chitosan was achieved by extracting chitin in 50 % sodium hydroxide with solid/liquid ratio = 1/20 at temperature of 100 °C for 300 minutes. The data obtained gave an average yield of chitosan from chitin were 72.6 %. The degree of deacetylation was 82.8 % was determined by means of FTIR spectrophotometer by the base line method ..

1.3.3 Preparation of irradiated chitosan and analysis of the hormone

The irradiation of chitosan was carried out in a Co-60 gamma irradiation source. The conditions of chitosan for irradiation were solid state, the irradiation dose used was 100 kGy with a dose rate of 7.5 kGy/hr.

The analysis of the hormone contains in degraded chitosan (1%) solution that induce the growth effect of plants are shown in Table 3. From that table it shown that chitosan containing gibberellic acid, 3-Indole acetic acid and zeatin which that compound known could increasing the growth of the root plant and decreasing drop off the flower that why the yield of the fruit increases, therefore increasing the crops of the harvest.

Table 3 Hormone in solution of 1 % degraded chitosan.*

Hormon		Concentration
Auxin	Indot Acetic Acid (IAA)	319,11 ppm
Sitokinin	kinetin	27.16 ppm
	zeatin	18.46 ppm
Gibberelin (GA)	GA3	252.48 ppm
	GA5	85.59 ppm
	GA7	101.02 ppm
Karbon		0.032 %

** analyzed by the Institute of Agriculture Bogor*

1.3.4 Field test of some plants

Some field test for chili, potato and carrot plant were done, to know the percentage of increasing the crops of the harvest using irradiated chitosan plus waste of chitin process compare with usually fertilizer used by the farmers.

(A) Chili plants

The total crop of the harvest of chili using irradiated chitosan and waste of chitin process compare with common fertilizer by the farmer shows in Table 4.

Table 4 The total crops of the harvest using irradiated chitosan + chitin waste process compare with commons fertilizer used for chili plants.

No.	Area for field test (Ha)	Total Crops Of the harvest (Ton)		Increasing of the total crop (%)	Age for the plants for harvest (month)	
		Chitosan + Waste of chitin	Common fertilizer		Chitosan + Waste chitin	Common fertilizer
1	2 x 0.2	3.2	2.1	52	6	7.0
2	2 x 0.2	3.8	2.4	58	6	7.0
3	2 x 0.2	3.5	2.3	52	6	7.0

As can be seen in Table 4. The combination of irradiated chitosan and waste of chitin showed strong effect of total crops of the harvest red chili plant. Visual observation shows that roots and leaves were found to develop at a faster rate. Results of field test showed that by spraying water contents of dry state irradiated chitosan made the productivity increase around of 52 ~ 58 %.

Fig. 2 Field test of irradiated chitosan on chili plants.

(B) Potato Plant

The total crop of the harvest of potato using reradiated chitosan and waste of chitin process compare with common fertilizer by the farmer shows in Table 5. It showed that using irradiated chitosan the yield of the harvest increases around of 31 ~ 34 %. The age of the plants for harvest also decreases, using common fertilizer after 4 month and by used of oligo chitosan was 3 month.

Fig. 3 Field test of irradiated chitosan on potato plants.

Common Fertilizer

+ Irradiated chitosan

Table 5 Total crops of harvest using irradiated chitosan + chitin waste process compare with commons fertilizer used for potato plants.

No.	Area for field test (Ha)	Total Crops Of the harvest (Ton)		Increasing of the total crop (%)	Age for the plants for harvest (month)	
		Chitosan + Waste chitin	Common fertilizer		Chitosan + Waste chitin	Common fertilizer
1	2 x 0.2	0.65	0.49	32.6	3.0	4.0
2	2 x 0.2	0.82	0.61	34.4	3.0	4.0
3	2 x 0.2	0.63	0.48	31.2	3.0	4.0

Irradiated chitosan shows strong effect on growth, amount of nitrogen fixing nodules and resistance to rust disease. Finally, these affect lead to an increase in crop of harvest.

(C) Carrot plant

The total crop of the harvest of carrot using reradiated chitosan and waste of chitin process compare with common fertilizer by the farmer shows in Table 6. It showed that using irradiated chitosan the yield of the harvest increases around of 53 ~ 55 %. The age of the plants for harvest also decreases, using common fertilizer after 5 month and by used of oligo chitosan was 3.5 month.

Table 6 Total crops of the harvest using irradiated chitosan + chitin waste process compare with commons fertilizer used for carrot plants.

No.	Area for field test (Ha)	Total Crops Of the harvest (Ton)		Increasing of the total crop (%)	Age for the plants for harvest (month)	
		Chitosan + Waste chitin	Common fertilizer		Chitosan + Waste chitin	Common fertilizer
1	2 x 0.2	8.75	5.70	53.0	3.5	5.0
2	2 x 0.2	11.5	7.42	54.0	3.5	5.0
3	2 x 0.2	9.20	5.90	55.0	3.5	5.0

Fig. 3 Field test of irradiated chitosan on carrot plants.

1.4 Conclusion

It is clear that the research give highlights the probability of utilizing. The waste product of the seafood industry (prawn, crabs shell) to products, which are useful for fertilizer and growth promoters for vegetable plants.

2. Economic Analysis of Chili Plant Using Oligo Chitosan Compare with Common Fertilizer

2.1 Economic analysis

The basic economic analysis got from the field test experimental for chili plant The field test was done in Cisarua village 1100 m osl with soil pH of 5,8. The area for the economic analysis was 1 Ha, could be planted by 18.000 chili plants. Analysis was for 6 months. The average yield of the crops using common fertilizer was 0.62 kg chili/plant and if using oligo chitosan + chitin waste 0.94 kg chili/plant.

The price of chili on the farmer was Rp.8.000,-. All the price calculation was in October 1, 2007 and change rate of $1 = Rp.9200,-

2.2 Calculation of amount of oligo chitosan used for 1 Ha of land area

- The price of mother liquor of oligo chitosan (5%) = Rp 30.000,- / L
- In application only 50 ppm /plants, every 3 day for 90 day by spraying with 300 mL water/plants.
- The area of the land was 1 Ha, could be planted of 18000 chili plant
- Oligo solution need for 18000 chili = 18000 plant x 300 mL/plant = 5400 L
- Volume of 5% mother liquor oligo Chitosan needs :

  V1.N1 = V2.N2 → V1 50000 ppm = 5400 L. 50 ppm

  V1 = 5.4 L
- For 90 day = 90/3 x 5.4 L = 162 L
- Cost = 162 L x Rp30.000,-/ L = Rp.4.860.000,-

2.3 Calculation of chitin waste as fertilizer was used for 90 day

- The price of chitin waste is Rp 1200,- /L
- For application much be dilution with water 1 : 50
- Same with application of oligo chitosan by spraying of 300 mL solution /plant.
- Solution of waste chitin need is = 1/50 x 5400 L = 108 L
- For 90 day =90/ 3 x 108 L = 3240 L
- Cost = 3240 L x Rp 1200,- = Rp.3.888.000,-
-

2.4 Cost for cultivation of chili plant:

There are 3 part of cost for cultivation of chili plant:

(1) Cost for land preparation
(2) Cost for seedling and plantation
(3) Cost for take care of the plans and harvesting

2.5 Production cost for cultivation of chili plant

(1) Cost for land preparation

No	Items	Cost (Rp)	
		Common treatment	Oligo Chitosan treatment
1	Land cleaning	Rp. 500.000,-	Rp. 500.000,-
2	Preparation of block for planting	Rp. 800.000,-	Rp. 800.000,-
3	Lime applied 1000 kg x Rp200,-	Rp. 200.000,-	Rp. 200.000,-
4	Labor for lime applied (2 xRp50.000,-)	Rp. 100.000,-	Rp. 100.000,-
5	Base fertilizer 20.000 kg x Rp 100,-	Rp.2.000.000,-	Rp.2.000.000,-
6	Labor for base fertilizer 6 x Rp50.000,-	Rp. 300.000,-	Rp. 300.000,-
7	Covering Plastic 12 roll x Rp 250.000,-	Rp.3.000.000,-	Rp.3.000.000,-
8	Labor for plastic covering	Rp. 300.000,-	Rp. 300.000,-
Total cost for land preparation		Rp.7.200.000,-	Rp.7.200.000,-

(2) Cost for seedling and plantation

No	Items	Cost (Rp)	
		Common treatment	Oligo Chitosan treatment
1	Chili seeds (200 gr)	Rp.200.000,-	Rp.200.000,-
2	Poly bag plastic 15 kg x Rp 15.000,-	Rp.225.000,-	Rp.225.000,-
3	Covering plastic 75 m x Rp.5000,-	Rp.375.000,-	Rp.375.000,-
4	Labor for seedling and plantation 3 person x 5 days x Rp.50.000,-	Rp.750.000,-	Rp.750.000,-
Total Cost for seedling and plantation		Rp.1.550.000,-	Rp.1.550.000,-

(3) Cost for take care of the plants for 6 months and harvesting

No	Items	Cost (Rp)	
		Common treatment	Oligo Chitosan treatment
1	Bamboo for sustain of plant 150 piece x Rp5000,-	Rp. 750.000,-	Rp. 750.000,-
2	Fertilizer :		
	- NPK: 300 x Rp.6000,-	Rp. 1.800.000,-	-
	- KNO_3 : 10 x Rp.10.000,-	Rp. 100.000,-	-
	- Urea : 400 kg x Rp.6000,-	Rp. 2.400.000,-	-
	- Leaf . Fert 10 kg x Rp15.000,-	Rp. 150.000,-	-
3	Oligo Chitosan : 162 L x Rp30.000,-/ L	-	Rp 4.860.000,-
4	Chitin waste : 3240 L x Rp 1200,-	-	Rp. 3.888.000,-
5	Insecticide : 20 L x Rp.150.000,-	Rp. 3.000.000,-	Rp. 3.000.000,-
6	Fungicide : 30 kg x Rp.50.000,-	Rp. 1.500.00,-	-
7	Bactericide : 1 kg x Rp.500.000,-	Rp. 500.000,-	-
8	Labor : 4 person x 6 month x	Rp.12.000.000,-	Rp.12.000.000,-Rp.
9	Rp.500.000/month	Rp. 2.000.000,-	2.000.000,-
10	Machinery (Sprayer, bucket,etc)		
Cost for take care of the plans and harvesting		Rp. 24.200.000	Rp. 26.498.000

(4) Total production cost

	Common treatment	Oligo Chitosan treatment
Cost (1) + (2) + (3)	Rp. 32.950.000,-	Rp.35.248.000,-
Miscellaneous expense (10%)	Rp. 3.295.000,-	Rp. 3.524.800,-
Total Production Cost	Rp. 36.245.000,-	Rp.38.772.800,-

2.6 Yield of the crop sales calculation

Common treatment

= 18.000 chili plants x 0.62 kg x Rp. 8.000,- = Rp. 89.280.000,-

Oligo Chitosan treatment

= 18.000 chili plants x 0.94 kg x Rp. 8.000,- = Rp. 135.360.000,-

2.7 Economic evaluation

2.7.1 Profit analysis

Profit analysis = Sales – Total production cost

	Common treatment	Oligo Chitosan treatment
Sales	Rp. 89.280.000,-	Rp.135.360.000,-
Total Production Cost	Rp. 36.245.000,-	Rp. 38.772.800,-
Profit	Rp. 53.035.000,-	Rp. 96.587.200,-

2.7.2 Break Event Point (BEP).

BEP = Total Production Cost/Total Plant

	Common treatment	Oligo Chitosan treatment
Total Production Cost	Rp. 36.245.000,-	Rp. 38.772.800,-
Total Plant	18.000	18.000
BEP	Rp. 2.014,-	Rp. 2.154,-

2.9 Return of investment (ROI)

ROI (%) = 100 x (Net Profit/ Total Prod. Cost) (%)

	Common treatment	Oligo Chitosan treatment
Net Profit	Rp. 53.035.000,-	Rp. 96.587.200,-
Total Production Cost	Rp. 36.245.000,-	Rp. 38.772.800,-
ROI (%)	146.32	249.11

2.10 Benefit cost ratio (B/C)

B/C = Total Sales/ Total Prod. Cost

	Common treatment	Oligo Chitosan treatment
Total Sales	Rp. 89.280.000,-	Rp. 135.360.000,-
Total Production Cost	Rp. 36.245.000,-	Rp. 38.772.800,-
B/C	2.46	3.49

Conclusion

The result shows that by using of oligo chitosan give more profit almost twice compare using common fertilizer and ROI, B/C shows a better value that mean have a better prospect for cultivation of chili plant.

The BEP value of using oligo chitosan was Rp. 2,154 and by using common fertilizer was Rp. 2,014.

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2. 3. 3 Progress of Agricultural Application of Degraded Chitosan in Thailand*

Siri-Upathum Chyagrit, Ruangphan Chanita

Chulalongkorn University, Thailand

1. Introduction

Thailand is an agricultural-based country. The utilization of chemicals for agricultural applications is becoming more and more essential, thus progressively increasing the amount of chemicals used for agricultural purposes. From plant hormones, fertilizers, insecticides to herbicides, the majority of these chemicals are imported products, annually worth thousands of million in Thai Baht.

There are five generally recognized classes of plant hormones; Auxin, Abscisic acid, Cytokinin, Ethylene and Gibbereliin. Most of these plant hormones are imported from overseas and, therefore, high-priced. As a result, domestic and economical materials, such as chitin and chitosan, are emerging as viable alternatives to replace these pricey chemicals.

Chitin is a natural, abundant, inexpensive, non-toxic and biocompatible polymer. Only cellulose is more bounteous than chitin, which make chitin an extremely crucial renewable resource that can easily be found as part of animals' and plants' physical structures. Chitosan is a derivative of chitin. The hydrolysis of chitin results in chitosan. Unique and beneficial properties of chitin and chitosan make them suitable for various applications, from agricultural to medical. In agricultural application, chitosan has proved to be a promising plant promoter. Chitosan has both direct and indirect effects on plants' growth, from strengthening roots' system, increasing resistance to pests and diseases, making plants healthy to extending shelf-life. The modifications of these natural polymers would make their applications even more fitting. Beside chemical and biological methods, radiation processing is one of the most convenient means for polymer modification, through crosslinking, grafting and degradation techniques. Radiation technology has been used commonly to modify polymers' physical properties, as well as their molecular weight. Radiation-induced degradation can reduce the molecular weight of chitosan to desired values so that it is suitable for specific applications. It is a well established fact that several properties of polymers are highly dependent on their molecular weight. The main chain scission induced by radiation will result in chitosan that becomes shorter in chain lengths, with random, smaller degree of polymerization (DP) and reduced molecular weight. Researchers have discovered that chitosan with DP in the range of 7 ~ 14 has the quality of a Phytoalexin inducer, which is beneficial for protection of various plants' diseases 1).

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* presented by Suwanmala Phiriyatorn

Chitosan with approximate molecular weight of 8 and 40 kDa is advantageous for agricultural applications, in terms of plants' rate of growth and germination, and resistance to disease, respectively [2] while chitosan with molecular weight between 30 ~ 41 kDa is most suitable for food additive and functional agent [3]. With the aforementioned reasons, the study to find chitosan with suitable molecular weights for plant growth promotion is highly interesting in such a way that it can be effectively applied to Thailand's domestic, agricultural products.

2. Experiments

Low molecular weight chitosan was prepared by gamma radiation degradation and molecular weight fractionation. The degradation of chitosan sample was performed by successive gamma irradiation of chitosan power with radiation dose of 100 kGy and then 10% (w/v) of the chitosan in 2.5% acetic acid was further irradiated at doses of 20, 40, 60, 70 and 80 kGy. The molecular weight of the irradiated chitosan was then determined by viscosity method, using Cannon Ubbelohde viscometer. In order to obtain the desired chitosan with Mv of about 20 kDa for further experiments, selective precipitation of 26 kDa chitosan using 0.75% NaOH solution was subsequently performed and optimized.

Chitosan at Mv of 4, 8, 12 and 20 kDa were selected for investigating the effect of chitosan molecular weight on the plant growth promotion. The study was done by measuring the height of three kinds of seedling (Kale (*Brassica Albloglabra*), lettuce (*Lactuca sativa Linn*), Chinese spinach (*Amaranthus Tricolor Linn*)) with 200 ppm chitosan at each molecular weight in a nutrient solution after 26 days.

3. Results and Discussion

3.1 Effects of radiation on chitosan's molecular weight

Irradiation in solid state at 100 kGy reduced the molecular weight of chitosan from 7.2 ~ 7.5 x 106 Da to approximately 148 kDa. Further irradiation of 10% obtained chitosan solution in 2.5% acetic acid at 20, 40, 60, 70 and 80 kGy resulted in chitosan with molecular weight of roughly 68, 26, 12, 8 and 4 kDa, respectively (Table 1), as determined by Dilute Solution Viscosity method. The molecular weight of chitosan dramatically decreases at low dose (0 ~ 40 kGy), while it gradually declines at high dose (40 ~ 80 kGy) (Figure 1). This can be explained in terms of molecular structure of chitosan. During the early stage, radiation has profound effects on amorphous regions, which are loosely and disorderly distributed, leading to remarkable reduction of molecular weight. Once the amorphous regions are destroyed, radiation will then start to disintegrate the crystalline regions.

Table 1 Effect of irradiation dose on molecular weight of chitosan.

Dose (kGy)	Average molecular Weight
100 (solid)	148,887 Da
100 (solid) + 20 (10% (w/v) solution in 2.5% acetic acid)	68,146 Da
100 (solid) + 40 (10% (w/v) solution in 2.5% acetic acid)	25,875 Da
100 (solid) + 60 (10% (w/v) solution in 2.5% acetic acid)	12,630 Da
100 (solid) + 70 (10% (w/v) solution in 2.5% acetic acid)	8,655 Da
100 (solid) + 80 (10% (w/v) solution in 2.5% acetic acid)	4,797 Da

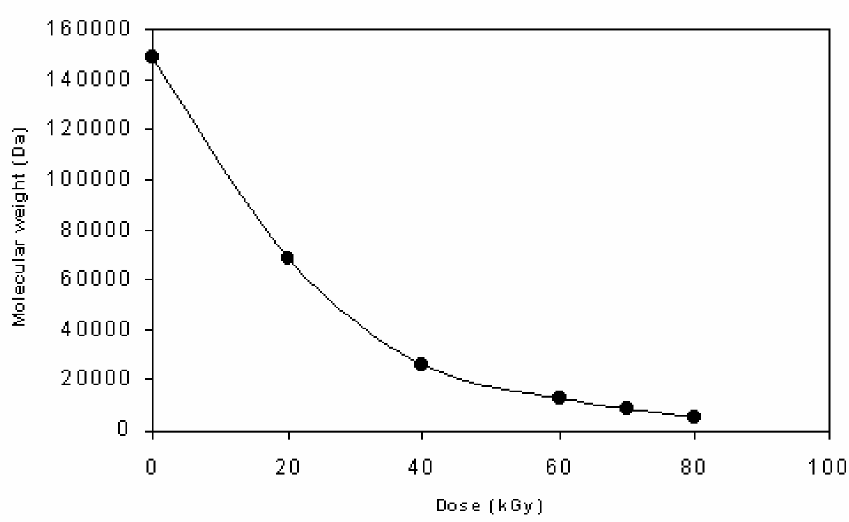

Fig. 1 Effect of irradiation dose on molecular weight of chitosan.

3.2 Effects of chitosan's molecular weight on plant growth rate

It was found that chitosan at Mv of 4 and 8 kDa possessed the highest rate of growth for kale (*Brassica albloglabra*) (Figure 2).

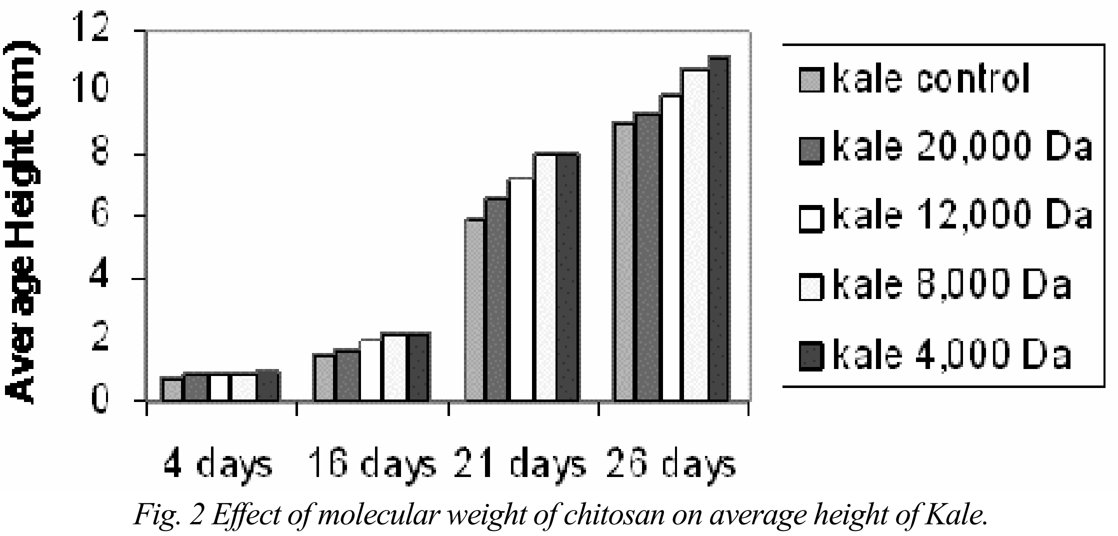

Fig. 2 Effect of molecular weight of chitosan on average height of Kale.

Chitosan of 20 kDa gave the highest growth for lettuce (Lactuca sativa Linn) (Figure 3) and Mv of 8 and 12 kDa gave the highest growth for Chinese spinach (Amaranthus tricolor Linn) (Figure 4).

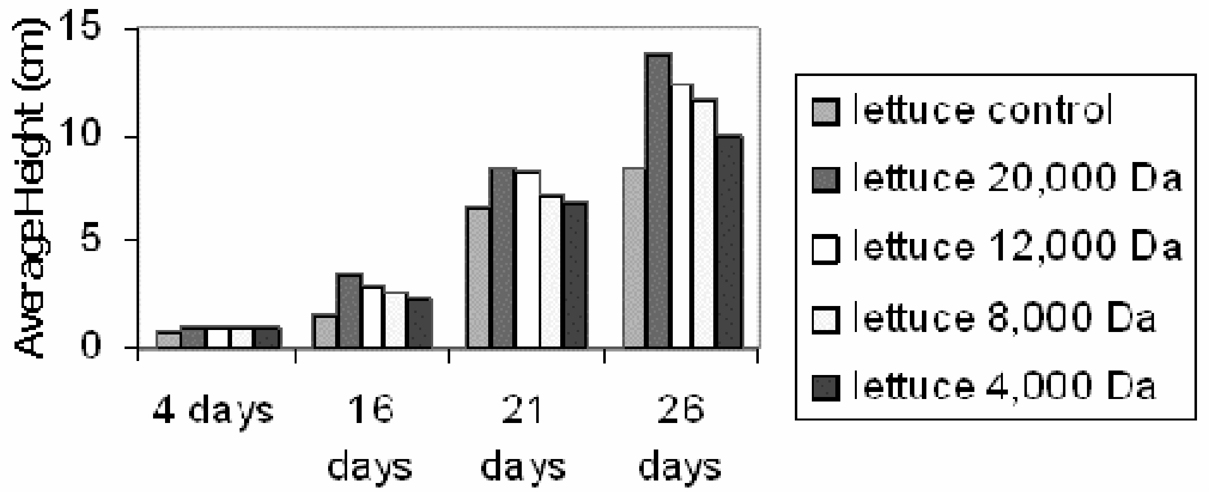

Fig. 3 Effect of molecular weight of chitosan on average height of lettuce.

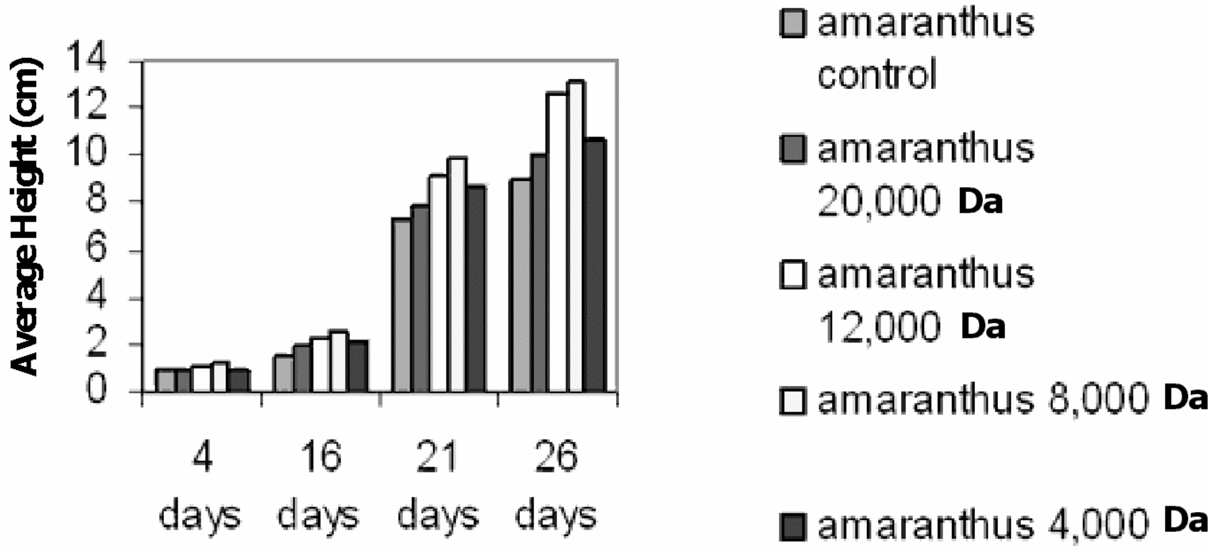

Fig. 4 Effect of molecular weight of chitosan on average height of lettuce.

The results have shown that each type of plant responds differently to chitosan with different molecular weights, depending on the absorptive abilities of their roots' system. It is obvious that oligochitosan has noticeable effects on plant growth rate, when compared with controlled fertilizer solutions. This stems from the fact that chitosan strengthens plants' roots, making their water and food absorption more effective. As a result, plants grow faster and become healthier, thus reducing their harvest stage. Moreover, chitosan also has bacterial-resistance effects, leading to plants growing without diseases.

Conclusion

Low molecular weight chitosan was obtained by gamma radiation degradation and molecular weight fractionation. oligochitosan has noticeable effects on plant growth rate. Each type of plant responds differently to chitosan with different molecular weights, depending on the absorptive abilities of their roots' system.

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2.4 Other Applications of Radiation Processed Natural Polymer

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2. 4. 1 Application of Radiation Degraded Chitosan in Aquaculture and Animal Feed

Guozhong Wu

Shanghai Institute of Applied Physics, Chinese Academy of Sciences

Abstract

Chitin is the second most abundant natural resource, mainly derived from the shell of crab and shrimp, fungi, etc. Chitosan is an amino-polysaccharide derived from chitin by deacetylation. At present, China produces about 30 thousand tons of chitosan every year, and more than 95% is exported to abroad. Chitosan can be degraded by three methods, i.e. chemical hydrolysis or oxidation, enzymatic catalysis, and radiation. The use of radiation to prepare low-molecular-weight chitosan has advantages over other methods. For example, the depolymerization of chitosan can be carried out in the solid state without destruction of chemical structure, which has been testified by the methods of DSC, FTIR, etc. Moreover, it is easy to control the molecular weight by simply controlling the radiation dose.

1. Use of Radiation Degraded Chitosan in Aquaculture

China shares 70% of artificial aquaculture products in the world, but antibiotics are widely used, causing a serious safety problem. Chitosan with low molecular weight is preferred for its extraordinary characteristics such as biocompatibility, biodegradablity, antibacterial effect, etc. Therefore it may be a substitute for pesticide or antibiotics in the field of aquiculture in China.

In cooperation with fishery pharmaceutical companies, we have done a lot of work on the application of chitosan in aquaculture since 2002. In 2003, we obtained a project of chitosan entitled “an alternative of antibiotics in aquaculture”. In 2004, we carried out lots of experiments on crab and fish in 20 hectare water area. It showed that low molecular weight chitosan was very effective for the disease caused by bacteria and partly effective for virus infected disease. The results also testified that oligochitosan could increase the proliferation of blood cells (Fig. 1) effectively.

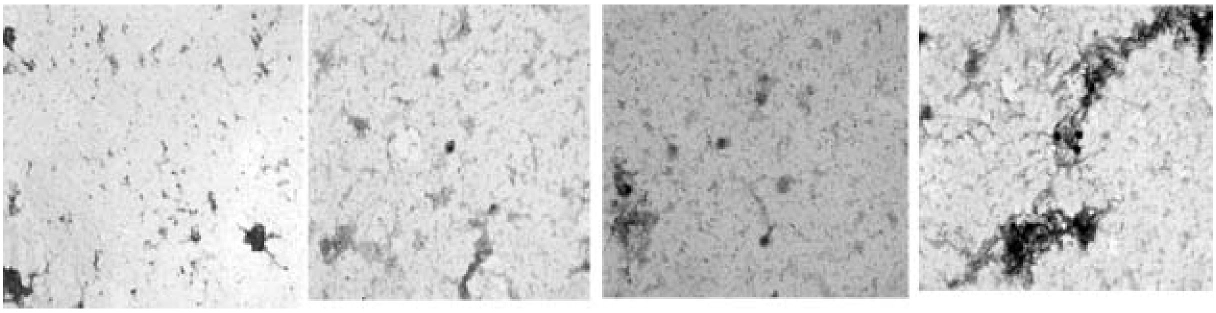

Fig.1 effect of oligochitosan on blood cell of fish and crab.

So far we have explored 6 kinds of chitosan and chitosan derivative products, and four of them have been commercialized. Among them, "Dafeng No.1" (Fig. 2) is very successful. Moreover, we signed cooperation contracts with five companies and they sold about 100 tons of liquid products in 2007. The market will become larger in the future.

Fig.2 Dafeng No.1.

2. Test of radiation degraded chitosan in animal feed

To apply radiation-degraded chitosan in animal feed as a special additive, a series of tests have been carried out on fish, pig, milk cattle and chicken respectively. To investigate the survival rate of Jian carps in the virus attack test, we fed them with chitosan as a feed additive for 30 days. The results showed that the pathogenic bacteria protective property was improved extremely by feeding chitosan at a dosage of 50 mg/kg ($P<0.01$) (Table 1). The serum lysozyme activity, serum antibacterial activity and number of carp blood NBT-positive cells were increased (Table 2), implying that chitosan might be a kind of good aquatic animal immune enhancer.

Table 1 survival of Jian carp in the virus attack test.

Group	Fish number tested	Fish number of survival	Survival rate (%)	Protective immunity （%）
Control	30	9	30	
VK3/50ppm	30	15	50	38.6
Chitosan/50ppm	30	21	70	57.1
Chitosan/100ppm	30	18	60	42.9

Experimental work was also done to study the effect of low molecular weight chitosan on the reproduction performance and blood biochemical index of weaned pigs. The results indicated that weaned pigs fed with low molecular weight chitosan improved reproductive performance obviously ($P<0.05$). At the same time, chitosan can also decrease the diarrhea rate, inhibit the growth of intestinal pathogen and promote beneficial bacteria breeding. The effect of chitosan at a dosage of 300 mg/kg was optimal. Based on the analysis of blood biochemical index, the physiology function of weaned pigs was increased at a certain extent by feeding low molecular weight chitosan..

Table 2 the effect of chitosan on the non-specific immunity index of Jian carp.

Group	Serum lysozyme activity	Serum antibacterial activity	Number of blood NBT-positive cells
VK3/50ppm	101±5.32	0.29±0.03	28±3.41
Chitosan/50ppm	118±5.95	0.38±0.05	43±8.25
Chitosan/100ppm	125±4.69*	0.42±0.03	61±5.58

In addition, a lot of effort was made to analyze the prophylactico-therapeutic effect of chitosan on subclinical mastitis of cow. The results indicated that feeding chitosan at a dose of 100-300 mg/kg can prevent the healthy diary cows from the invasion of pathogenic factors. In addition, the intensity of negative mastitis was decreased for the slight to heavy mastitis cows by adding chitosan at a dose of 50-300 mg/kg after 2-3 weeks. After 5 weeks, the mastitis remission rate was 83%-100% and the cure rate reached 33%-66%. With the increase of chitosan dose, the remission rate and cure rate were also increased step by step. Compared to the basal diet group, the effect of direct injection chitosan to the udder of diary cows was better and faster, though slightly weaker when compared to the antibiotics control group. Therefore, injecting the udder of diary cow directly was recommended.

Finally, the effect and mechanism of chitosan on broiler chicken's growth performance was intensively studied. Four hundred 1-day-old Avian broiler chicken were randomly divided into four groups, with 4 replications per group. The control group (group A0) was fed with corn－soybean meal basal diets, the trial groups (group A1,A2,A3,A4) were fed with basal diets added with 5 mg/kg flavomycin and 25, 50, 100 mg/kg chitosan, respectively. The test period was 40 days. The results showed that the average daily gain weight（ADGW）of the trial groups (group A1, A2, A3, A4) was increased by 2.04% ($P<0.05$), 4.01% ($P<0.05$), 6.05% ($P<0.05$) and 5.05% ($P<0.05$) compared to the control group (group A0). The ADGW of group A2, A3, A4 was increased by 2.08%, 4.06% ($P<0.05$) and 3.06% compared to group A1. The feed gain ratio (FGR) of the trial groups (group A1, A2, A3, A4) was decreased by 7.73% ($P<0.05$), 7.22% ($P<0.05$), 10.82% ($P<0.01$) and 9.28% ($P<0.01$) compared to group A0. The FGR of trial group A3 and A4 was decreased by 3.35% and 1.68% compared to group A1. The eviscerated weight, semi-eviscerated weight, breast meat percentage, thigh percentage, abdominal fat rate（$P>0.05$）and liver function（$P<0.05$）of broiler chicken were also improved by adding flavomycin and chitosan.

3. Developing trend of chitosan industry in china

China is the biggest supplier of chitosan, its domestic use is very limited yet. It is urgent to explore more chitosan derivatives instead of exporting as a cheap raw material. Though research on chitosan and chitosan-relevant materials is very active in China, more “real” applications and commercial products are required.

2. 4. 2 Poly(vinyl pyrrolidone)-Chitosan Implant for Endoscopic Treatment of Vesicoureteral Reflux

Lorna S. Relleve[a], **Lucille V. Abad**[a], **Charito T. Aranilla**[a], **David T. Bolong**[b],

Carlo C. Bisnar[b*], **A. M. dela Rosa**[a]

[a]Philippine Nuclear Research Institute
[b]Urology Section, Department of Surgery, University of Santo Tomas Hospital
* Corresponding author

Abstract

Radiation-crosslinked poly(vinyl pyrrolidone) (PVP)-Chitosan was prepared as a potential injectable implant for endoscopic treatment of vesicoureteral reflux (VUR). The physical and histological properties of PVP-Chitosan implant in comparison with the commercial dextranomer/hyaluronic acid copolymer (Deflux) have been evaluated in vivo by subcutaneous and abdominal injection in rats over a period of 6 months. The PVP-Chitosan implant was easily injected through 26-gauge needle. Monthly gross examination of the implanted sites showed no significant decrease in volume of implant and no local inflammatory reaction. Histological findings indicated no evidence of migration to the distant organs after 6 months of implantation. Results of this study indicated that PVP-Chitosan implant has properties of a good tissue augmenting substance such as stability, biocompatibility and non-migration but long-term studies are needed to evaluate its therapeutic efficiency.

1. Introduction

Vesicoureteral reflux refers to the retrograde flow of urine from the bladder into the upper urinary tract (Figure 1). It predisposes an individual to renal infection by facilitating the transport of bacteria from the bladder to the upper urinary tract1). It is the most common urologic anomaly in children and it is a risk factor for progressive renal damage. Endoscopic treatment of VUR involves the introduction of an injectable material into the wall of the bladder near the opening of one or both ureters under the cystoscopy (Figure 2) 2). A variety of implants have been used but safety and efficacy have precluded their widespread use 3~6). A known stable subureteral implant approved by the US FDA is the dextranomer/hyaluronic acid copolymer (Deflux). The dextranomer microspheres are 80 to 120 microns in diameter forming a network of crosslinked dextran polysaccharide molecules that prevent degradation and migration. One milliliter of Deflux costs approximately US$700~800 and one refluxing ureter would more or less needs 1 ml of this implant.

The need for a stable locally available and less expensive bioimplant must be pursued to promote endoscopic treatment of VUR especially with all the advantages of this procedure such as minimally invasive technique, absence of significant postoperative complications, safety of the available injectable materials and high success rate. Polymeric implants can be prepared by chemical or radiation crosslinking to produce insoluble gels[7 ~ 10]. This study aims to develop a cheaper alternative to the Deflux from radiation-crosslinked PVP-Chitosan. Radiation processing offers a number of technical advantages when compared with chemical methods. The radiation-processed materials contain no residuals of toxic substances required to initiate chemical reactions like crosslinking. The physical and histological properties of PVP-Chitosan implant in comparison with Deflux will be presented in this paper.

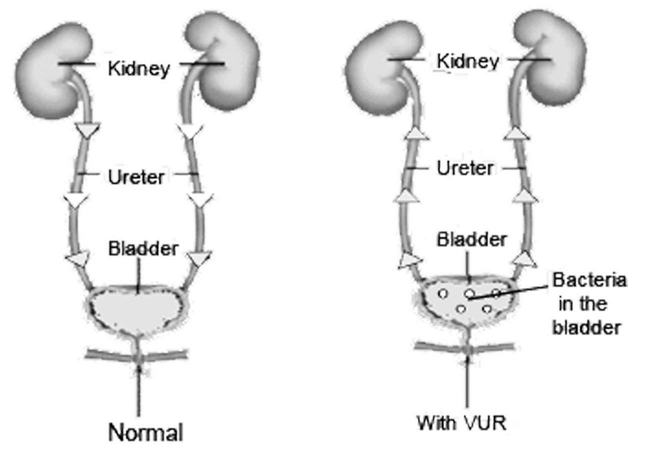

Fig 1. Normal Urinary system and urinary system with VUR.

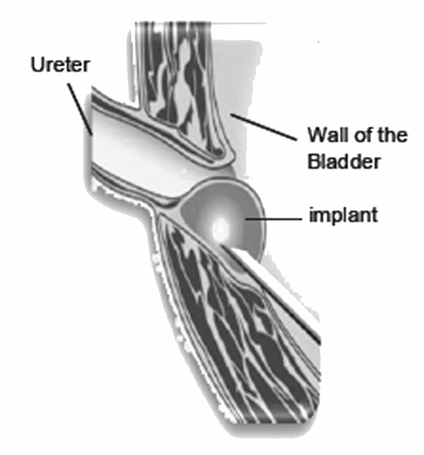

Fig. 2. Endoscopic treatment of VUR[2].

2. Methodology

2.1 Preparation of PVP-chitosan implant

Solution containing 5% PVP (Kollidon 90F) and 2% chitosan (Mv 4.8 x 10^5) in 1.5% acetic acid was irradiated at 15 kGy by γ-rays. After irradiation, the gel formed was neutralized and homogenized at 15,000 rpm. The resulting PVP-Chitosan microgel was dispersed in aqueous medium, transferred in a 5 cc needleless plastic syringe, sealed in laminated foil pouch and sterilized at 25 kGy. Viscosity was tested by passage of gel implant through gauge 26 needle.

2.2 Subjects and implantation

Twenty-four 1 year old male Sprague-Dawley rats were sheltered in a controlled environment: in a single animal house in separate cages each with well-regulated room temperature; and same time and amount of feeding. Simple random assignment was done to divide the subjects into two groups: 18 rats were assigned to the PVP-Chitosan group while 6 rats were under the Deflux group. All the rats in both groups were weighed and sedated by intramuscular thigh injection with 10 mg or 0.2ml ketamine hydrochloride. After sedation, each of the rat's abdomen was shaved and sprayed with disinfectant solution using isopropanol benzalkonium chloride (Cutasept). The PVP-Chitosan group (18 rats) received 2 subcutaneous injections of 0.4 ml PVP-Chitosan gel each using G26 needle, one on the right and the other on left hemiabdomen. Since Deflux is too expensive, the

Deflux group (6 rats) received only 1 subcutaneous abdominal injection of 0.4 ml Deflux each also using G26 needle. The subcutaneous abdominal implants of 0.4 ml each formed a total of 42 abdominal subcutaneous nodules: 36 nodules in the PVP-Chitosan group (18 rats x 2 injections / rat) and 6 nodules in the deflux group (6 rats x 1 injection / rat). The volume (horizontal diameter x vertical diameter x height) of each subcutaneous nodule formed by the implants were measured using a caliper initially by a personnel immediately after implantation and then by another personnel once a month for 6 months blinding the second personnel from the measured initial implantation volume of the subcutaneous nodules. Gross inflammatory reaction such as erythema, abscess, and tissue necrosis were also noted during these periods. All the rats were sacrificed 6 months post-implantation. The implanted sites which formed a pseudocyst on the rats' subcutaneous tissue were dissected free from the surrounding tissues. All the implants were extracted from the pseudocysts and the volume of the retained implants were taken by a personnel (blinded from the initial volume of implant injected) by immersing the implants in a graduated cylinder containing isotonic saline solution.

2.3 Histological examination

The histological examination was done by a single blinded pathologist. All the pseudocysts formed by the implanted sites (36 PVP-Chitosan group + 6 Deflux group = 42 total number of pseudocysts) were examined for any granuloma formation, foreign body reaction, scar formation, and inflammatory reaction. Inflammatory reaction or presence of neutrophils, lymphocytes, eosinophils, and plasma cells were graded as follows: absent (none found), mild (1 -100 cells/hpf), moderate (100 ~ 200 cells / hpf), and severe (>200 cells/hpf). Migration potential of the implants were also tested by histological examination of each of the rat's liver, kidneys, and lungs; and noting for any inflammation, irritation, foreign body response, tissue necrosis, or scarring.

2.4 Statistical analysis

To test the homogeneity of the population, to compare the differences in volume of subcutaneous nodules after 6 months from implantation and difference in volume of subcutaneous nodules between the treatment groups, and to compare the differences in implant volume after 6 months from implantation and differences in implant volume between treatment groups, T-test is used in the assumption that all variances are equal (Levene's Test). To test the significant difference in inflammatory response based on neutrophil, eosinophil, lymphocytes and plasma cells scores in between the two treatment groups, Mann Whitney Test was used. SPSS ver 11.5 was used in statistical analysis. Significance level was set at $p < 0.05$.

3. Results and Discussions

To be an effective tissue augmenting or bulking agent for treating VUR, the ideal material should flow readily through a small gauge needle, resistant to degradation, be biocompatible, elicit minimal inflammation, maintain its periureteral configuration over time and should not migrate to locally or to distant sites 11). Degradation and migration have been undesirable characteristics that have haunted clinicians in adopting many of the materials used with injection therapy to date12). Figs. 3a-c shows the PVP-Chitosan implant injected in the rat's abdomen. The viscosity of the Chitiosan-PVP gel was adequate enough to be injected from a 5 cc syringe and easily passed through a G26 needle which is smaller than the standard Deflux metal needle (3.7FR x 23G [tip] x 350 mm) used in actual periureteral injection of Deflux in patients with VUR. No obstruction of the needles was observed at injection. F

Figs. 3. a) Subcutaneous and abdominal injection of PVP-Chitosan gel in rat b) subcutaneous nodules formed by the implant and c) implant retained after 6 months from implantation.

The properties of PVP-Chitosan and Deflux implants after six months implantation are summarized in Table 1.

Table 1 Properties of PVP-Chitosan and Deflux implants (6 months post-implantation).

Properties of implants	PVP-Chitosan implant	Deflux implant
Gross examination of the implanted sites	No gross local inflammatory reaction	
Decrease in volume of subcutaneous nodules	0.0345 cm^3	0.0252 cm^3
	No significant difference (p = 0.794)	
Decrease in volume of implant retained	0.0556 ml	0.0500 ml
	No significant difference (p = 0.611)	
Inflammatory response	Higher lymphocytes and plasma cell score	Lower lymphocytes and plasma cell score
	No statistical significant difference in neutrophil (p = 0.539) and eosinophil (p = 0.539) score	
	Absence of granulation tissue, foreign body reaction and scar formation	
Migration potential	No inflammation irritation, foreign body reaction, tissue necrosis, nor scarring in liver, kidneys, and lungs	

Both groups grossly retained their subcutaneous nodules and the implants within these nodules were retained 6 months post implantation showing the comparable stability of these two implants. Fig 3c shows the stability of PVP-Chitosan implanted for a period of six months. The observed decrease of subcutaneous nodule volume and initial volume of the PVP-Chitosan group from implantation to 6 months post-implantation is still clinically and statistically comparable with the Deflux group.

Grossly no erythema, abscess formation, nor tissue necrosis were seen in both groups. The mild local inflammatory reaction of the PVP-Chitosan group as demonstrated by the presence of some lymphocytes and plasma cells on histological examination is still acceptable since there was no presence of gross inflammation, erythema, and abscess formation. This is also the inflammatory reaction seen in other implants which is still acceptable as long as there is absence of granuloma formation, foreign body reaction, and scar formation. In a study on the histological findings of those treated with Deflux, even this particular implant show histological findings of inflammation such as that of the giant cell type, inflammatory cell infiltration, and fibrotic pseudo-encapsulation of the implant; but still with good results and outcome[3)].

Non-migratory property of the PVP-Chitosan implant was also demonstrated by unremarkable findings in the distant organs such as the liver, kidneys, and lungs. Although more appropriate migration studies such iodine labeled nuclear tracer migration determination and electron microscopic examination for the molecular size of this new implant was not done, the histologic studies on distant organs serves as a preliminary test to the non-migratory property of this implant. Because of its N-acetylglucosamine repeating units, chitosan binds to growth factors such as fibroblast growth factor and platelet-derived growth factor promoting fibroblast and collagen formation13-14). The PVP may have been quickly dispersed by the body and replaced by fibrin. This fibrin holds other components in place such as in our study, chitosan, while the surrounding area becomes organized by the host fibroblast into collagen 15). After subjecting this newly synthesized implant to its preliminary experimental study, it showed promising results as a possible ideal tissue augmenting implant for endoscopic treatment of vesicoureteral reflux plus the advantage of being a lot cheaper and being readily available in the country.

4. Conclusion

The newly synthesized radiation-crosslinked PVP-Chitosan implant has properties of a good tissue augmenting or bulking substance such as ease of injection through a small gauge needle, stability, biocompatibility and non-migration. Results of the studies indicated that PVP-Chitosan implant could be a potential alternative to the commercially available implant for endoscopic treatment of vesicoureteral reflux but long-term studies are needed to evaluate its therapeutic efficiency.

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2. 4. 3 Metal ion Adsorption by Carboxymethyl Chitin and Chitosan Hydrogels

Masao Tamada

Quantum Beam Science Directorate, Japan Atomic Energy Agency

Abstract

Chitin (Cht) and chitosan (Chts) were chemically modified to water soluble derivatives of Carboxymethyl Cht (CMCht) and Chts (CMChts). The high concentration of CMCht and CMChts gave their paste-like state. The high energy irradiation could lead hydrogels of CMCht and CMChts in this state. The preferential concentrations of CMCht and CMChts in the water for radiation crosslinking were 40% based on the Charlesby-Rosiak equation. Hydrogels of CMCht and CMChts degraded slightly faster than unirradiated CMCht and CMChts. Since noble metal such as Pd, Au, and Pt could be adsorbed by hydrogels of CMCht and CMChts, the hydrogels have the possibility for the application in the recovery of noble metals in industrial waste water.

1. Introduction

Metal ion adsorbent has practically used as the exchange of ions and the removal of toxic ions such as lead and cadmium. Such commercialized adsorbent resins were generally synthesized by copolymerizing the precursor monomer, chloromethystylene, and crosslinker, divinylbenzene. The resulting crosslinked resin has the convertible site of -CH_2Cl in chloromethystylene moiety to the functional group having the affinity against metal ions. This precursor resin can be chemically modified to metal ion adsorbent having –SO_3, -COOH, and -NH_2. However, these resins are derived from petroleum products. For the security of petroleum resources and the decrease of environmental burdens, the natural occurring polymers should be used for the raw materials for metal ion adsorbents. In the natural occurring polymers, chitin and its deacetylated derivative, chitosan, are considered to be the most interesting raw material for the metal ion adsorbents due to the possessing of amine group which has affinity against metal ions. Amine groups can recover several kinds of metal ions such as copper, mercury, uranium, lead and chromium, molybdenum and vanadium, as well as noble metals, platinum and palladium 1). The most common chemical modification is crosslinking by using glutaraldehyde as a crosslinking agent to prepare the metal ion adsorbent. Chemical modification of chitosan increase the chemical stability of the adsorbent in acid media and, especially, decrease the solubility in most mineral and organic acids 2). Such modified chitosan has been used for metal ion recovery with chitosan in acid media. Without any crosslinking agent, high energy radiation can induce the crosslinking in the derivatives of polysaccharides 3). In the present paper, the possibility of crosslinking of chitin and chitosan was considered by chemical modification and irradiation conditions 4). The obtained hydrogels of chitin and chitosan was evaluated from swelling, biodegradability, and metal ion adsorption 5).

2. Crosslinking of Carboxymethyl Chitin and Chitosan

Intrinsic chitin and chitosan were decomposed by high energy irradiation. However, chemical modification of these polymers can overcome this property. Carboxymethylated derivatives, carboxymethyl chitin (CMCht) and carboxymethyl chitosan (CMChts) can be crosslinked in those paste-like states. The paste-like state was composed of 20 - 40 % of CMCht or CMChts which was mixed homogenously with water. The hydrogel preparation is as follows: The degree of substitution (DS) which indicates the number of original H atoms of hydroxyl groups replaced by carboxymethyl group in molecule of CMCht and CMChts were 0.81 and 0.91, respectively. The average molecular weights estimated by gel permeation chromatography were 2.5x104 for CMCht and 6.0x103 for CMChts. Degree of deacetylation values were 24.6% and 84.0% for CMCht and CMChts, respectively. The kneaded pastes of CMCht and CMChts were pressed at 200 kPa for 45 min to obtain film, 1 mm thick, and then sealed in air-free polyethylene bags. The paste films were irradiated with electron beam of 1kGy/pass.

Figure 1 shows the effect of dose on the gel fraction of crosslinked hydrogels in CMCht and CMChts in the concentration of 20, 30, and 40%. The gel fraction of radiation crosslinked hydrogels was determined gravimetrically by weighing the insoluble part after extraction of soluble part with deionized water for 5 days at room temperature, occasionally shaken and with daily changed water. The gel fraction was calculated by the following equation:

$$\text{Gel fraction (\%)} = (Gd/Gi) \times 100$$

where Gi is the initial weight of dried hydrogel after irradiation and Gd is the weight of insoluble part after extraction with deionized water.

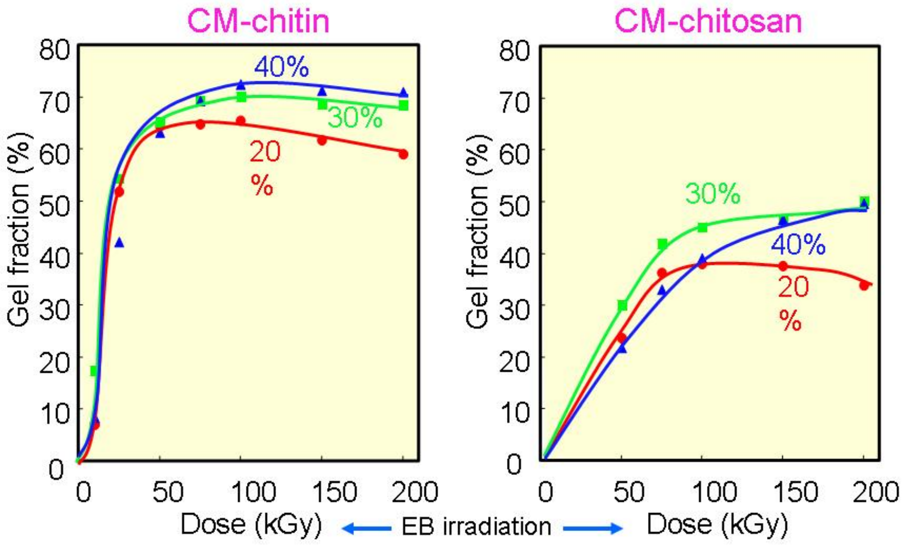

Fig. 1 effect of dose on the gel fraction of crosslinked hydrogels in CMCht and CMChts.

After EB irradiation of 50kGy, the gel fraction were 60 - 65% and 20 - 30 % for CMCht and CMChts. Gel fraction of CMCht did not change so much with the increment of irradiation dose. In the case of CMChts, the gel fraction reached 35 - 40 % at 100 kGy. Only 40% of CMChts went up to 50%. The gel fraction was not strongly affected by concentration of CMCht and CMChts and the gel fraction of 20 - 40% of CMCht and CMChts were located in the mentioned ranges. However, for very higher polymer concentration of 50%, gel fraction was lower than that at 40 % concentration. This is because, the CMCht and CMChts are not homogenously distributed in entire volume and some insoluble regions of polymer exist at such high concentration.

The gelation dose (Dg); minimum required energy to initiate gelation process, and the ratio of scission to crosslinking densities (p_0/q_0); yields of crosslinking and degradation are the most important factors which describe the efficiency and character of crosslinking reactions. Dg and p_0/q_0 values can be calculated based on Charlesby-Rosiak equation:

$$s+\sqrt{s}=\frac{p_0}{q_0}+\left(2-\frac{p_0}{q_0}\right)\frac{D_v+D_g}{D_v+D}$$

where s is sol fraction, p0 degradation density; average number of main chain scission per monomer unit and per unit dose, q0 crosslinking density; proportion of monomer units crosslinked per unit dose, D absorbed dose, Dv virtual dose; a dose required to change the distribution of molecular weight of the certain polymer, Dg gelation dose; minimum required energy to start gelation process. This equation was derived by incorporating the change of molecular weight distribution accompany with irradiation.

Table 1 show that crosslinking dose, ratio of degradation to crosslinking, yields of crosslinkig (G(x)) and scission (G(s)) of CMCht and CMChts by EB irradiation. The CMCht was crosslinked much easier than CMChts since gelation doses are 8.65 kGy for CMCht and 27.0 kGy for CMChts at 40%. It is due to the fact that the molecular weight of CMCht is about 4 times larger that that of CMChts. Lowest p0/q0 ratio appeared for polymer concentration of 40 % for CM-chitin as well as for CM-chitosan, which means that this concentration is the optimum for crosslinking reaction. The Swelling, in grams of absorbed solvent per gram of dried gel, was calculated as follows:

Swelling = (Gs - Gd)/Gd

where Gs is the weight of hydrogel in a swollen state. Swelling experiments were conducted by immersing a dried gel of about 100 mg in deionised water at room temperature. After an equilibrium water uptake was reached, i.e. when the mass of the gel at two consequent weighing did not differ by more than 0.5%, the hydrogel was filtered by stainless steel net of 30 mesh and lightly blotted out by filter paper to remove surface water prior to weighting.

Table 1 Crosslinking dose (D_g), ratio of degradation to crosslinking (p_0/q_0), yields of crosslinking ($G_{(x)}$) and scission ($G_{(s)}$) of CMCht and CMChts by EB irradiation.

Concentration of polymer (%)	Dg (kGy)	p_0/q_0	$G_{(x)}$ x 10^7 (mol/J)	$G_{(s)}$ x 10^7 (mol/J)
CM-chitin				
20 %	9.63	0.93	0.78	1.44
25 %	9.22	0.86	0.95	1.64
30 %	8.37	0.80	1.19	1.91
40 %	8.65	0.68	1.40	1.91
50 %	27.79	0.74	0.57	0.85
CM-chitosan				
20 %	47.79	1.41	1.18	3.33
25 %	48.89	1.23	1.11	2.72
30 %	34.09	1.15	1.73	3.97
40 %	27.00	0.99	2.44	4.84
50 %	49.68	1.19	2.07	4.93

Figure 2 shows the relationship between gel fraction and swelling of CMCht and CMChts in various concentrations. The correlations were divided into two categories. In the both cases of CMCht and CMChts hydrogels shows the similar tendencies. There are linear relationship between gel fraction and swelling of CMCht and CMChts. The swelling decreased with increase of the gel fraction. CMChts hydrogels shows lower swelling than CMCht hydrogel.

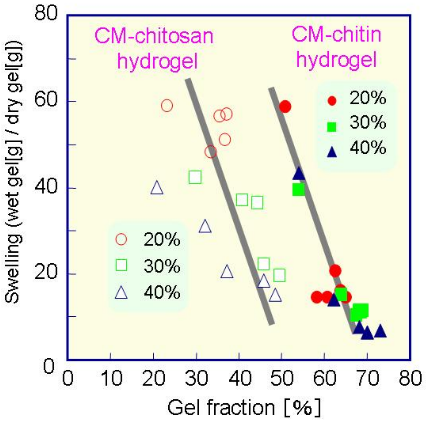

Fig. 2 Relationship between gel fraction and swelling of CMCht and CMChts.

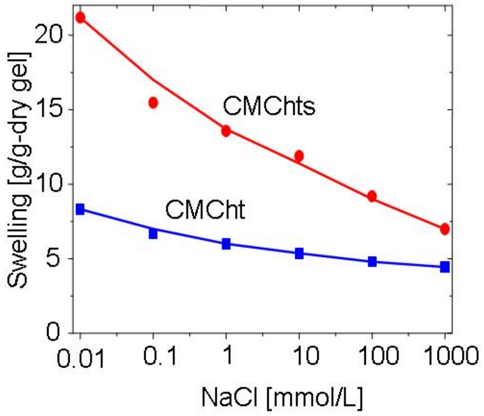

Fig. 3 Swelling behaviors as a function of NaCl concentration for CMCht and CMChts hydrogels.

Figure 3 shows the swelling behaviors as a function of NaCl concentration for CMCht and CMChts hydrogels. The degree of swelling decreases continuously with the increasing ionic strength of the solution. With increasing of salt concentration it interacts with the CMCht or CMChts molecules causing significant reduction of swelling. Positive ions of the salt screen electrostatic interactions of the carboxyl, and negative ones of those of amine groups. It results in a marked reduction in the repulsive forces of charged segments of the crosslinked polysaccharide network and consequently leads to the gel contraction. Therefore, the osmotic swelling pressure of the mobile ions inside the gel decreases, and so the hydrogel collapses more in the case of CMCts.

3. Biodegradability of CM-chitin and Chitosan Hydrogels

Natural polymers inclusive chitin and chitosan were renewable sources and spontaneously degraded by naturally occurring microorganisms. Such polymers increase no burdens to natural environment since they do not produce any toxic waste products during degradation process.

3.1 Enzymatic degradation

Enzymatic degradations of CMCht and CMChts hydrogels were carried out in a phosphate buffer solution at pH 8.0 containing chitinase and at pH 5.6 containing chitosanase enzymes, respectively. The enzymatic degradation is expressed by weight loss. Figure 4 shows the enzymatic degradation of Cht, Chts and their CM-hydrogel. They lost its weight sharply in 20 h. At 50 h, the weight losses of Cht and Chts were higher than the corresponding CM-hydrogels. Enzyme degradation of the hydrogel was less effective than each Cht and Chts. Carboxymethyl groups may lead the structural hindrance for enzyme which fit to the structure chitin or chitosan molecules.

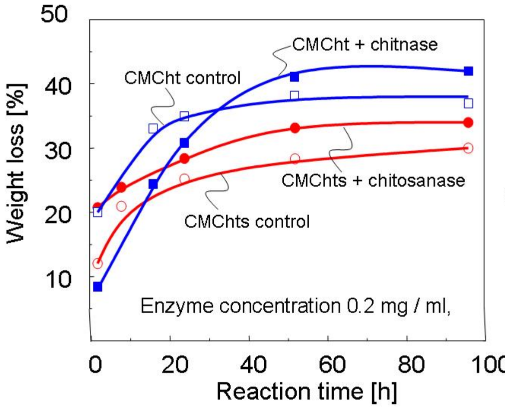

Fig. 4 Enzymatic degradation of Cht, Chts and their CM-hydrogel.

3.2 Soil burial test

Natural degradation process of radiation synthesized CMCht and CMChts hydrogels has been evaluated in soil burial test at the depth of 8 cm under the surface in Takasaki, JAEA area. Figure 5 shows the films of CMCht and CMChts hydrogels, 1mm thick, before and after keeping in soil for 10 weeks from October to December. The size and thickness of samples kept in soil become smaller then their initial ones. In the case of CMCts even creation of some small wholes is noticeable. It can be concluded that prolonged storing of these samples in the ground would cause their complete

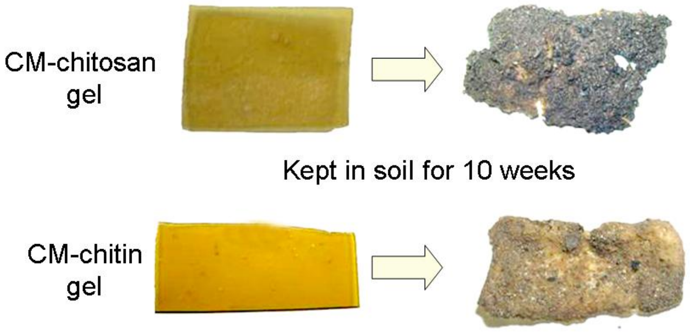

Fig. 5 Soil burial tests of CMCht and CMChts hydrogels, 1mm thick, before and after keeping in soil for 10 weeks.

disintegration as a result of bacterial activity.

3.3 Biodegradation under controlled conditions in composed soil.

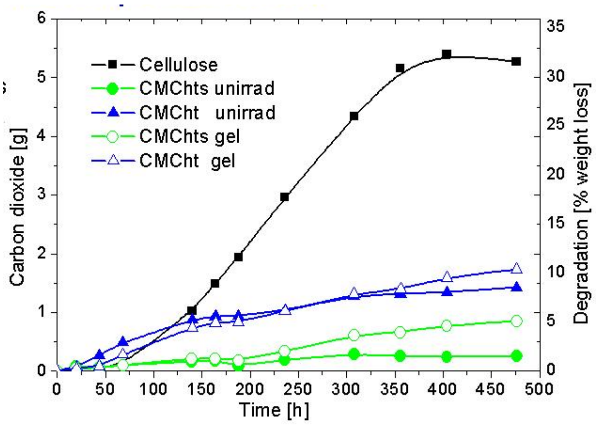

Fig. 6 Microbial degradability of hydrogels in composted soil with MODA.

The microbial degradability of hydrogels in composted soil was evaluated by Microbial Oxidative Degradation Analyzer (MODA) with measurements of produced CO2 gas. Hydrogels of 10 g was mixed with rinsed sea sand - 450 g, and compost (water content 52%) - 120 g, and then placed in a heated reactor at 35ºC. The CO2 was collected quantitatively by soda lime and the mass of produced carbon dioxide was calculated as a difference in the weight of the two last columns at the beginning and the end of the test. Figure 6 shows the amount of produced CO2 which was recalculated to a total degradation percentage. After 504h (21 d), CMCht lost 8 % and CM-chitosan 4 % of their initial weight, whereas their unirradiated counterparts 6 and 2 %, respectively. The degradation of both hydrogels is more effective then their initial polymers. Crosslinking is accompanied by degradation of polymers. It is apparent than that these shorter chains undergo biodegradation more efficiently than the crosslinked hydrogels.

4. Metal ion Adsorption with CM-chitin and Chitosan Hydrogels

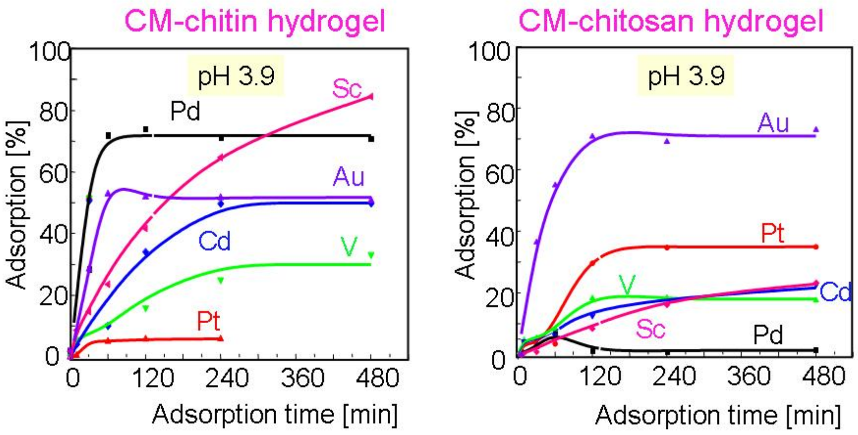

Fig. 7 Batch adsorptions of various metal ions onto CMCht and CMChts hydrogels

Batch adsorption of metal was carried out as follows: The hydrogels of 50 mg was put into 100 ml of citric buffer solution at pH 3.9 containing ca. 100 ppb of metal ions at room temperature. After 2 h of adsorption, the metal ion concentration in solution was measured by inductively coupled plasma mass spectrometer (ICP-MS). Figure 7 shows the adsorptions of various metal ions onto CMCht and CMChts hydrogels. The CMCht hydrogel adsorbed the Pd, Sc, Au, Cd, V, and Pt in the order of high adsorption at 240 min. The adsorption yield of Sc still increased and at

480 min Sc attained the highest adsorption percentage in all metal ions. In the case of CMChts, Au, and Pt was preferentially adsorbed. Palladium, gold, and platinum are expensive noble metals because of their rare occurrence in the nature.

They are commonly used in industry due to their excellent catalytic and conductive properties. The selectivity CMCht and CMChts hydrogels to noble metals can be applied to their recovery from industrial waste solutions. The best results for both hydrogels were obtained for gold ions, Figure 8 shows the adsorption of gold ions as dependence of solution pH. The maximum metal ions uptake is observed at the pH 2.0 for CMCht and CMChts hydrogels. At this pH, functional groups of both polymers exist in their ionized forms what facilitates metal ions adsorption through electrostatic interaction forces. The maximum adsorption of gold ion was obtained by isotherm adsorption. The maximum capacities were 53.3 and 39 μmol/g for CMCht and CMChts hydrogels.

Figure 9 shows the desorption of the gold ion treated with HCl solution. The elution of the gold ion from hydrogels became effective in the high concentration of HCl. After desorption of gold ion, the regenerated hydrogel can be used for the metal adsorption again.

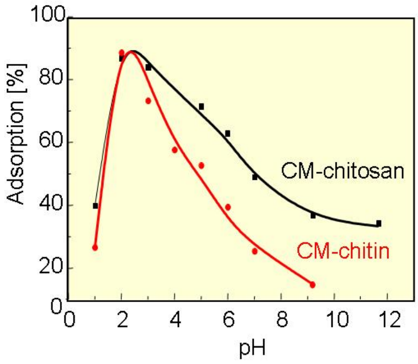

Fig. 8 Adsorption of gold ions in various pH solutions

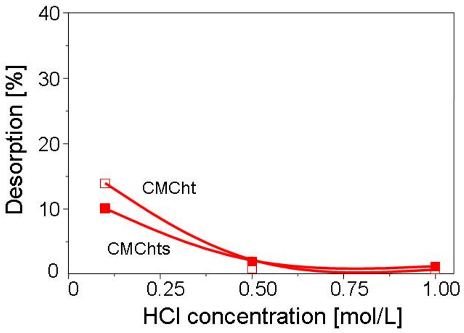

Fig. 9 Desorption of the gold ion treated with HCl solution

5. Conclusions

Carboxymethylated Cht and Chts, CMCht and CMChts, could be crosslinked with high energy irradiation at their past-like state. The gel fractions were 60 - 65% and 20 - 30 % for CMCht and CMChts after EB irradiation of 50 kGy. The preferential concentrations of CMCht and CMChts in the water were 40% based on the Charlesby-Rosiak equation. The enzyme degradabilities of CMCht and CMChts were maintained even after their crosslinkings. In the soil burial test, the degradations of both hydrogels were confirmed. Microbial oxidative degradation revealed that hydrogels of CMCht and CMChts degraded slightly faster than unirradiated CMCht and CMChts. This is due to the decrease of molecular weight accompanied with radiation crosslinking. CMCht hydrogel adsorbed Pd, Sc, Au, Cd, V, and Pt and CMChts Au, and Pt. In the adsorption of gold ion, the optimum pH was 3. The maximum capacities were 53.3 and 39 μmol/g for CMCht and CMChts hydrogels. The adsorbed gold ions on hydrogel were quantitatively eluted by HCl solution. Hydrogels of CMCht and CMChts have the possibility for the application in the recovery of noble metals in industrial waste water.

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2. 5 Activities and Achievement of RCA

2. 5. 1 IAEA/RCA Activities on Radiation Processing

Lucille V. Abad
Philippine Nuclear Research Institute

Radiation processing either by gamma of e-beam has been applied in many fields and has been widely accepted for use in many areas of the global economy. Among the well established technologies are sterilization, polymer crosslinking/grafting, tire component curing, conservation of art objects and irradiation of selected food items.

The International Atomic Energy (IAEA) through its technical co-operation programs, coordinated research projects, consultants and technical meetings and conferences is promoting the peaceful use of nuclear science and radiation technologies. Due to the IAEA's support, some new radiation technologies (e.g. hydrogel dressings, sulfur-free radiation vulcanized latex, growth promoting oligomers, superabsorbents) were developed and transferred to Member States over the past decade. Other promising applications the IAEA has supported are flue gas, waste water and sludge treatment.

The IAEA has been organizing many meetings and research coordinated research projects (CRP) in which trends and new developments have been discussed and technical work conducted along this field. Special attention was given to the radiation processing of natural polymers under the framework of the Regional Cooperative Agreement (RCA) for Research, Development and Training Related Nuclear Science and Technology for East Asia and the Pacific. This region is especially rich in respect to wide variety of indigenous natural polymers such as rubber, chitin/chitosan, carrageenans, alginates and silk. It has organized the following research and technical cooperation projects since 1998.

- CRP on Radiation Processing of Indigenous Natural Polymers (1998 -2000)
- RAS 8/096 "Modification of Natural Polymers through Radiation Processing" (2003-2004)
- RAS 8/098 "Radiation Technology for Development of Advanced Materials and for Protection of Health and the Environment" (2005-2006)
- RAS/8/106 "Radiation Processing Applications for Health and the Environment" (2007-2008)

Under these projects, work was focused on achieving the following:

- Development of applications in lower molecular weight polysaccharides in the area of agriculture as plant growth promoter.

- Utilization of specific properties of natural polymers as an additive to produce radiation processed hydrogels.
- Development of methods for producing radiation crosslinked completely biodegradable hydrogels.
- Exploration of possibility of using radiation modified materials or methods for environmental remediation.
- Utilization of radiation technology for environmental remediation.

Through these projects, quite a number of developed products have been commercialized.

- View gel (PVA gel for wound dressing commercialized July 2004 in Japan)
- Gel Protector for shoe sore prevention (PVA gel commercialized in Japan)
- Non-bedsore mat (CMC hydrogel commercialized in Japan)
- Burn Caring (Wound dressing commercialized in China)
- P-chitosan (Wound Dressing commercialized in Vietnam)
- Hizel (Wound Dressing commercialized in India)
- Cligel (Wound Dressing commercialized in Korea)
- T&D (alginate product, commercialized Year 2000 in Vietnam)
- Olicide (chitosan product, commercialized Year 2002 in Vietnam)
- Osan (chitosan based product, commercialized Year 2002 in Thailand)
- Gold Rice (Rice growing Protectors, chitosan, commercialized year 2003 in Vietnam)
- Stop (Chitosan product in complex with metal ions, as nematocide, commercialized Year 2004 in Vietnam)
- Esllon (Sago starch hydrogel face mask commercialized in Malaysia)
- Thai silk soap product (commercialized in Thailand)

RAS 8/098

IAEA RCA RAS 8/098 entitled "Radiation Technology for Development of Advanced Materials and for Protection of Health and the Environment" was implemented in 2005-2006. This was created with the objective of enhancing RCA Member States' capabilities in applying radiation technology for advanced materials development, natural polymer processing, and assurance of health safety and protection of environment. This was participated by Fourteen (14) member states: Bangladesh, China, India, Indonesia, Japan, Korea, Malaysia, Mongolia, Myanmar, Pakistan, Philippines, Sri-Lanka, Thailand and Vietnam. The following are the major achievements of the member states.

Bangladesh was able to produce the following materials: a) hydrogels with good physical properties (PVP-Agar, PVP- PVA-Agar, PVP-kappa-carrageenan), b) Bio-blends from naturally occurring polymers (polysaccharides) as hydrogels, packaging materials, et. and c) good quality fiber reinforced polymer. The properties of their blend rubber were also improved. A demonstration plant at a cost of 5.3 million USD has been implemented by the financial assistance of the government of

Bangladesh to facilitate the transfer of technology of their products to private entrepreneurs.

China was able to prepare new products such as a) metal nanoparticles (Ag, Au, Pt) in carboxymethylated chitosan, b) PVP/CMC blend hydrogels for wound dressing, c) CM-chitosan hydrogels for the adsorption of metal ion and d) amphiphilic gel based on methacryloxyethyl dimethyloctane ammonium bromide for the adsorption of organic solvent. Hydrogels for wound/burn dressings has already been commercialized. Radiation degradation of chitosan with suitable additives for industrial preparation of oligo chitosan was developed. The quality of oligo chitosan produced by radiation method is similar to that gained by enzyme. The cost of production of oligo chitosan by radiation is lower than enzymatic method, so radiation degradation is good for producing oligo chitosan. Technique of preparing oligo chitosan has been transferred to the company, and a pilot plant was built in 2006. It has built an industrial facility for EB treatment of Flue gas in Beijing in 2005.

India is developing: a) PVA/EDTA and polyethylene amine hydrogels for metal ion absorption and b) hydrogel dressing containing silver nano-particles c) acrylic acid grafted polyethylene sheets d) nanoparticles of SiO2 for improvement in surface properties and e) crosslinked chitosan for chromium uptake. Hydrogel dressing based on PVA-Polysaccharides (Hydroheal) has already been commercialized by a multinational company. Radiation hygenized sludge was demonstrated as crop promoter on pilot scale. EB curing of organic-inorganic hybrid coating was also demonstrated on lab scale.

Indonesia has carried out field test of oligo chitosan as growth promoters for chili and potato plants. It has prepared medical grade irradiated chitosan for health care applications. Trial test of irradiated chitosan for food preservation (Tofu, fish ball) was also done. Hydrogels for wound dressing have been prepared from chitosan-PVA and Carrageenan-PVA hydrogel. Preclinical test of PVP - Honey hydrogel as burn dressing has been done.

Korea has built new facilities to accommodate relevant industries around the center. Among these are a) two Co-60 irradiators of 420 k curie, b) one electron accelerator of 10 MeV) one ion beam accelerator of 300 keV, and d) one gamma irradiation farm. It has organized a national seminar on radiation processing of natural polymer, a conference on the use of radiation and radioisotopes, and a workshop on radiation, nano and biotechnology. An industrial waste water treatment plant at Daegu Dyeing Industrial Complex has been built in 2006. A sludge disinfection pilot plant has also been built at Daejeon in 2006

Malaysia has transferred the development of sago hydrogel by radiation processing for wound dressing and facemask to the local company. Facemask or biogel mask, i.e. for skin protection, has been produced at commercial scale, whereas, hydrogel for wound dressing is still waiting for clinical trial. Bioform and Biofilm based on radiation crosslinking of sago starch-polymer blend have also been transferred to the local company for pilot scale production trial. On the other hand, palm oil acrylate resins and its application for pressure sensitive adhesive are ready to be transferred to end user. Other products namely nanoclay composites and micro-nanogel are still at the laboratory stage. For environmental project, laboratory scale research on electron beam treatment of volatile organic compounds generated by municipal solid waste incinerator is still on going under the CRP of the IAEA. On the other hand, a joint developmental project between Nuclear Malaysia, local university and company on the integrated system for the treatment of industrial wastewater which include electron beam processing is still pending and waiting for financial support from the government.

Myanmar has synthesized a degraded chitosan hydrogel beads which will be developed for controlled drug delivery system.

Pakistan has developed: a) PVA/CM-Chitosan Hydrogel for healthcare application and b) CM-chitosan/acrylic acid hydrogel for the removal of toxic metal from industrial effluent.

The Philippines has successfully carried out animal testing of the injectable gel from PVP-chitosan for the cure of vesicoureteral reflux (VUR). It has developed CMC-carrageenan hydrogel. Studies on its possible application as a drug release system, metal adsorbent, superabsorbent, etc. will be studied in the future. A letter of intent by a private company (St. Rafael) has been signed for the transfer of technology of the PVP-carrageenan hydrogels.

Sri-Lanka has conducted animal testing of PVP-carrageenan-agar hydrogels for burn/wound dressing. Clinical evaluations for PVA/Agar/Carrageenan will be conducted in near future. Studies on the effect of irradiated chitosan powder and solution on shelf life extension of papaya by controlling anthracnose disease in Papaya (Red Lady and Rathna) have been initiated. Studies on the exploration of viable metal adsorbent (Lead and Cadmium) using Carboxymethyl Cellulose have been also initiated. Investigation of the metal sorption ability of the composite, identification of the individual material and composite characteristics, and optimization of parametric conditions were carried out. Super-absorbent hydro-gel was prepared using Sodium Carboxymethyl Cellulose with the locally available Carboxymethyl Cellulose (CMC).

Thailand has developed: a) Polymeric chelating resins containing the hydroxamic acid groups from poly(methyl acrylate)-grafted cassava starch for metal adsorption, b) PVP-grafted–cassava starch, and c) polyvinyl alcohol/silk fibroin (PVA/SF) hydrogel. Radiation induced admicellar polymerization of silica surface has been successfully carried out. It has commercialized a Thai silk soap product and oligochitosan solution used as plant growth promoter.

Vietnam has prepared a plant growth promoter from radiation degraded alginate. The plant growth promoter (Anti-fungal) prepared from radiation degraded chitosan has been produced at the pilot scale and is partially being commercialized. Super water absorbents prepared by radiation grafting of acrylic monomers onto cassava starch has been studied and is now being pilot scale tested. The products have potential to be used as soil moisture conditioner to reduce watering or overcoming draught stress of plants. The products can also be used for controlling fertilizer consumption. Crosslinking of PVA/CM-chitosan/carrageenan for preparation of wound dressing hydrogel has been carried out. The products are under clinical testing.

Regional activities were also conducted under RAS 8/108.

- The IAEA/RCA regional training course on “Recyclable Radiation Processed Polymeric Products” was conducted in Ho Chi Minh, Vietnam from 9-13 May 2005.
- The IAEA/RCA regional training course on “Clean Water and Air – Advanced radiation processes for air, water and soil pollution control” was held in Beijing, China last June 27-1 July 2005.
- IAEA/RCA Regional Training Course on Applications of Radiation in Nanotechnology: an executive summary, 27 February ~ 10 March 2006, Kuala Lumpur and Bangi, Malaysia
- Regional meeting on Health Care Stimuli Responsive Radiation Processed Materials, 26-30 June 2006, Dhaka, Bangladesh

Some of the identified constraints in the implementation of RAS 8/108 are the following:
a) Constraints faced in R & D work (product development)

- Lack of experts and trained researchers
- Lack of materials and equipments
- Lack of facilities (irradiation, testing)
- Lack of commitment of private counterpart to carry out research

b) Constraints faced in carrying out pilot testing / trialing of developed products

- Lack of EB facility
- Lack of technical expertise in scaling up to pilot plant (technical gaps)
- Lack of equipments
- Identifying and selecting industrial partner for pilot scale trial
- Selection of suitable machine and processing system
- Finances for setting up plant

c) Constraints faced in commercializing products after successful pilot testing / trialing

- Evaluation of market demand of the products
- High cost of radiation processed products
- Acceptance of new products by end-users
- Scaling up to industrial production
- Difficulty of convincing entrepreneurs to buy the technology
- Finances for start up of commercial plant
- Market penetration

- Public acceptance for radiation technology

RAS 8/106

IAEA/RCA RAS 8/106 (2007-2008) entitled “Radiation Processing Applications for Health and Environment” is currently being implemented. It aims to:

- To apply radiation processing to natural polymers for use in health and environment sector
- To establish radiation processing technology for environmental remediation
- To transfer and to promote the utilization of the radiation processing technology to end-users in health and environment sector.

The following are the Regional Training Courses/Seminar scheduled to be organized in 2007 and 2008:

1) Regional training course on the promotion of radiation technology utilization, 9 ~ 13 July 2007 in Philippine.
2) Regional training course on Radiation Processing for basic and medium level personnel, 6 -10 August 2007 in Malaysia
3) Regional Training Course on Applications of Nanotechnology, Q4 in India/Pakistan.
4) Regional Executive Management Seminar for Policy makers and entrepreneurs, 2008, Korea/Japan.

In a meeting held by all participating members of RAS 8/106 and representatives from FNCA last April 23-27, 2007 in Bangkok, Thailand, proposals have been made regarding a possible collaboration between RCA and FNCA. This collaboration was made to avoid duplication and to synergize the activities of each group. This will further strengthen the radiation processing program in the region. In that meeting, the following agreements were reached:

1) Identification and establishment of single team of experts in each country to implement joint activities.
2) The RCA and FNCA have its own annual workshop and it will continue for efficient project implementation
3) Non members of FNCA of RCA member countries may be invited to attend FNCA workshop related to commercialization of radiation processed products and they are to be supported by IAEA.
4) On the job training on product development leading towards commercialization, if needed, to be supported by IAEA through fellowship or scientific visit and MEXT nuclear scientist exchange program and/or ANTEP.
5) Selection of a few high priority products such as hydrogel for wound dressing and super-absorbent for commercialization through collaboration between FNCA and RCA.
6) Identification of the current status of R& D work, pilot scale testing and product commercialization, identification of constraints faced at each stage and means of overcoming

the constraints.

7) Exchange of project information through PLCC and FNCA Project Leader by both leaders attending the RCA and FNCA workshops and presenting the status and planned activities under each program in this project area to avoid duplication of activities and facilitate the collaborative work.

2. 5. 2 Radiation Processing of Natural Polymers - Applications in India*

Sanju Francis

Radiation Technology Development Section, Bhabha Atomic Research Centre

1. Radiation Processing in India

Radiation processing is being used in India on commercial basis since 1974 with operation of ISOMED plant for medical products sterilization and electron beam machine (ILU-6) in 1988. Large Scale gamma facilities in India is listed in Table 1. Table 2 shows the list of electron accelerators for radiation processing in India.

Table 1 Large Scale gamma facilities in India is listed.

Facility	Designed Capacity	Application
ISOMED	37.0 PBq	Radiation sterilization
RASHMI	18.5 PBq	Radiation Sterilization
SARC	18.5 PBq	Radiation Sterilization
RAVI	18.5 PBq	Multi-purpose
SPICE Irrd.	37.0 PBq	Multipurpose including spices
Organic foods	37.0 PBq	Radiation Sterilization*
A.V.Prpcessor	37.0 PBq	Radiation Sterilization*
Universal ISOMED	37.0 PBq	Radiation Sterilization*
VARDHAN	37.0 PBq	Radiation sterilization*
MICROTROL	37.0 PBq	Radiation Sterilization*
SHRI	18.5 PBq	Hygienization of sewage sludge
KRUSHAK	11.1 PBq	Onion irradiation, Mango Irradiation

*Established during 2005-2006

Table 2 Electron Beam facilities in India.

Facility	Designed Capacity	Application
ILU-6	2-MeV, 20 kW	Multi-purpose
NICCO	3-MeV, 150 kW	Wire & cable
Radiant	1.5 MeV, 15 kW	Wire & Cable
500-keV	500 KeV, 10 kW	Surface curing, R&D
3-MeV	3-MeV, 30 kW	Under construction
10-MeV	10-MeV, 10 kW	Under construction
ELV-8	2-MeV, 50 kW	Wire &Cable industry, Under construction

Total installed capacity = 285 kW

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*This text was arranged by the Secretariat of FNCA EB Project, Japan based on a document (Power Point file) presented by the author at the Workshop.

2. Radiation Processing of Natural Polymers in India

Activities of research and development on radiation processing of natural polymers in India are as follows:

1) PVA-Polysaccharides hydrogel wound dressings (HDR)/healthcare
2) Superabsorbent Materials, CMC-Ricehusk
3) Chitosan Degradation/Crosslinking - applications
4) Radiation processing of Levan for FOS
5) Radiation grafting of monomers: antibacterial properties

2.1 PVA-polysaccharides hydrogel

Hydrogel wound dressings (HWD) are produced for healthcare from PVA-Polysaccharides hydrogel. Ingredients are poly(vinyl alcohol) (PVA), natural polysaccharides like agar and distilled water. These ingredients are dissolved in water at high temperature. The solution is filled in trays and irradiated to 25 kGy with γ-rays. The role of natural polysaccharides was investigated (Table 3)[1] .

Table 3 Role of natural polysaccharides in radiation formation of PVA–hydrogel wound dressing.

	PVA/Agar/Carrageenan				
	8/0/0	8/1/0	8/0/1	8/1/1	8/0/2
Elongation (%)	30	410	93	180	250
Tensile strength (gm/cm^2)	45	240	125	217	411
H_2O(%)	25	58	90	120	157

About 120000 pieces can be irradiated at ISOMED Radiation sterilization Plant to make HWD. The technology was transfer to the three companies, ABS Medicare (Figure 1), Dr Reddy's Laboratories (Figure 2) and VIRIDIS BIOPHARMA, earning about 3 million rupees as technology transfer fee alone.

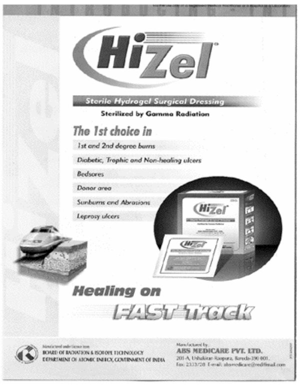

Fig.1 HWD by ABS Medicare.

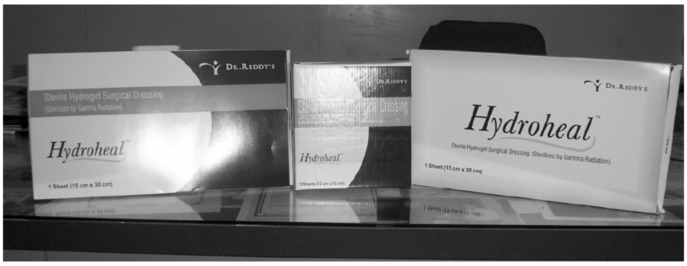

Fig. 2 HWD of Dr Reddy's Laboratories Hydroheal.

Iodine- Hydrogel also developed. Iodine forms a blue-black complex with PVA hydrogel and is released to the wound in sustained manner. Development of Silver based antibacterial hydrogel dressing is carried out [2]. Silver nanoparticles formed in hydrogel matrix containing polysaccharides. Figure 3 shows the absorbance spectra of high molecular weight PVA containing 2 mM Ag^+ at various doses.

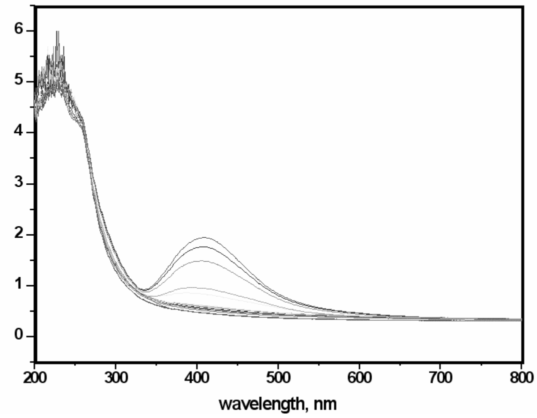

Fig. 3 Absorbance spectra of Silver nanoparticles containing PVA hydrogel.

There is a gradual increase in the intensity of the plasmon band at 400 nm at lower doses, resulting in the yellow colored Ag sol. At the dose of about 3 kGy, a slight red shift in its l max is observed. At higher doses, there is a small decrease in the intensity along with a little broadening of the Ag plasmon band, without any other significant change in the nature of the absorption spectra. After the complete reduction of Ag+ ions, on further irradiation (at 70 kGy), a yellow colored weak gel-containing Ag nanoparticles is formed due to the crosslinking of PVA chains, without much change in the spectral characteristics. The Ag nanoparticles have antibacterial activity against *E. Coli* and *MRSA*.

2.3 Radiation synthesis of superabsorbent polymers

A series of superabsorbent hydrogels were prepared from carrageenan and partially neutralized acrylic acid by gamma irradiation at graded doses up to a maximum dose of 50 kgy[3]. It was found that the incorporation of even 1% carrageenan (sodium salt) increases the eds of the hydrogels from 320g/g to 800g/g

2.4 CMC-rice husk composite

CMC can also be crosslinked to form gels at 25 kGy with degree of swelling 90-120 (1g absorbing 90-120 gm of water) which retains its structure in swollen state[4]. Rice husk which is normally burnt, is a by product of rice mills contains 35 % cellulose, 25% hemicellulose, 20% lignin, 3% crude protein and 17 % silica can be a good source of C, Si and N. A mix of 1:1 of 20% CMC and rice husk formed a hydrogel at 25 kGy which has significant property of water retention and contained depolymerized rice husk due to radiation processing. In swollen state, it was observed that the husk was coated with CMC gel.

3 Radiation processing of chitosan

3.1 Radiation degradation of chitosan

Chitosan was degraded by irradiation. Figure 4 illustrated the radiation degradation processes. Plant growth promotions of irradiated chitosan and alginate in wheat were demonstrated.

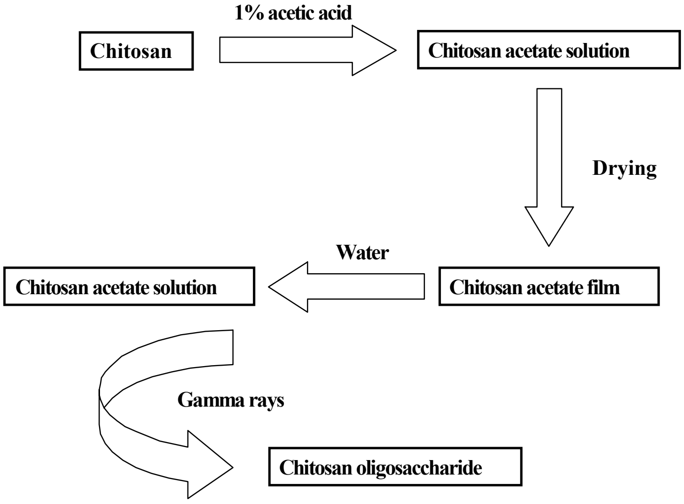

Fig.4 Radiation degradation processes of chitosan.

3.2 Radiation crosslinking of chitosan

For various applications of chitosan such as protein separation, removal of metal ions from the solution, effluent treatment, control drug delivery etc. it is necessary to crosslink it. Chemical reagents such as glutaraldehyde, epichlorohydrin etc. are being used to achieve crosslinking. However these reagents react through $-NH_2$ group of chitosan. Thus, radiation crosslinking of chitosan using CCl_4 as sensitizer was developed[5)]. Figure 5 shows the radiation crosslinking processes of chitosan.

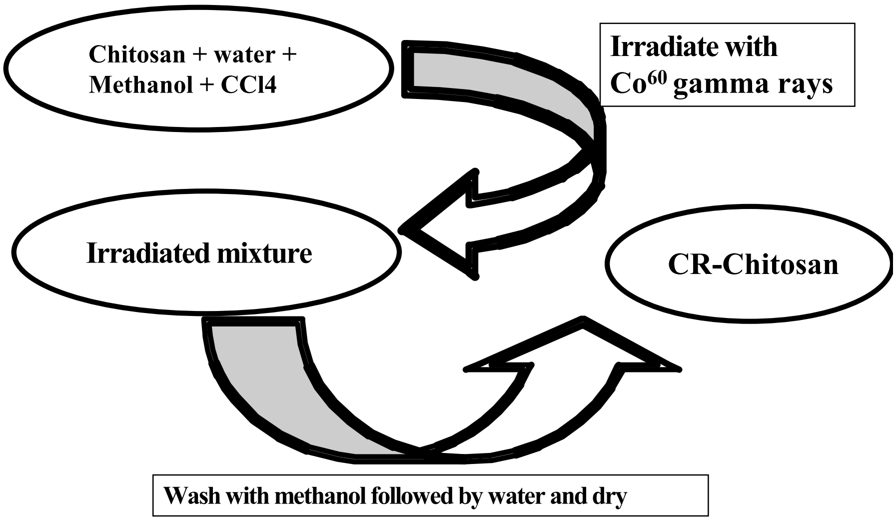

Fig. 5 Radiation crosslinking processes of chitosan.

3.3 Applications of radiation crosslinked chitosan

The radiation crosslinked chitosan was applied as meta ion bsorbant[6)]. Maximum adsorption capacity of Cr(VI) on the three samples namely CH, CRC and CRCH were calculated to be around 16 mg/g (Figure 6).

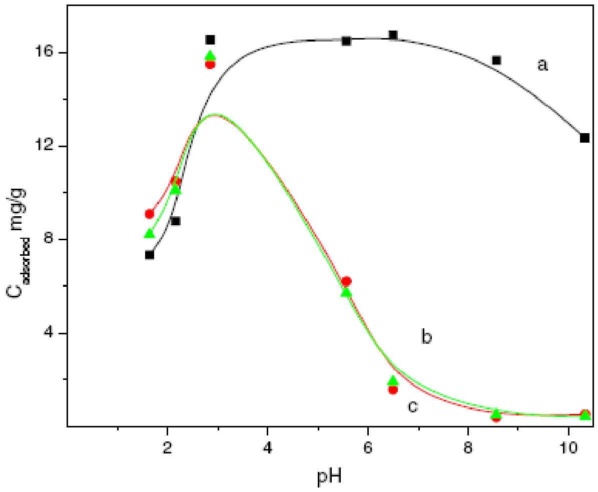

Fig. 6 Effect of pH on the uptake of Cr(VI) from aqueous solution by chitosan samples: (a) CRC; (b) CH; (c) CRCH.

4. Radiation degradation of Levan

Levan (Figure 7) is a homopolymer made of fructose units connected by β 2,6 glycoside and β 2,1 glycoside in the branch. Levan is mainly produced by microorganisms like *Bacillus subtilis, Acetobacter xylinum* etc. Fructo-oligosachharide (FOS) is the low MW Levan (5-9 DP) which has found many applications. (prebiotic properties, decreases serum cholesterol, phospholipids & triglyceride, Low calorie sweetener, Non-carcinogenic). Radiation degradation of levan was studied. Figure 8 shows molecular weight change with irradiation dose.

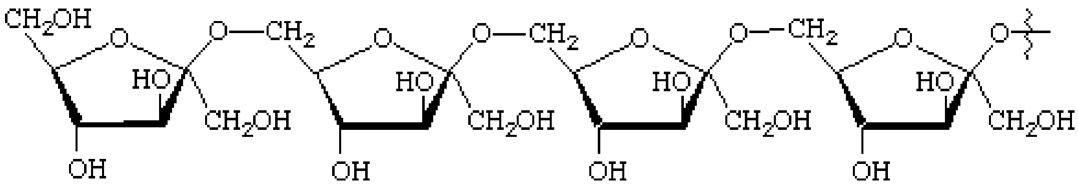

Fig.7 Chemical structure of Levan.

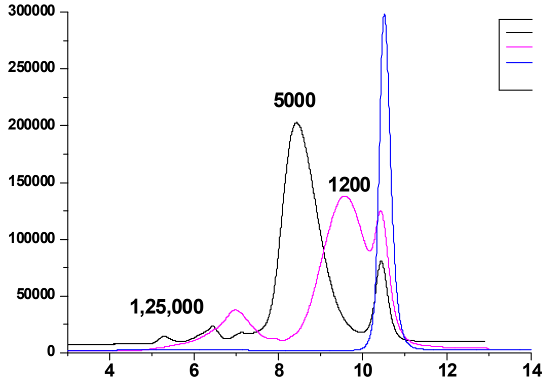

Fig. 8 Effect of radiation on 10 % Levan solution.

5. Radiation Modification of Natural Rubber and Radiation Induced Grafting

Effect of styrene-butadiene rubber latex addition on radiation vulcanization of natural rubber latex 7) and radiation grafting of methyl methacrylate on radiation crosslinked natural rubber film 8) were carried out. Radiation induced grafting of vinylbenzyltrimethylammmonium chloride (VBT) onto cotton fabric 9) and radiation-induced grafting of acrylamide onto guar gum in aqueous medium10) were published.

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2. 5. 3 R & D Activities on Radiation Processing of Natural Polymers in Pakistan

Tariq Yasin

Pakistan Institute of Engineering and Applied Sciences

1. Introduction

The fishery industry in Pakistan is well established and is growing very fast. The annual production of shrimp is ~ 45,000 metric ton, out of which ~ 20,000 metric ton is exported. The annual production of crab is 250 metric ton. The estimated production of waste from these materials is approximately 20,000 metric ton, which is a huge quantity. This crustacean waste generated by fishery industries containing chitin, a natural polymer, can be extracted by chemical treatments. Deacetylation of chitin gives chitosan which is soluble in dilute mineral acids. Presently, the main consumer of this waste is animal feed industries. Pakistan Atomic Energy Commission (PAEC) has started research program on Radiation Processing of Natural Polymers in cooperation with IAEA and RCA in order to convert this sizable waste into value added products. This report describes some of our obtained results on radiation processing of natural polymer and its applications

2. On Going Radiation Processing Activities

PAEC is actively pursuing research and development program in different fields of radiation processing and its applications in healthcare, agriculture and environment. One of the PAEC's main objectives is to work in collaboration with industries to familiarize them with the new applications of radiation technology and to enhance the capabilities in order to compete with the international market. Recognizing the growing importance of radiation processing of natural polymers in particular and for cable and wire in general, the PAEC has made significant contribution in research and development of this advance technology. Sterilization of disposable material by using radiation is a routine process since 1987 at Pakistan Radiation Services (PARAS), Lahore. A lab scale facility has been developed at PIEA to analyze and characterize radiation processed material.

2.1 Radiation degradation of chitosan

A study has been carried out on degradation of chitosan using radiation and chemical methods. Chitin was extracted from crab shells waste and different reaction parameters have been studied. After demineralization and deproteinization chitin with yield of 15% was obtained. Chitin was deacetyled with 50% NaOH for different time intervals. The obtained chitosan has molecular weight in the range of 2.2 x105 to 0.73 x105 (Table 1). This chitosan was then used for radiation as well chemical degradation and their degradation effects on chitosan were characterized by FTIR, viscometry and UV-VIS spectroscopy.

Table 1 Effect of refluxing time on viscosity average molecular weight of chitosan

Reflux time (hrs)	Hr (mL/g)	Hsp (mL/g)	[η] (mL/g)	Molecular Wt. (Mv)
5	1.1874	0.1874	6.92	2.2×10^5
6	1.1511	0.1511	5.734	1.6×10^5
7	1.1017	0.1017	3.922	0.95×10^5
8	1.0854	0.0854	3.355	0.73×10^5

In radiation degradation process, chitosan sample was divided into the following four sets:

Set-1: Chitosan powder

Set-2: Chitosan powder wetted with few drops of water

Set-3: Chitosan powder having 0.5% H_2O_2

Set-4: Chitosan powder was dissolved in 2% acetic acid solution and then added 1% H_2O_2

All four different sets of chitosan were subjected to gamma radiation ranging from 10 kGy to 150 kGy. This study revealed that the physical state of chitosan and degradation promoters greatly effect the degradation process by radiation. Low degradation products were obtained in case of powder chitosan whereas higher degradation products were obtained in solution chitosan (Figure 1). Same results were obtained in case of combined (radiation and chemical) degradation.

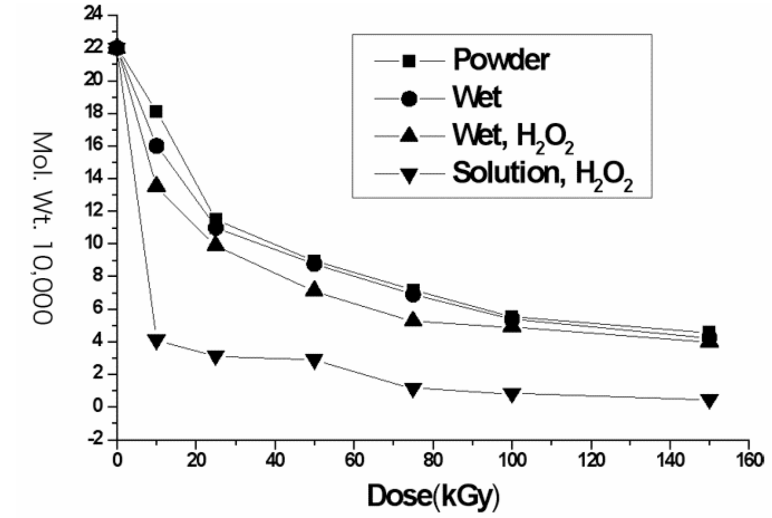

Fig. 1 Radiation dose vs. molecular weight chitosan.

The data in above figure shows that the degradation of chitosan can be tailored by using different procedures. Range of molecular weight has been obtained using gamma radiation and/or hydrogen peroxide. The degraded chitosan retained the chitosan backbone structure and degradation reaction take place at glycosidic linkage (C-O-C). The formation of carbonyl groups at the chain end is confirmed by FT-IR and UV-VIS spectroscopy. In all cases, a decrease in viscosity and viscosity average molecular weight is observed. It shows that as the radiation dose increases, the viscosity of chitosan decreases in following order:

Powder chitosan > Wet Chitosan > Wet Chitosan + H_2O_2 > Chitosan solution + H_2O_2

This study revealed that degradation of chitosan could be tailored by using different procedures. Range of molecular weight has been obtained using gamma radiation and/or hydrogen peroxide. The degraded chitosan retained the chitosan backbone structure and degradation reaction take place at glycosidic linkage (C-O-C). The formation of carbonyl groups at the chain end are confirmed by FT-IR and UV-VIS spectroscopy.

2.2 Post harvest fruit preservation

Chitosan form semi permeable coating, which can be used to increase the shelf-life of fresh fruits. In this study, a native Southeast Asian variety of citrus fruit called Kinnow was selected. It is one of the most important fruit crop successfully grown in Southeast Asian countries. Citrus fruits are very susceptible to be attacked by pathogenic fungi due to its low pH, high moisture content and many nutrients. For increasing its shelf life as well as maintaining its quality, irradiated and unirradiated chitosan coatings on Kinnow mandarin has been tried and their effect up to 12 weeks storage period has been investigated.

The effect of coating with irradiated chitosan (CHIirr, $Mv = 5.14 \times 10^4$) and unirradiated chitosan (CHIun, $Mv = 2.61 \times 10^5$) on post harvest preservation of Kinnow (Citrus Reticulata B) has been studied. 1% and 2% coatings of both CHIirr and CHIun were used and the fruits were stored at 4 °C in 80% relative humidity for 12 weeks. Changes in weight loss, ascorbic acid, titratable acidity, total soluble solids, reducing, non-reducing and total sugars were periodically measured during storage. Physical characteristics such as general appearance in color and shape of the fruits and organoleptic evaluation were also carried out. All chitosan coating reduced the weight loss and respiration rate during storage. It also delayed and minimized the changes in: ascorbic acid contents, titratable acidity etc and maintained eating quality of fruits till 3 months as compared to untreated fruits.

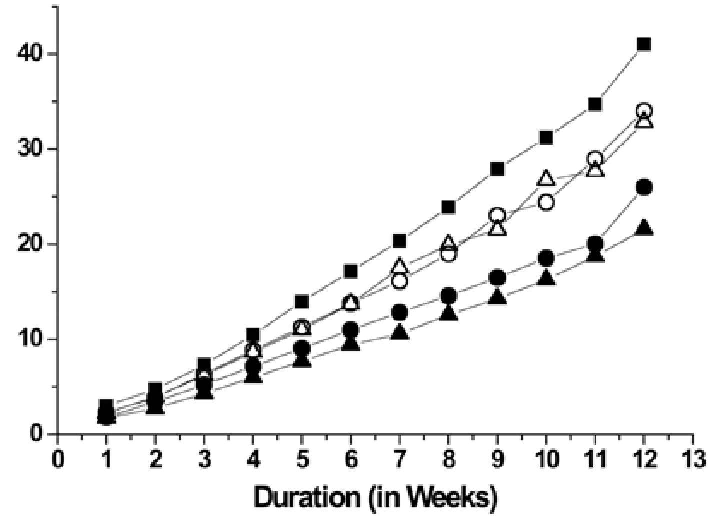

Fig. 2 Changes in percentage weight loss of citrus fruits coated with unirradiated, irradiated chitosan and the control during storage at 4 °C. (-■- CHIcon, -○- CHIun1, -●- CHIun2, -△- CHIirr1, -▲- CHIirr2.

Figure 2 shows that weight loss increases with increase in storage period and minimum weight loss was observed in chitosan coated fruits as compared to uncoated one. Moisture loss through respiration is the main process leading to weight loss of pulp and peel of Kinnow fruit. Weight loss in fruit coated with CHIcon fruits was 3% on 1st week and 41% on 12th week. This is a maximum weight loss as compared to chitosan treated fruits because chitosan coating provides barrier between inner and outer environment of the fruit and decreases rate of transpiration. By comparing chitosan coated fruits, it can be concluded that minimum weight loss of 25% was observed in CHIirr2 on 12th week. The minimum weight loss in CHIirr2 is due to its high rate of respiration which in turn increases the metabolic activities inside the fruit as a result of the ripening of the fruit.

In citrus fruit, changes like ascorbic acid content, acidity and other internal changes are affected as fruits are kept in storage so these undesirable changes reduce and eventually damaged the quality of the fruit. Chitosan coating showed its ability to minimize these changes to successive extent. Figure 3 explains the effect of different chitosan coatings on ascorbic acid during storage. This figure shows a decrease in ascorbic acid contents as storage period increases. Chitosan coated fruits demonstrated a small decrease in ascorbic acid as compared to controlled ones. This decrease in ascorbic acid reduces the eating quality of citrus fruits. Ascorbic acid contents of 54.77 mg /100 ml of juice were obtained at the start of the experiment and maximum loss of 16.01 mg /100ml was observed in CHIcon on 12th week. Minimum loss in ascorbic acid was observed in 2 % coated fruits. In CHIirr2, ascorbic acid contents at the end of experiment were 26.00 mg /100 ml of juice whereas in CHIun2 it was only 22.12 mg /100 ml of juice.

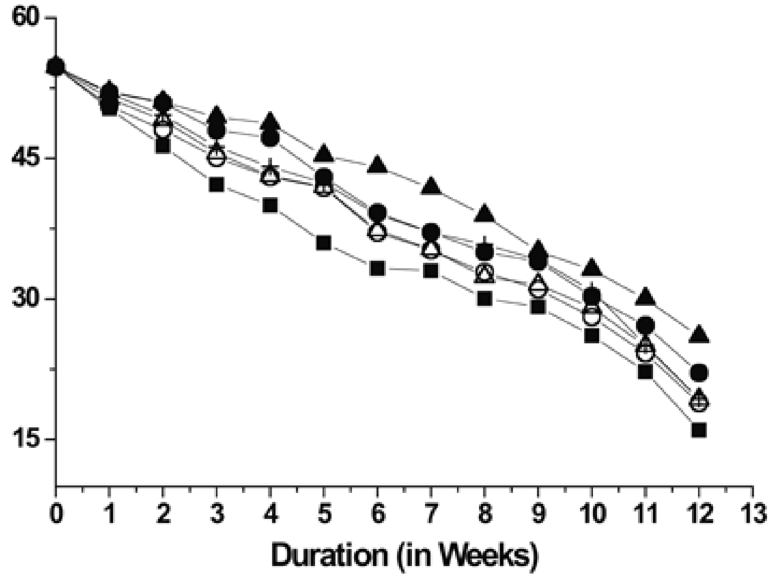

Fig. 3 Effect of unirradiated, irradiated chitosan coatings on ascorbic acid contents of Kinnow and the control during storage at 4 °C. (-■- CHIcon, -○- CHIun1, -●- CHIun2, -△- CHIirr1, -▲- CHIirr2).

The results showed that coating of Kinnow with chitosan provides an active package on fruits. Coating of 2% irradiated chitosan was effective enough to decrease the respiration rates and delays ripening by suppressing the evolution of ethylene and carbon dioxide. It maintained the active ingredients of the fruit with minimum loss and also kept its organoletic properties. In addition, against the growing awareness of consumers around the world about the chemical preservatives, chitosan can be a good alternate due to its non toxic and biocompatible nature.

2. 5. 4 Research & Development on Radiation Processing in Sri Lanka

S. S. Kulatunge[a], L. Motha[b], Y. Sultanbawa[b], S. Malavipathirana[b], A de Silva[b],
S. Nanayakkara[b], I. G. N. Hewajulige[b], K. R. C. de Silva

[a]Atomic Energy Authority of Sri Lanka, [b]Industrial Technology Institute*

Abstract

Research on radiation processing of natural polymer such as polysaccharides of chitosan, cellulose, carrageenan has been carried out in Sri Lanka since the year 2004. The research group have been involving in development activities on application of chitin & chitosan for wound dressing, irradiated chitosan on shelf life extension of fruits such as papaya, banana, mangoes, radiation crosslinked super-absorbent hydrogel from sodium carboxymethyl cellulose by radiation processing. Hydrogels prepared with PVA/Carrageenan/Agar has been studied on guinea pigs to determine the wound healing effect. Irradiated chitosan powder and chitosan solution was studied in vitro and found chitosan solution (1%) directly subjected to irradiation dosages even at 5 kGy was highly effective in control of anthracnose causing organism of papaya. In vivo studies with irradiated 1 % chitosan solution on Rathna & red lady variety of papaya shows better control of spoilage of papaya to a considerable extent. The government of Sri Lanka (Ministry of Science & Technology and Atomic Energy Authority) is in the process of establishing the first government owned Multipurpose Gamma Irradiation Facility and it will be helpful to transfer the output of R&D in radiation processing.

1. Introduction

Radiation Technology has been successfully utilized to modify natural polymers such as natural rubber, polysaccharides of chitosan, cellulose, starch, carrageenan and alginate. Radiation processing of these polymers has shown promising results and achievements for different applications such as wound dressing in medical, plant growth promoter and fertilizer in agriculture, slow drug release materials in pharmaceutical and super-absorbent in agriculture & industry. At present there is no value addition to the shells and carapace from the shrimp processing industry except for some drying and powdering for the poultry industry. The volume of by-products from the shrimp industry in Sri Lanka amounts to about 3000 mt/year, which has become an environmental hazard and a waste disposal problem for the shrimp export industry. The processing of shrimp uses about 40% for products and 60% is by-products. The potential products from these by-products are shrimp powder; shrimp flavor extract, Chitin, chitosan and glucosamine.

Chitin is a polysaccharide made from N-acetyl-D-glucosamine units. It is the second most abundant biopolymer next to cellulose. Chitosan is prepared by the N-deacetylation of chitin. The applications of chitin derivatives in industry are due to its polyelectrolite properties, the presence of reactive groups functional groups, gel forming ability, high adsorption capacity, biodegradable ability and bacteriostatic and fungistatic properties. Many applications of chitin and chitosan have been identified in the medical and veterinary fields, pharmaceutical, cosmetic, agriculture, food, environment and textile fields.

The research group on Radiation Processing Applications for Health and the Environment consists of Atomic Energy Authority (AEA), Industrial Technology Institute, University of Kelaniya and National Aquatic Research Authority focused on research and development activities on application of chitin & chitosan for wound dressing ,irradiated chitosan on shelf life extension of fruits such as papaya, banana, mangoes, development of radiation crosslinked super-absorbent hydrogel from sodium carboxymethyl cellulose by radiation processing.

2. Application of Carrageenan, Chitin & Chitosan in Wound Dressing

At present chitin has been extracted from farm shrimp (*penaeus monodon*) and lagoon shrimp (*penaeus indicus*). Extraction process included deproteinization with Sodium hydroxide (NaOH) and demineralization with Hydrochloric acid (HCl). After extraction the chitin was deacetylated with concentrated NaOH. The process has also been scaled up for pilot scale preparations. Chitosan have shown an inhibitory effect on the growth of phytopathogenic fungi and bacteria and induce resistance of plant to fungal and viral infections. Hydrogel can be described physically as three-dimensional networks from hydrophilic polymers. Depending on the type of hydrogel they contain varying percentages of water, but altogether do not dissolve in water. Despite their high water content, hydrogels are capable of additionally binding great volumes of liquid due to the presence of hydrophilic residues. Hydrogel were prepared using PVA, Carrageenan and Agar. Animal studies on guinea pigs were carried out to determine the wound healing effect. Obtaining of ethical clearance is in the process by the AEA & ITI and clinical trials are planned in two hospitals in Colombo and Ragama in Sri Lanka.

3. Effect of Irradiated Chitosan on Shelf life Extension of Papaya

In Sri Lanka a fungal disease in papaya called anthracnose is caused by *Collectortichum gloeosporioides* which causes about 30-40% post harvest losses of papaya. Chitosan extracted from locally available head and shell waste of prawns was powdered and irradiated at different doses. Similarly chitosan solutions were irradiated at different doses. Antifungal activity of irradiated chitosan powder and irradiated chitosan solution was tested in-vitro and effective dosage for complete control of the pathogen was investigated. It was found that chitosan powder is not effective in controlling the post-harvest fungus on papaya. However chitosan solution (1%) directly subjected to irradiation dosages even at 5 kGy was found to be highly effective in in-vitro control of anthracnose causing organism of papaya.

Studies were conducted to apply 1% irradiated chitosan solution in vivo on growth of pathogen of Rathna and Red Lady variety of papaya for shelf life extension in order to reduce post harvest losses. It was determined the disease development of both papaya varieties stored at low temperature (13.5°C) for two and three weeks (in vivo).

Table 1 Shelf life extension of two papaya varieties with 1% irradiated chitosan solution.

Condition	Disease development(%)			
	Rathna Variety		Red Lady	
	2 weeks	3 weeks	2 weeks	3 weeks
Control	60	80	80	80
Unirradiated 1% chitosan solution	30	48	50	58
Irradiated 1% chitosan solution	20	40	30	48

4. Development of Super-Absorbent from Sodium Carboxymethyl Cellulose

Sodium carboxymethyl cellulose (CMC) is a water-soluble natural polymer derivative. It can be modified to prepare biomaterials such as super absorbent hydrogel with properties such as non-toxicity, degradability and good biological compatibility. Super absorbent polymers are those, which can absorb several hundred times their dry weight of water and retain it even under pressure. Super-absorbent hydrogel was prepared using Sodium Carboxymethyl Cellulose with the locally available CMC. The optimum conditions of the properties such as gel fraction, swelling ratio and swelling time under different irradiation doses, vacuum conditions and CMC concentrations were evaluated for the prepared hydrogel. The results obtained so far suggest that the optimum gel fraction of 50% and swelling ratio of 45% was obtained (in 0.9% NaCl solution) when irradiated at 60 kGy and the Na-CMC concentration of 20%. Also the kinetic studies on the experiment showed that the swelling time is 16 hrs for 20% Na-CMC. Swelling properties of the gel prepared under vacuum condition was better when compared to the trials done under normal air conditions.

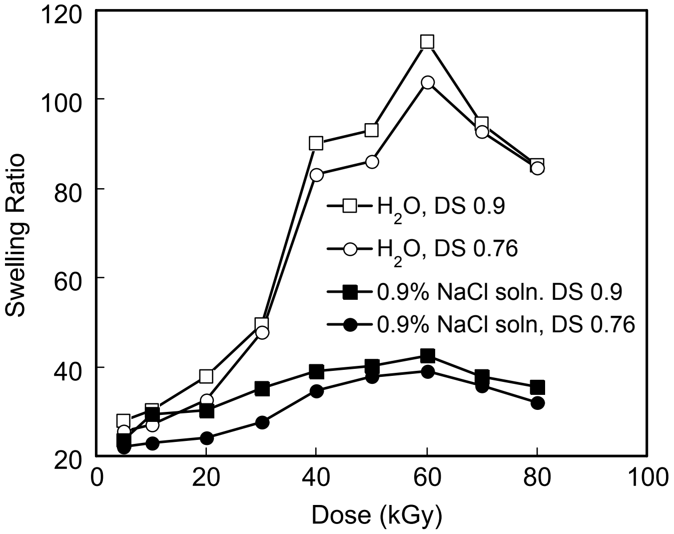

Fig: 1 Swelling behavior of 20% CMC.

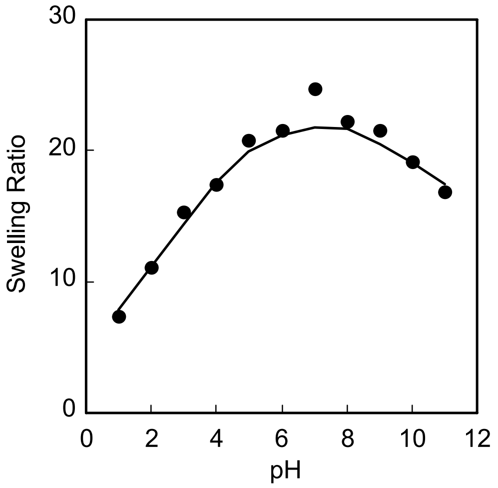

Fig. 2 Swelling behavior of CMC with different pH.

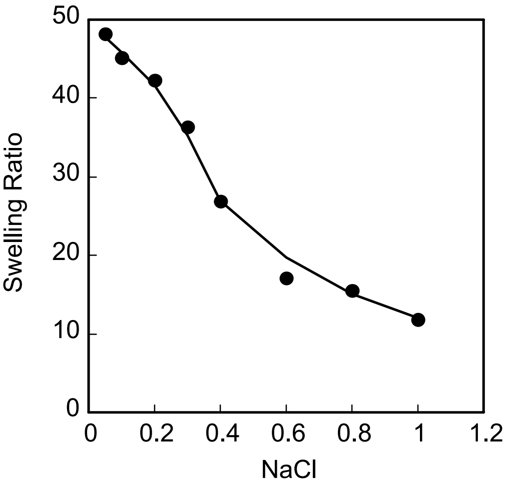

Fig. 3 Swelling behavior of CMC with inorganic salt.

5. Super- absorbent hydrogel in Animal Waste Management

Pig dung has become a disposal problem in Sri Lanka. Presently it is mixed with saw dust to make fertilizer. How ever it requires about period of 4-6 months to make the fertilizer and a strong smell is emitted which is not acceptable. Further more saw dust is now being gradually phased out due to the carbon treaty. As such gamma radiated carboxymethyl cellulose (CMC) has been tried to study the feasibility of using it as a strong absorbing agent of moisture and since it is biodegradable the time period it will take for the pig dung to become fertilizer. Preliminary studies on management of water of pig excretions by CMC have been carried out.

6. Modification of Biodegradable Polymers by Radiation Processing for Metal Adsorbent

Studies were focused so that exploration of viable metal adsorbent through radiation modified polymers that can be used for the adsorption of metal ions from the solution in contact. Natural polysaccharide derivatives were modified, in this regard, by both radiation and incorporation of biodegradable fabric materials such as cotton fabric and cotton gauze to form a composite. Carboxymethyl cellulose which is a readily available, economical, water soluble anionic polysaccharide has been used as the base material to be incorporated with fabrics. Further, cotton - cellulose; the core material is widely available natural polymer with advanced characteristics of biodegradability, water absorption etc. with no other artificial polymer can compete. Desirable properties associated with both CMC and cotton cellulose along with radiation processing collectively contributed to form a viable metal adsorbent. In this regard, radiation crosslinking by means of Electron Beam (EB) source was used to qualify CMC/cotton composites to meet the objectives. Further, prior to investigation of the metal sorption ability of the composite, identification of the individual material and composite characteristics, and also optimization of parametric conditions were carried out towards gel content, swelling, mechanical properties etc. Metal sorption characteristics were understood towards Lead (Pb^{2+}) and Cadmium (Cd^{2+}).

7. Commercialization of Radiation Processing in Sri Lanka

Sri Lanka has only one commercial gamma irradiation facility to sterilize rubber gloves owned by private sector and dedicated for their products. The present activity is around 1.5 MCi and upgradeable to 4.5 million curie. The government of Sri Lanka is in the process of establishing the first government owned Multipurpose Gamma Irradiation Facility with the initial loading of 150 kCi and up gradable to capacity of 3 MCi. A suitable land has been selected and purchasing of the land and tender has been advertised internationally for the irradiator plant to establish the above facility. The main end users will be medical products manufacturers such as natural rubber glove, food industry in the country.

Acknowledgment

The Atomic Energy Authority and Industrial Technology Institute appreciate the cooperation given by International Atomic Energy Agency through RCA and the FNCA on behalf of Government of Sri Lanka. The authors wish to thank all the members working in the national research program for their valuable contribution to the project a success one.

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3. Progress in Radiation Processing -Lecture at Seminar

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3.1 Introduction to Radiation Processing

Tamikazu Kume

Takasaki Advanced Radiation Research Institute, Japan Atomic Energy Agency

1. Introduction

Nuclear technology such as γ-rays, electron beams and ion beams irradiation is widely used in industrial, medical and agricultural fields. The purpose of radiation application is aiming at increasing welfare and quality of our life. Radiation technology applied to medical care is widely known as X-ray diagnosis but the contribution of radiation processing to our daily life is not well known even though it is effectively used in industry and agriculture. The main radiation processing in industry is the modification of polymers, i.e. heat shrinkable tube, radial tire, plastic foam, etc. in a car, heat resistant wire and cable, semiconductor, floppy disk, etc. in a computer, and sterilization of medical devices (Figure 1). In Agriculture, radiation has been used in various fields such as food irradiation, sterile insect technique, mutation breeding, etc. contributing for human being to supply foods and sustainable environment.

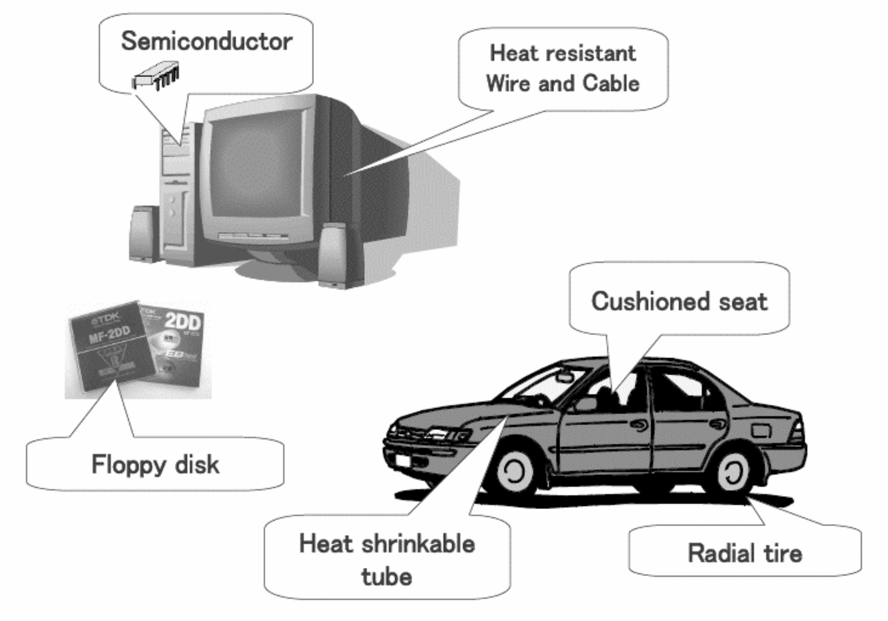

Fig. 1 Radiation processing products using in a car and computer.

2. Radiation Modification of Polymers

Radiation induces the ionization or excitation of atoms or molecules in materials and can induce chemical reactions without using catalyst at room temperature. Principle and features of gamma and electron beam (EB) irradiation on polymers are shown in Figure 2. Main processes are 1) crosslinking, 2) degradation, and 3) graft polymerization.

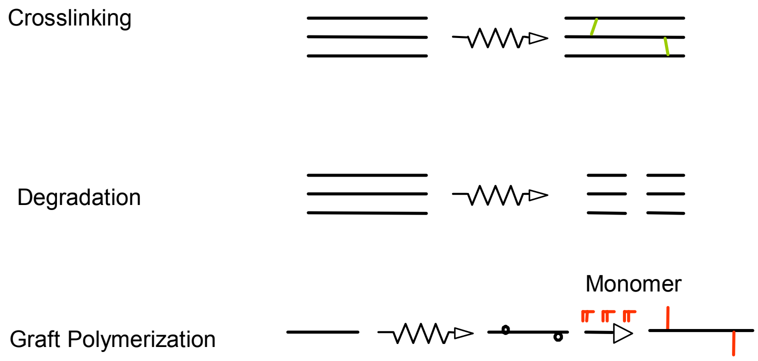

Fig. 2 Principle and features of gamma and EB irradiation.

Radiation processing of polymers has been used in various commercial products (Figure 3). The radiation crosslinking is the most commonly used for radiation processing in industry and its share is over 99% of whole radiation processing. Radiation crosslinking of polymers such as polyethylene, polyvinyl chloride and rubber improves their thermal resistance, chemical resistance and mechanical properties.

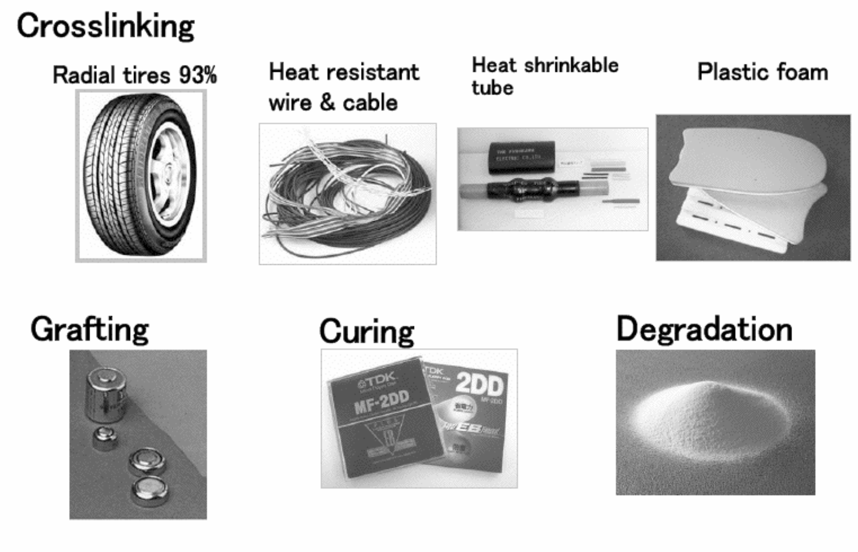

Fig. 3 Commercial products of radiation processing.

Wires and cables insulated with radiation crosslinked heat resistant polymer are used for the automobile, telecommunications, and the aerospace instruments. Heat shrinkable material induced by crosslinking is widely used for packaging, wire insulation and corrosion protection of pipeline welds. In the automobile tire industry, radiation processing is used to crosslink rubber molecules to improve physical properties for the production of radial tires. Graft polymerization is useful for modification of polymers. Acrylic acid grafted polyethylene fibers are used as battery separator. The radiation graft polymerization can be applied for the preparation of absorbents for various pollutants from water and air.

3. Radiation Sterilization

Radiation is widely used for sterilization of medical products to avoid disease infection. About 60% of disposable medical products are sterilized by radiation and remaining by ethylene oxide (EOG) and autoclave. ^{60}Co γ-ray is used for sterilization but high energy (10MeV) electron accelerators are being introduced because of better public acceptance and economics for large throughput. Radiation is commercially used for sterilization of medical products, food packaging materials and laboratory animal feeds (Figure 4).

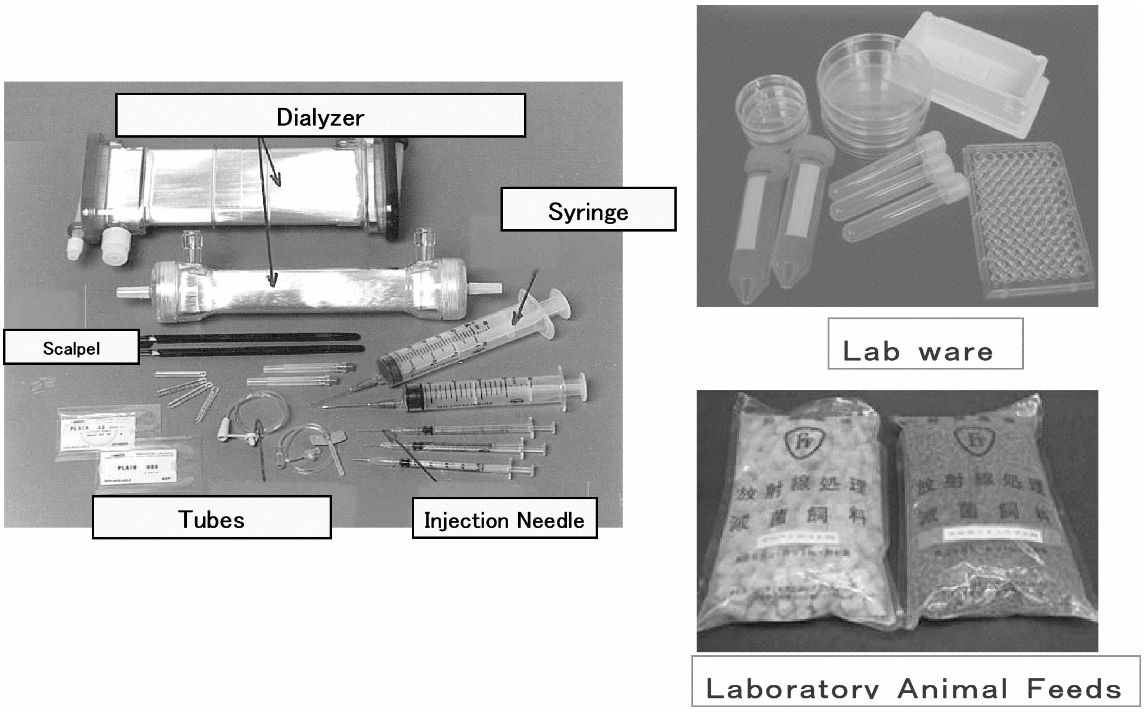

Fig. 4 Radiation application for sterilization.

4. Food Irradiation

Irradiation for foods has been used to control harmful bacteria, to eliminate insects from fruits and vegetables, to control sprouting and ripening, replacing methyl bromide fumigation which depletes the ozone layer. Currently FAO/IAEA reported that the food irradiation was approved in 57 countries on 8 classes of food items. The commercial food irradiation is developing rapidly in Asia and the total volume is reached to 180,000 ton in 2004 (Table 1). In Japan, only sprout inhibition of potato is approved and commercialized since 1974. The irradiation of potato in Shihoro, Hokkaido is continued more than 30 years but other food item is not approved in Japan. Recently it is expected to commercialize the radiation processing of spices.

Table 1 Food irradiation in Asia.

Country	Food items	Volume (ton)	
		2002	2004
China	Garlic, Rice, Corn, Orange, Apple, Meat	100,000	140,000
Vietnam	Frozen shrimp, Frozen fog leg, Spices	5,200	14,200
Indonesia	Spice, Cocoa	5,000	7,000
Japan	Potato	8,000	8,000
Malaysia	Herbs	500	3,500
Korea	Potato, Onion, Garlic, Spices	3,300	3,500
India	Onion, Spices, Potato, Meat	1,000	1,500
Thailand	Herbs, Spices, Fermented sausage	1,130	3,000
Bangladesh	Dry fish, Spices	229	
Philippines	Spices, Onion	90	103
Pakistan		27	50

5. Mutation breeding

The radiation-induced changes in DNA sequences have resulted improved mutant crops demonstrating 1) disease resistance, 2) early maturity, 3) drought tolerance, and 4) better yield. New mutant varieties give us useful gene resources for the security of food resources, the conservation of our ecosystem, and the promotion of new industries. Plant mutation breeding has been investigating for long time in many countries and the induced species were more than 2,500 in the world. Using radiation technique 161 varieties including 137 varieties induced by γ-ray irradiation were developed in Japan. Many new species of rice, barley, wheat, beans, fruits including pears resistant for black spot decease, grass, vegetables, etc, were developed for decease resistant species.

Recently, a lot of fascinating new mutants are generated by ion beams. Ion beams can frequently cause large DNA alterations such as inversion, translocation and large deletion rather than point mutation, which result in producing characteristic mutants otherwise attainable. Ion-beam irradiation of *Arabidopsis* seeds has produced the UV-B-resistant, the frilled-petal, and other novel mutants. The features of ion beams in the mutation induction seem 1) to induce mutants with high frequency, 2) to show a broad mutation spectrum, and therefore, 3) to produce novel mutants. New mutants of chrysanthemum and carnation with complex and striped flower-color, and new flower-shape have been produced and commercialized. Recently new variety of chrysanthemum reducing axillary buds was induced by ion beams and commercialized in Japan.

6. Radiation Processing of Natural Polymers

Polysaccharides such as chitosan and sodium alginate were easily degraded by irradiation and induced various kinds of biological activities, i.g. anti-microbial activity, promotion of plant growth, suppression of heavy metal stress, phytoalexins induction. The main advantage of radiation processing of polysaccharides are as the following:

1) the degradation reaction can be performed at room temperature,

2) after processing, the degraded polysaccharides can be used without purification,
3) the simplicity of controlling the whole process; and
4) large-scale application.

Radiation degraded chitosan was effective to enhance the growth of plants in tissue culture (Figure 5).

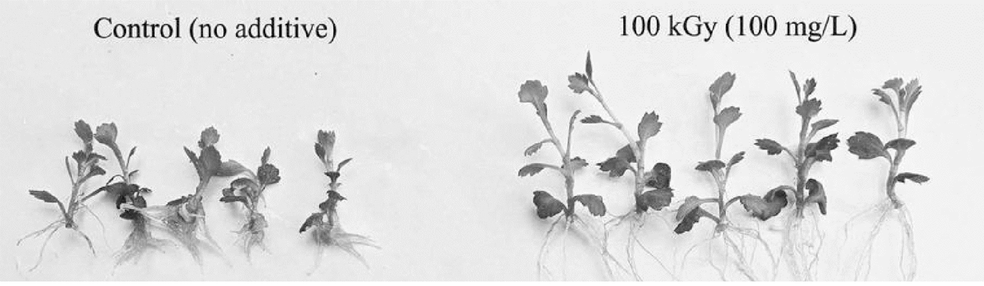

Fig. 5 Growth enhancement of chrysanthemum by irradiated chitosan.

Polysaccharides have been recognized as a degradable type of polymer. We found carboxymethyl-cellulose (CMC) can be crosslinked under certain radiation condition at a high concentration (50-60%) in an aqueous solution. It is assumed that high-radiation crosslinking of CMC was induced by the increased mobility of its molecules in water and by the formation of CMC radicals from the abstraction of H atoms of macromolecules of water radiolysis. Carboxymethyl-starch (CMS) and carboxymethyl-chitin/chitosan (CM-chitin/chitosan) could be crosslinked as same as CMC and these crosslinked polysaccharides produced the biodegradable hydrogel for medical and agricultural use (Figure 6).

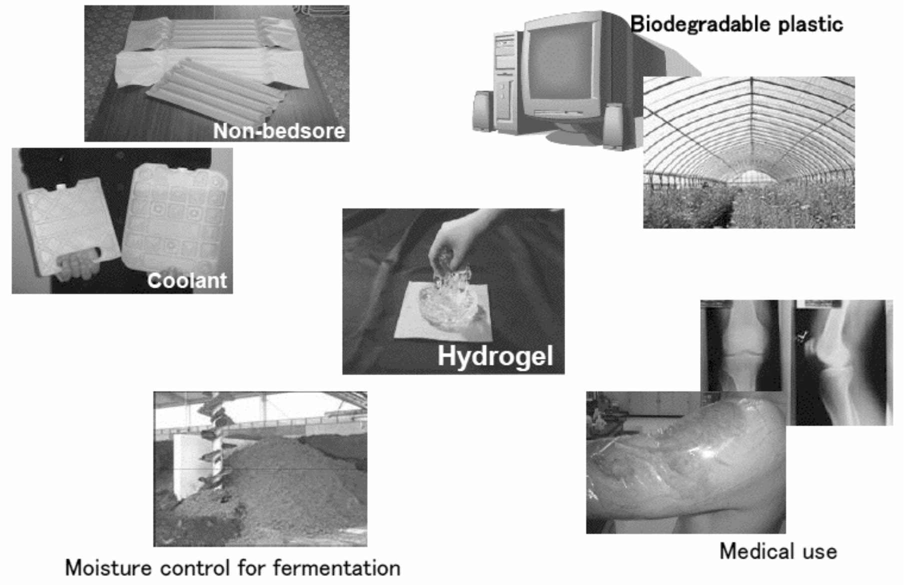

Fig. 6 Application of crosslinked natural polymer.

3.2 Radiation Processing in Vietnam During the Period of 2005-2007

Nguyen Quoc Hien, Tran Khac An

Research and Development Center for Radiation Technology, Vietnam Atomic Energy Commission

Abstract

Radiation technology has been increasingly applied in many countries including Vietnam. This report reviews R&D works, manpower, irradiation facilities and service irradiation in the period of 2005-2007. The orientation of the development for radiation technology in the country and co-operation programs of the Research and Development Center for Radiation Technology (VINAGAMMA) are also briefly outlined as well.

1. Introduction

In the initial years major emphasis was on the use of isotope gamma sources (mainly Cobalt-60) because of the large penetration for irradiation of thick materials. In recent years, electron beam accelerators (EB) have emerged as preferred alternative for industrial radiation processing because EB offered the advantages such as 1) increased public acceptance, 2) ability to combine with the industry for online processing and 3) provide higher dose rates resulting high throughput [1-2]. An upper energy limit 10 MeV for electrons and 5 MeV for the converted X-rays has been imposed for the accelerators to ensure that no radioactivity is induced in the irradiated material. This report reviews R&D works, manpower, irradiation facilities and service irradiation in Vietnam in the period of 2005 ~ 2007.

2. Present Status and Activities

2.1 Irradiation facilities

Table 1 The list of irradiation facilities [3].

Owner	Source and main characteristics	Installed year
Nuclear Research Institute, Dalat	Co-60 Cell, 2 kCi	1981
Nuclear Research Institute, Dalat	Co-60 Chamber, 10.5 kCi	2007
Hanoi Irradiation Center	Co-60 Irradiator, 20 kCi	1991, in upgrading
VINAGAMMA Center	Co-60 Irradiator, 370 kCi	1999
Binh Duong Irradiation Co.	2 Co-60 Irradiator, 400 kCi	2005 and 2006
SonSon Co.	2 LINAC, SureBeam, 5MeV/150kW	2003 and 2005 X-ray

At present VINAGAMMA Center has planed to install an EB 10MeV/15kW in the years 2008.

2.2 Manpower

Table 2 Staff and education level.

Organization	Total	Education level			
		Ph. D.	M.Sc.	B.Sc./Eng.	Technician
Hanoi Irradiation Center	18	2	3	6	7
Nuclear Res. Institute, Dalat	13	-	4	5	4
VINAGAMMA Center	25	2	4	12	7
Total	56	4	11	23	18

There are 56 peoples belong to Vietnam Atomic Energy Commission working on the field of radiation processing.

2.3 R&D projects

- Grafting of monomers onto natural polymer for heavy-metal ions adsorbent
- Preparation of hydrogel and super water absorbent for medical and agricultural applications
- Production of oligomers by degradation of polysaccharides
- Preparation of biodegradable materials
- Modification of water soluble polymer used for improvement of crude oil recovery
- Preparation of nanomaterials (nanogel, nanoparticles)
- Calculation of dose rate distribution in irradiation volume.

2.4 Irradiation service

Table 3 Irradiation service at VINAGAMMA Center.

	Year			Total
	2005	2006	2007 (June/2007)	
Time of irradiation (h)	8,147	7,642	2,763	18,534
Medical supplies (m^3)	666	1,374	619	2,659
Food (ton)	5,683	4,264	1,740	11,687

It was estimated that the amount of irradiated food of two private companies (SonSon Co. and Binh Duong Irradiation Co.) was of 6,400 tons for 2005 and 39,000 tons for 2006 [3)] [3].

2.5 IAEA TC-project

- VIE/8/017: Upgrading of irradiator at Hanoi Irradiation Center
- VIE/8/018: Application of electron beam for preparation of biomaterials

3. Concluding Remarks

For the research and application of radiation technology effectively in future, the following contents are outlined.

- Active contribution on technology transfer of well established radiation applications to industry
- Orientation of R&D projects for potential applications
- Stepping up fundamental research especially on modification of polymer materials and nanocomposites
- Installation of EB with energy in the range of 1-3MeV in near future for R&D purposes
- Recruitment and training of young staff for research, management and trading as well
- Pushing up international cooperation in fundamental research and technology transfer especially with EB applications.

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3.3 Radiation Processing of Polymer in China

Guozhong WU

Shanghai Institute of Applied Physics, Chinese Academy of Sciences

Radiation processing has been increasingly applied in industry, agriculture, medical health and environmental conservation. Industrial radiation processing depends mainly on two kinds of ionizing radiation equipments: electron beam accelerator and cobalt-60 source. Radiation can induce chemical reactions in the solid, liquid or gas phase without using any additives. The unique characteristic brings many advantages in chemical industry such as energy saving, easily handling.

Radiation processing of polymeric materials is one of the most active branches of radiation applications in China. The modification of polymer by radiation includes crosslinking, degradation, grafting and polymerization. Various products of heat shrinkable materials, cable and wire constitute a large proportion of radiation products. In addition, polyethylene foam (crosslinking), PTC materials (crosslinking), PTFE micropowder (degradation), battery membrane (grafting), adhesive and thickener (polymerization) are also an essential parts of them. For example, by combination of radiation and further milling, PTFE can be crushed into micropowder (Fig. 1).

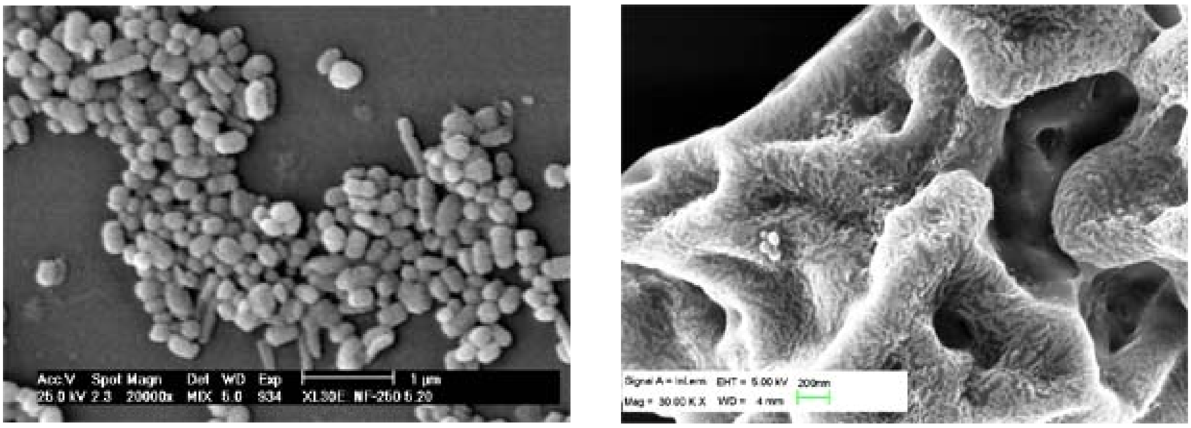

Fig. 1 SEM of PTFE micropowder.

The other field of possible application is the processing of natural polymers. Chitosan is one of such polymers and has unique characteristics. Radiation processing can modify the molecular weight, hydrophilicity and mechanical properties of chitosan without using any toxic additives. A good example is the fabrication of antibacterial rayon fiber (Fig. 2) by adding irradiated chitosan micropowder into viscose before wet spinning.

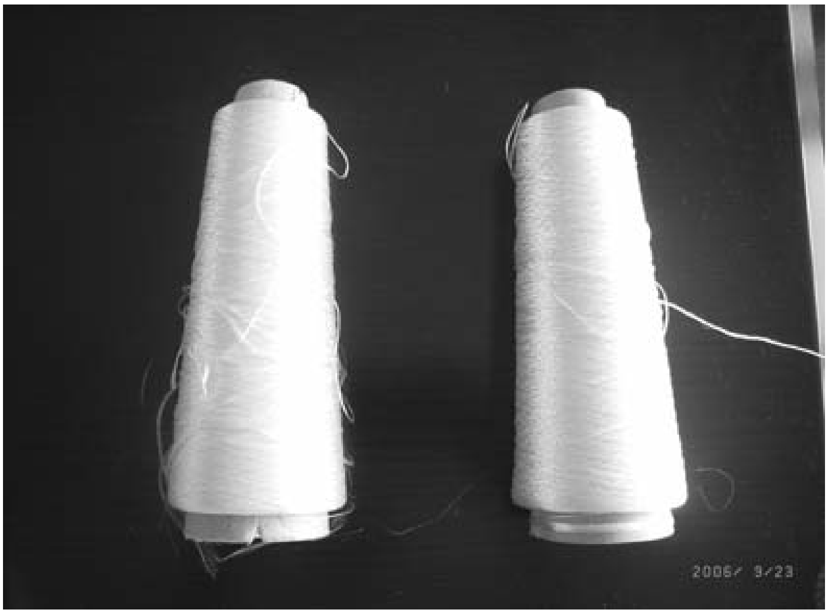

Fig. 2 antibacterial rayon fiber.

Based on the statistics provided by China society of Isotope & Radiation Processing, the number of accelerators in China increased from 49 in 2000 to 120 in 2007. With the rapid development of China economy, more automobiles have entered into families. There will be a fast growing of automobile industry in the near future. It is estimated that China will become the world largest automobile market, producing 20 million cars per year by 2020. Thus there is also a huge market for vehicle materials such as heat-shrinkable tube, polymer foam and tire. In addition, the fast development of nuclear power plant leads to the great need for radiation-resistant cables, wires, tubes, etc. By 2020, 30 nuclear power stations will be completed in China. Moreover, export of radiation processed polymer materials have been growing fast in recent years and thereby it is possible to set up factories in foreign countries especially in the developing Asian countries.

What's more important, China government pays great attention to radiation processing. For instance, in 2004, Chinese National Development & Reform Commission (NDRC) supported 21 projects relevant to non-power nuclear application, 8 projects for radiation processing of polymer (battery membrane, rubber modification, heat-shrinkable material, etc.) and 3 projects for accelerator fabrication.

In general, China will grow into the largest nation of radiation processing of polymer in the near future on account of the number of accelerators for industrial use and market value. However, many important technologies are still not available. Technology such as improving the quality of tire and polypropylene foam is still not mature. China should look for a wide range of international exchange and cooperation. Developing advanced high add-value products is very important and high attention should be paid to this issue.

3.4 Radiation Processing Program at the Malaysian Nuclear Agency

Khairul Zaman Hj. Mohd Dahlan

Malaysian Nuclear Agency

Abstract

Radiation processing technology has been proven to enhance industrial efficiency and productivity, improve product quality and competitiveness. For many years, varieties of radiation crosslinkable materials based on synthetic polymers have been studied at the Malaysian Nuclear Agency either in the form of thermoplastic resins, polymer blends or composites. At present, effort is focused towards developing new materials based on natural polymers such as natural rubber and rubber based products, palm oil and palm oil based products and polysaccharide. Hydrogel based on sago starch has been developed and commercialized for face mask. As for wound dressing application, sago hydrogel is still subjected to the clinical evaluation. Sago starch has also been modified for biodegradable products such as bio-film and bio-foam for packaging purposes. On the other hand palm oil based acrylate resins have been synthesized at the Nuclear Malaysia for pressure sensitive adhesive and printing ink applications. Meanwhile, natural rubber is used in a polymer blend and composites for automotive components. All of these products are at various stages of commercialization.

1. Introduction

As a government research institute, research activity of Nuclear Malaysia is designed to meet the country development plans and aspiration of developing knowledge driven economy (k-economy). It is recognized that knowledge is the main driving force for economic growth of a country. In this connection, R & D program is designed to generate knowledge that can meet market needs and generate new economy so as to enable country to sustain the economic growth in a long term.

Under the 9th Malaysian Plan, 2006-2010, greater emphasis is given on developing a few niche areas which include advanced materials, advanced manufacturing and nanotechnology. Science and technology fund that include R & D and Commercialization of Technology has increased by 57% to RM5.2 billion. In this regards, high priority is given to the research project that is market-driven and will increase the rate of commercialization.

In the light of IMP 2 and 9th Malaysian Plan, the current industrial application of radiation processing fits in well into the country's development program. The radiation processing technology is used either for radiation services or as an integral part of the manufacturing process for the production of flame/fire resistant wire and cable, heat shrink tube and heat shrink film. Radiation processing is used mainly for sterilization of medical products and for crosslinking of polymeric materials. Radiation processing has been proven as a unique and commercially viable process

In Malaysia, there are several irradiation facilities. Gamma irradiation facilities provide irradiation services mainly for sterilization of medical products. Whereas, electron beam accelerator is used either as an integral part of the manufacturing process for crosslinking of heat resistance wire and cable, heat shrink packaging film and sterilization or as irradiation services for heat shrinkable tube. Malaysian nuclear agency is the only institution that provides electron beam irradiation services in Malaysia.

Nuclear Malaysia is equipped with two electron beam machines, a 3.0MeV, 90kW and a 200keV, 4kW. Another electron beam accelerator of 1.0MeV, 40 mA current has been procured from Russia and will be delivered by end of 2007. Gamma irradiation plant and Gammacells are also available with the Cobalt-60 strength of 1 MCi and <20 kCi respectively. Two laboratory units of UV irradiation system of 100 Watt/cm2 mercury lamp and high-powered fusion lamp with conveyor system for curing of surface coating are also available.

Gamma irradiation and electron beam plants are well equipped with the handling facilities that enable them to provide irradiation services to industry. The irradiation facilities are also being used for research on materials modification by crosslinking, grafting and degradation. In line with the 9th Malaysian Plan, the R&D is aimed at producing advanced material through enhancing and providing high value added to the indigenous resources of natural polymer such as polysaccharides, lignocellulosic materials, palm oil and natural rubber by modification using radiation technology. In this connection, most of the research and development projects have niche or specific applications such as heat/fire resistant properties, high performance surface materials, biodegradable materials and thermoplastic elastomer materials. The following are projects that have been conducted in relation to radiation modification of polymer, polymer blend and composites:

1. Heat and flame retardant polyolefin compounds for wire insulation
2. Heat shrinkable compounds for flexible tubes
3. Radiation resistance PVC compounds for medical products
4. PVC-ENR radiation curable compounds for automotive components
5. Liquid natural rubber as compatibilizer for thermoplastic elastomer blends
6. Radiation curable resins from palm oil such as polyurethane palm oil acrylate, epoxidized palm oil acrylate.
7. Pressure sensitive adhesive from palm oil based resins
8. Abrasion resistant and hard coating radiation curable materials
9. Agro-fiber polyolefin composites
10. Sago starch hydrogel for biogel mask and wound dressing
11. Biodegradable sago starch film and foam for packaging

2. Scope of Research and Development

2.1 Natural Polymer Modification

Scope of research covers modifications of polysaccharide – sago starch, chitin/chitosan, carrageenan and palm oil based resins for cosmetic, healthcare and medical applications. It also covers development of biodegradable materials for foam product and packaging film for industrial usage. The scope of research also includes synthesis of nano-material based on natural polymer.

2.1.1 Polymer, Polymer Blend and Composite

Scope of research covers blend of two different polymers such as natural rubber and polyolefin, natural rubber and polystyrene, epoxidized natural rubber and polyvinylchloride, etc. It also includes agro-fibers polymer composites, development of flame retardant and heat resistance compounds and heat shrinkable materials. The scope of research also includes synthesis and production of nanoparticles for various applications such as nanoclay polymer composites and nanosize inorganic fillers.

2.1.2 Radiation Curing and Synthesis of Acrylate Resins

Scope of research covers the application of low energy electron beam radiation and UV radiation for modification and curing of thin layer polymeric materials, which are mainly used in coating of various substrates, printing inks and adhesive. It also includes the synthesis of new resins from natural resources such as palm oil and natural rubber and to develop radiation curable acrylate resins. The scope of research also includes the development of nanosize silica coatings for high scratch and abrasion resistant properties.

2.1.3 Radiation Conservation of Environment

Scope of research covers the applications of radiation technology for treatment of industrial wastewater, volatile organic compounds and solid polymer waste for the purpose of recover, recycle, reuse and safe handling of the waste and where possible to add value to the waste.

3. R & D value Chain and Support Facilities

Radiation processing is seen as the alternative to the conventional chemical processing. Laboratories for polymer processing, polymer testing and analysis, surface modification, physical testing and evaluation, thermal analysis are geared towards providing international standard services to researchers. To interface the laboratory results with the commercial industrial processing requirement, pilot scale facilities for polymer compounding, extrusion profile, injection molding and coating of wire are available for upgrading and scaling up developmental work.

The typical R & D cycle (Figure 1) is as follows i.e.:

- Laboratory scale research
- Developmental or pilot scale research

- Technology transfer and commercialization

Each product has to go through the above stages of development in order to determine its technical and economic viability. At the laboratory research, the Radiation Processing Technology Division is well equipped with polymer processing facility such as melt blend mixers, compounder/extruder, cold and hot roll pressed, hot and cold press, table top injection molding machine, rheometer, etc. Subsequently, the materials will be subjected to physical, mechanical, analytical and thermal analysis in order to establish the material specifications.

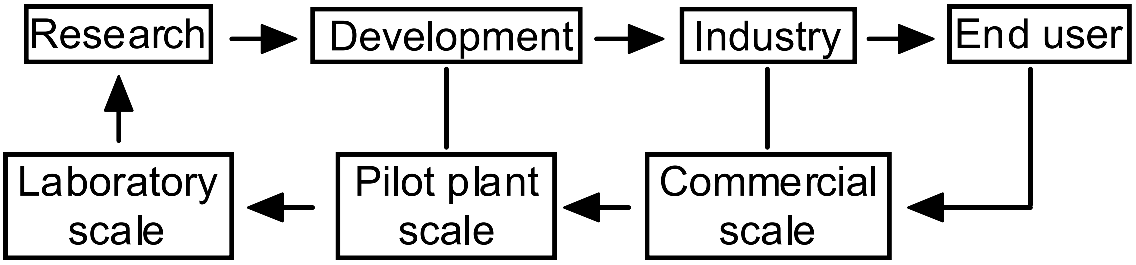

Fig. 1 R & D Cycle.

For the physical and mechanical testing, the Division has sufficient equipment such as several tensile machines, impact tester, and hardness tester; melt flow indexer, scratch and abrasion testers, adhesion tester, etc. For analytical and thermal analysis several equipment are available such as FTIR, STEM, GPC, HPLC, DSC, DMA and TGA. Where do we go after this level of research?

The government research institutes carry out most of the research activities in relation to new material development. Meanwhile, R & D by the industrial sector is more focus on product improvement and problem solving in nature. Therefore, the industrial sector depends very much on the government research institute to develop the materials from laboratory to the commercial products. This would require facility that can convert the results from laboratory to the industrial requirement. Usually at this stage, it involves the development of process and products at the minimum level of industrial processing, i.e. pilot scale. Currently, Nuclear Malaysia has six pilot scale facilities as follows:

- Gamma sterilization plant with the maximum Co-60 strength of 2.0 MCi for sterilization of medical disposable items, irradiation of food items, herbal and other products (SINAGAMA)
- Electron beam processing facility for crosslinking of tubes and wire & cables (ALURTRON)
- Continuous gamma irradiation of latex using gamma pilot plant (RAYMINTEX) – Gamma facility is designed specifically for irradiating natural rubber latex (liquid) to

produce pre-vulcanized latex for dipped products such as surgical gloves, balloon, condom etc.

- Pilot plant to process animal feeds from palm oil empty fruit bunches wastes using gamma irradiation (STERIFED).
- Flue gas treatment using electron beam accelerator: a semi-pilot scale of the out put of 400 cubic meter/hr gas from diesel generator.
- Synthesis plant of 30 liter for palm oil based acrylates.

For the polymer materials processing, several machines have been installed such as a twin-screw compounder of 15 ~ 50 kg/hr out put, extrusion machine for profile and for continuous products such as for insulation of wire and injection molding machine of 60 ~80 ton clamping force. These machines are crucial for inter-phasing the laboratory scale research with the industrial scale requirements. Several work for the processing of new compounds using the above machines have been established and ready to be transferred to industry such as:

- Hydrogel from sago-starch for facemask has been commercialized – Figure 2
- Hydrogel from sago starch for wound dressing is in the process of commercialization
- Starch modified compounds for biodegradable packaging film – in the process of commercialization – Figure 3
- Starch modified compounds for biodegradable foam products – Figure 3
- Flame retardant compounds for wire insulation – in the process of commercialization – Figure 4
- Heat shrinkable compounds for tube – in the process of commercialization – Figure 5
- PVN-ENR compounds for under-hood automotive parts – Figure 6.
- Radiation resistant PVC compounds for medical product disposable items – in the process of commercialization – Figure 7.
- Agro-fibers polymer compounds – in the negotiation and promotion stage

On the other hand, the acrylate based oligomers as one of the important ingredients for radiation crosslinkable compounds synthesized from palm oil products have also been developed and a semi-pilot scale synthesis facility has recently been installed. With this pilot scale facility, market acceptance tests can be conducted. Several applications of acrylate-palm oil oligomers are pressure sensitive adhesive, printing ink and coatings.

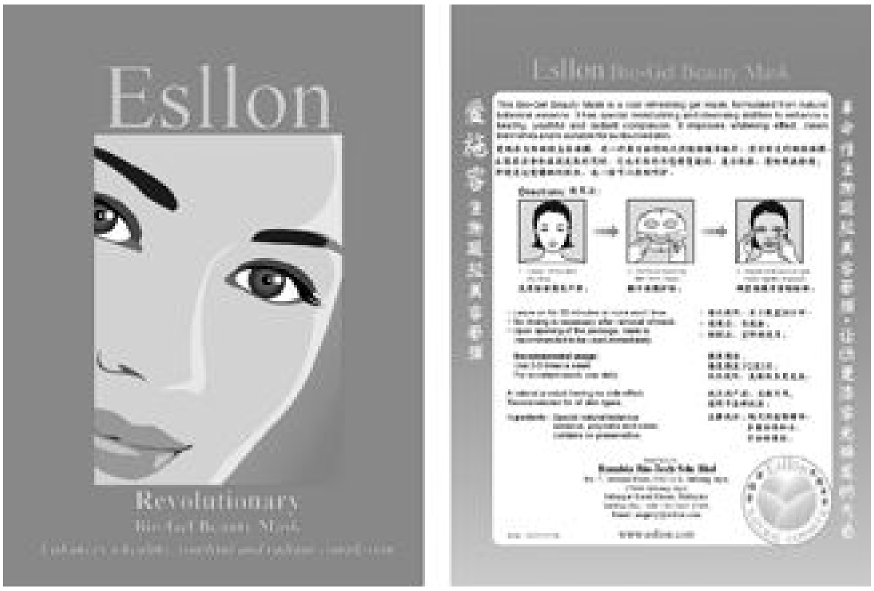

Fig. 2 Sago hydrogel for biogel mask.

Fig. 3 Sago based biodegradable foams and films 2picts.

Fig. 4 Heat and flame retardant compounds.

Fig. 5 Heat shrinkable tubes.

Fig. 6 Thermoplastic elastomer products.

Fig. 7 PVC radiation resistant tube.

4. Technology Transfer and Commercialization

The third stage of the R & D cycle is the transfer of technology to the industry. At this stage, the industrial partner should have full commitment to push further the development of the products to the market. Two important components of the technology transfer are the technical component and market component. The technical component involves the production of the materials or products at the sufficient quantity and standard quality. In this aspect, continuous involvement and support from research institute is a must. On the other hand, the industrial partner should take the lead to carry out the market acceptance test, evaluation and marketing. In Malaysia, the technology transfer can be carried out in several ways such as:

- The industrial partner makes available their existing plant at their factory for the industrial pilot trial cum commercial production trial
- The industrial partner provides fund to buy pilot plant facility
- The industrial partner pay for the trial run conducted oversea at the machine manufacturer facility.
- Government provides financial support through Science Fund, Techno Fund and the Commercialization of Research and Development Fund (CRDF) for pilot scale trial, production, market acceptance tests and market promotion (Table 1).

Table 1 Government funding to support R & D and Commercialization.

SCIENCE FUND	TECHNO FUND	CRDF
		SME
• Laboratory scale • 2 ~ 3 years • Research institute and university only	• Pilot scale developmental stage • Requested by industry/ university or research inst. • Must have Univ. or Res. Inst partners. • Grants • Incubator system	• Commercialization • Marketing • Matching grants (1:1) • Requested by company

In most cases, the industry chooses the last option whereby they will request government funds for the commercialization of the research finding.

After the successful pilot scale trial, it is important for the project group to follow through the development of the project up to the initial commercial production. The role of inventor in every stage of R & D till commercialization is essential. Scientists today should equip themselves with the knowledge on market needs and trends in their own fields. They should be sensitive to the political, economy and social changes around them.

5. Conclusion

In the past several years, there is a significant progress and development on the application of radiation processing in Malaysia. Government continues to support R & D in this field by providing the necessary infrastructure, facility, training and research funds. Various mechanisms for commercialization are also in placed to facilitate the transfer of technology from laboratory to industry.

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3.5 Coating and Printing with Electron Accelerator

Masakazu Washio

Research Institute for Science and Engineering, Waseda University

1. Introduction

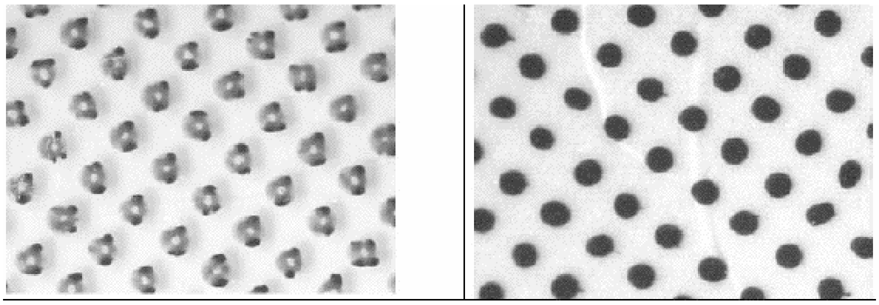
The electron beam processing (EB processing) has been started in 1950's in the filed of crosslinking of polyethylene for the purpose to adding the high temperature durability and to giving memory effects on the products. In nowadays, the EB processing technologies are applied to wide fields of the manufacturing such as the tires, the plastic forms and the poly-electrolyte membranes for button type batteries, etc. The EB processing has been well-known as the technology for the high production rate and the highly functionalized material production. This is true; however, the technology should be noted as the one of the most promising technology with low emission of CO_2 (i.e. so-called green technology) by the high efficiency conversion from wall-plug electricity to electron beam and the high reaction efficiency in the materials. In the viewpoint of this fact, EB processing is one of the key technologies for the various kinds of manufacturing processing In this paper, the applications and advantages of low energy electron beam below 300keV and especially, extremely low energy electron beam with the energy of several tens of keV are described.

2. Electron Beam for Printing Application

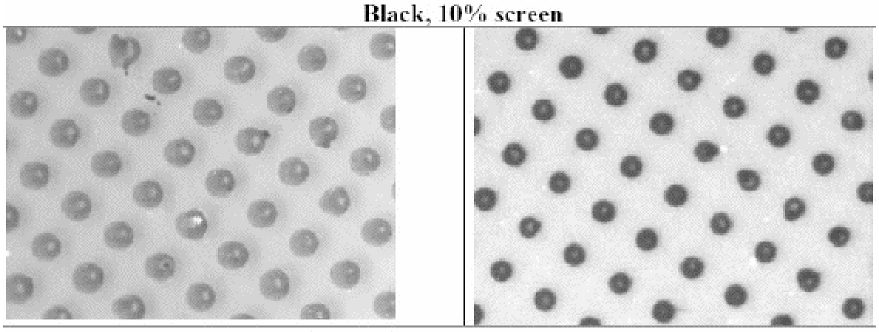
An application to the printing technology was started in 1970's not only in U.S.A. but also in Japan. In U.S.A., the technology has been used as the high production rate and cost effective processing. The customers in Japan did not accept the relatively low printing quality using EB processing, which may due to with the lack of insufficient technology development. Thus, the technology has been shrunk in Japan for long time by lack of the merits as the EB application. Very recently, new development of the EB printing technology has been conducted by 3 companies, which are the manufactures of the EB machines, the printing machines, and EB curable chemicals, named ESI, COMEXI and Sun-chemical, respectively. Development of the EB printings with the new team is succeeded in the very good quality with low energy consumption for the Wet-Flex printing. The high quality of dots and no dots gain have been achieved as shown in Figure 1. As is the case, the development of new technology on EB processing should be conducted by the sophisticated expert team on each machineries and/or manufacturing.

3. Advantages of Extremely Low Energy Electron Beam

The extremely low energy electron beam has been pointed out as the technology of very high dose rate on the surface region of materials and without or slight damages for bulk materials. This is realized by the very high LET features in the region less than 100 keV electron beam energy. The stopping powers for various kinds of materials are shown in Figure 2. One can see the increase of stopping powers less than the energy of several hundreds of keV for the various materials.



Black, 10% screen



Reflex Blue/Violet, 10% screen

Fig. 1 Printings for conventional wet flex (left) and EB wet flex printing (right).

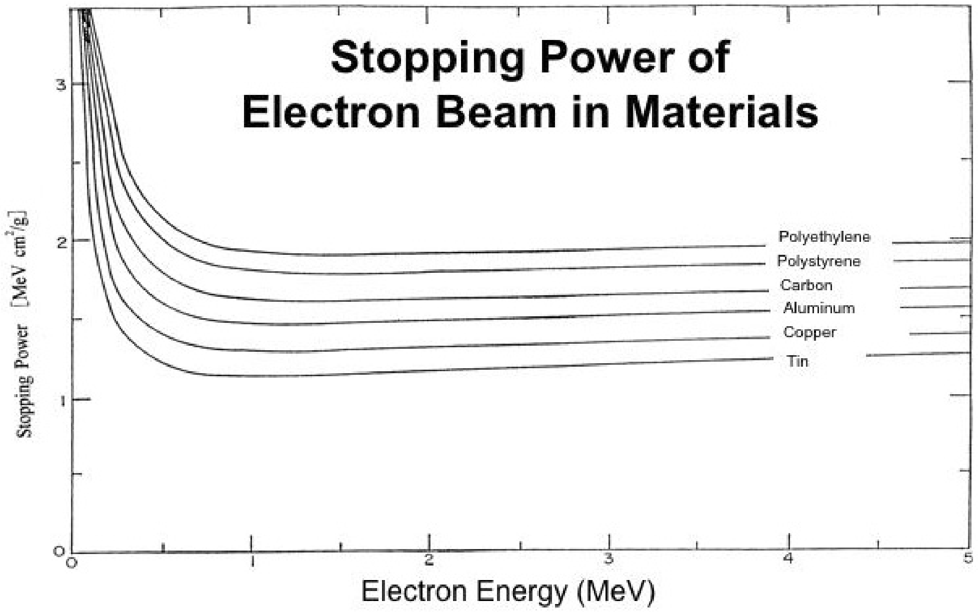


Fig. 2 Stopping power dependences with the electron energies for the various materials.

The EB machines with extremely low energy are developed by some companies in Japan. Figure 3 shows the photographs of Min. EB and EB-engine, which are developed by Ushio Electric Co. Ltd. and Hamamatsu Photonics Co. Ltd.

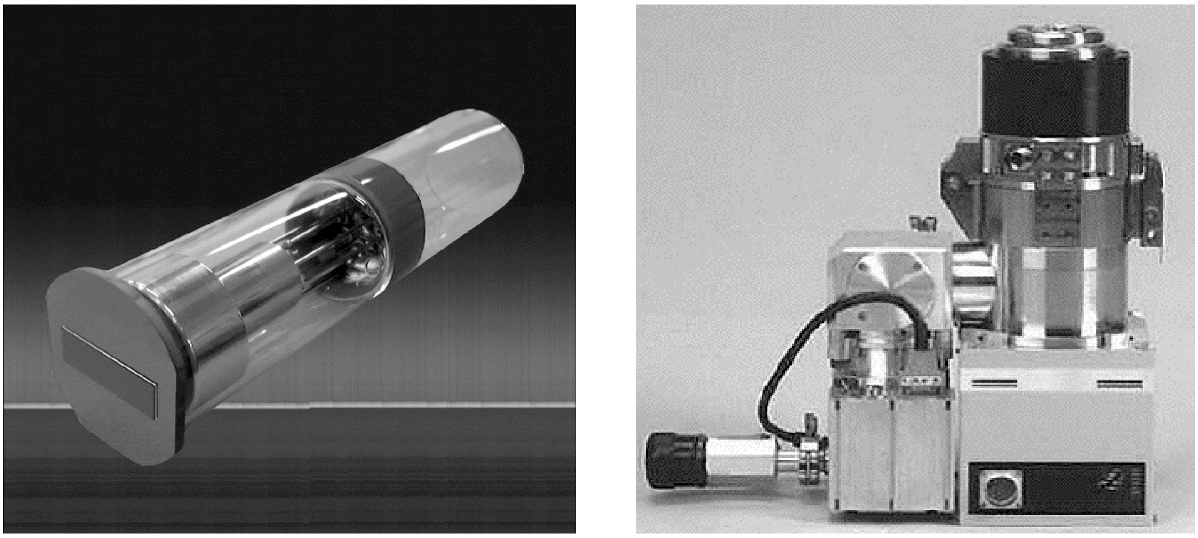


Fig. 3 Photographs of the Min. EB (left) and EB-engine (right) developed by Ushio electric Co. Ltd. and Hamamatsu Photonics Co. Ltd.

By using Min. EB, the very high grade (high gross) printing with very high pigment density has been demonstrated as shown in Figure 4.

Fig. 4 Sample of EB printing by Min-EB with high pigments densities.

4. Electron Beam Application for Film Manufacturing

An advanced process development for direct film manufacturing by low energy EB (less than 300keV) machine has been done by CI chemical Co. Ltd. in Japan. This technology enables to realize the relatively low cost manufacturing system for various kinds of films by same production line. Table 1 shows comparison between EB and conventional film manufacturing methods.

Table 1 Comparison between EB curing and conventional method for film manufacturing.

Methods		Initial Investment	Size Flexibility	Performance
EB Curing		Middle	High	Fine
Pressing		Large	High	Moderate
Extruding	Non-ex	Middle	Low	Moderate
Extruding	Ex	M to L	Middle	Moderate
Flowing		Large	Low	Moderate

The products manufactured by the process have been demonstrated as the materials with the high durability against the sunlight exposures. Hence, the films have been applied for building outside wall surface. The example of the application is shown in Figure 5

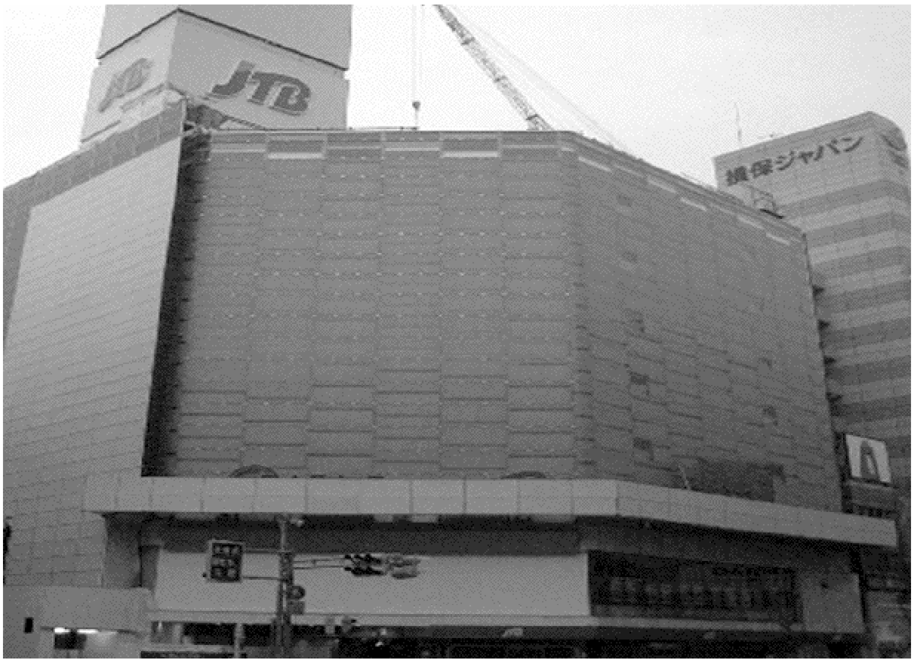


Fig. 5 Outlook of EB film applied fro building outside wall surface.

5. Summary

As described above, the low energy electron beam applications for surface coating, film manufacturing and printing are the stage of industrialization. Nevertheless, the further extensive development should be required to be conventional techniques as the manufacturing technology for these applications. The low energy EB processing will be one of the most energy saving and environmental effective technology.

3.6 Automobile Parts by Radiation Crosslinking

Fumio Yoshii

Japan Atomic Energy Agency

1. Introduction

Radiation crosslinking, graft polymerization and degradation are useful technologies to improve polymer materials. The crosslinking causes improvement in strength, heat stability and processability to gives network structure for polymer materials and hence crosslinked materials are used in various fields, especially car parts. Electron beam (EB) of short time irradiation is used for these modifications. Irradiated (pre-vulcanized) before sulfur vulcanization rubber tires, heat resistant wires/cables, shrinkable tubes and foams of car parts are achieved by EB crosslinking. Polyethylene and polyvinyl chloride are used in cables and wires, polypropylene in plastic foams and natural rubber etc. In this paper radiation processing of tire, wire/cables, foams, shrinkable tubes and circuit protection devices (CPT) are explained.

2. Tires

In Japan 92% of radial tires are pre-vulcanized to improve processability before sulfur vulcanization as shown in Figure 1.

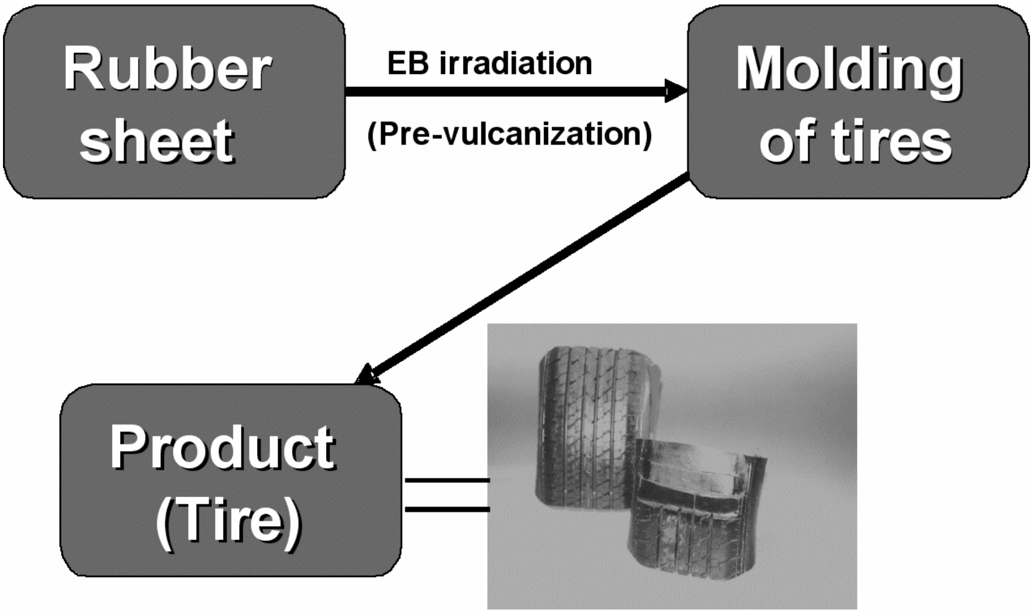


Fig. 1 Irradiation (pre-vulcanization) of rubber tire.

Performance of tire depends on formation precision of various rubber components/compound.

Pre-vulcanization by irradiation of rubber sheet can give suitable hardness and green strength to easier further process. Sulfur, additives such as acceleration agents for vulcanization and zinc oxide are kneaded in rubber sheet and after that, this sheet is irradiated for pre-vulcanization. Irradiated rubber sheet is cut to length of tire, wound on tire drum together with cord such as polyester and then molded by tire molding machine to form tire. Since irradiation has enhanced green strength and hardness of rubber sheet, cords relocation during tire molding can be prevented. Finally, sulfur vulcanization of tire is done at high pressure and temperature. The main advantages of irradiation lead to improvement of quality and reduction of rubber materials.

3. Plastic Foams

Ceiling and instrument panel in cars are mainly formed by PP foam. Application of EB irradiation in plastic foam production enhances melt viscosity (melt strength) of PP. As shown in Figure 2 PP is irradiated before foam formation. Foaming agent such as azo compound (decomposition temperature, 170 to 200℃) is kneaded with PP at molten state and then the mixture is molded into sheet at the same temperature. The sheet is irradiated to obtain crosslinking structure and next heated above decomposition temperature of foaming agent. Because of high melt viscosity of PP material after crosslinking, gas (nitrogen gas) formed during decomposition of foaming agent is trapped in material and causes formation of PP foam sheet. In case of unirradiated sample, foam is not formed because the gases diffuse out from low melt viscosity PP sheet.

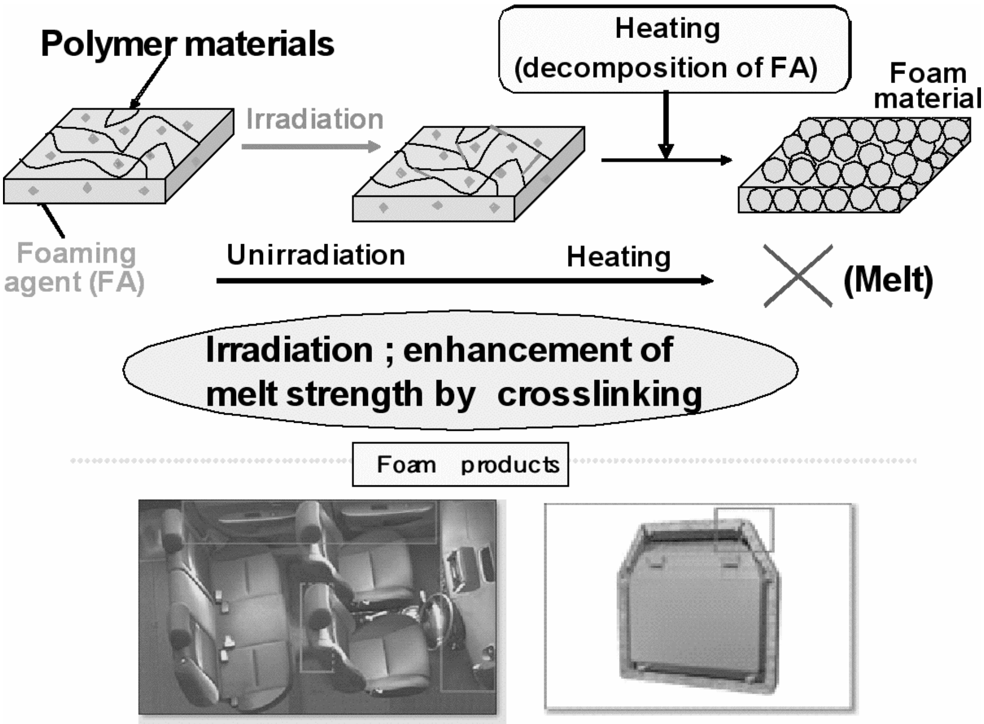


Fig. 2 Production of foam using EB and its application on the car parts.

4. Wires and Cables

Many wires and cables are used in car. Wires used in car have to be durable at high temperatures such as 100℃. Radiation crosslinking is useful technology to induce heat resistance for wire made from olefin polymer. Polymers that found the application in this field are: polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and polyurethanes. In case of crosslinked PVC, life time at 100℃ increased 10 times from 1,000 hrs.

5. Shrinkable Tubes

Shrinkable tubes are well used to cover terminals and condensers and to bundle wires in the car. Production of shrinkable tubes is shown in Figure 3. Firstly, plastic tube is irradiated to induce crosslinked structure (Figure 3a). Irradiated tube expands at above melting point of polymer tube and fixes at room temperature (Figure 3b). After that, expanded tube shrink up to original size by re-heating (Figure 3a). The uncrosslinked sample cannot expand for flowing at over melting point. The crosslinked structure is necessary for production of shrinkable tubes as well as heat resistant wires. Figure 3c shows shrinkable tubes. Narrow part of tubes is original size and larger parts are expanded parts at high temperature. Furthermore, as shown in Figure 3d, transparent shrinkable tube was formed from radiation crosslinked poly(lactic acid)1). The tube bundled the wires.

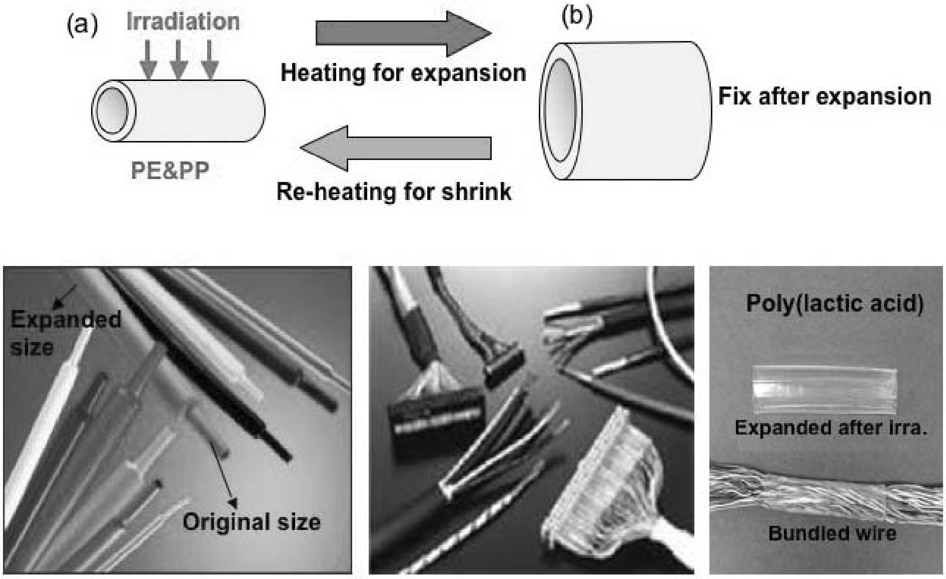


Fig. 3 Production of shrinkable tubes and its application in the car parts.

6. Circuit Protection Devices

Up to now, to prevent over current and heat in the car, fuse has been used for long time. Recently, Circuit protection devices (CPT) have been used instead of fuse. The CPT is thermistor (Positive Temperature Coefficient, PTC) of polymer system. Circuit protection devices are used in principle when electric resistance of polymer increase remarkably with elevated temperature by over current. Polyethylene kneaded with conductive materials such as carbon black, carbon fiber and metal powder forms PTC by radiation crosslinking. Figure 4 shows relationship between temperature and electric resistance of PTC. Conductive materials are trapped in crosslinked matrix of polymer. Distance between conductive materials at low temperature, below melting point, is very narrow and hence conduction circuit is formed by channel effect (a area). In this case, electric resistance shows low value for area at low temperature. But electric resistance increases extremely with increasing temperature (b area). This is due to that distance between conductive materials is far by expand of polymer matrix and melting of crystalline parts. As a result, structure of conduction circuit is destroyed (b area). Crosslinked polymer matrix can keep the shape even at high temperatures, above melt temperature (c) and keep high electric resistance. Current in PTC is stopped and then, temperature of PTC is reduced. While for uncrosslinked PTC, conductive materials coagulate due to melting (d) of polymer and conduction circuit in lower electric resistance is formed (d), so that abnormal fever often occur (e). Chemical crosslinking using peroxide at molten state is difficult to form PTC such as (a) structure to retard crystal growth. Accordingly, radiation crosslinking is desirable to form PTC.

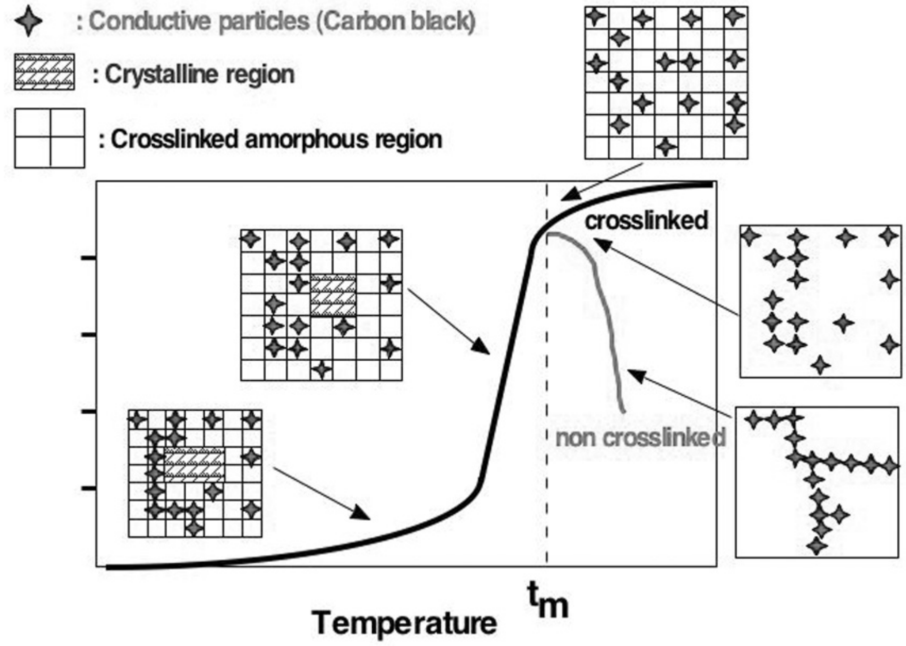


Fig. 4 Principle of circuit protection device

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3.7 Production of Hydrogel Wound Dressing by Radiation

Kazuki Isobe

Nichiban Co., Ltd.,

1. Introduction

It has been thought that making a dry scab helps to cure a wound faster. However, recently a treatment of a wound according to moist healing theory which cure a wound without making a scab is becoming popular. Accordingly, we prepared a highly stable sheet type hydrogel in a short period by radiating electron beam to an aqueous solution of a polymer. The hydrogel is not soluble in water and keeps suitable moist environment for wound healing. Therefore, a hydrogel a wound dressing, Viewgel^{R} in which represents a registered trademark and is referred to Viewgel hereinafter, is developed and released from July of 2004. In this paper we report the process of the development of Viewgel.

2. Selection of Hydrogel Material

2.1 Preparation of sample for evaluation

The electron beam crosslinking method does not use a crosslinking agent and a pure gel can be made in a short period without worrying about residual crosslinking agent. Therefore, a highly safety water soluble polymer for medical use(based on materials listed in the Japanese Pharmacopoeia etc.) is prepared in an aqueous solution, and is transformed into a hydrogel suitable for a wound dressing by radiating electron beam. The gel sheet is made by radiating a suitable dose of electron beam on the viscous solution made of materials in the Table 1 is coated on a flexible plastic film with a thickness of 1.2 mm.

2.2 Physical property evaluation method

The hydrogel for a wound dressing needs properties such as exudate absorbability, non-solubility and a suitable mechanical strength. The absorption rate while being soaked in physiological saline solution is used to evaluate the exudate absorbability, and the gel internal strength is used to evaluate the mechanical strength.

Gel internal strength : A special tape is attached on the surface of the gel with a width of 25mm and is made to detach with a destruction of gel from the inside. It is then loaded on a tensile tester the stress is measured while the tape is detached at the rate of 300mm/min.

Absorption rate : A 3x3cm sample is made and the initial weight is measured. Then it is soaked in a physiological saline solution for 24 hours and is retrieved. The water on the surface is wiped out, and the final weight is measure again. The absorption rate is calculated by the following equation.

Absorption rate (%)={(weight after 24 hours－initial weight)/initial weight} × 100

2.3 Result on gel properties measurement

Table 1 shows the properties of tested hydrogel. The results show that the electron beam crosslinking gel of poly(vinyl alcohol) (PVA) shows higher mechanical strength than other hydrogels, and has good exudate absorption suitable for a wound dressing. Based on the results, we designed the hydrogel wound dressing by selecting PVA as a main polymer.

Table 1. Tasted polymers for Hydrogel wound dressing

Polymer	M.W. ($\times 10^3$)	Content (%)	Appropriate Dose for Gelation (kGy)	Internal Strength (N/25mm)	Swelling Ratio (%)
Poly(vinyl alcohol)	75	20	20	2.0	265
Poly(vinyl pyrrolidone)	1500	20	10	0.6	525
Poly(acrylic acid)	360	20	20	0.8	102
Poly(ethylene oxide)	500	8	10	0.2	214
Hydroxypropyl Cellulose	150	6	10	0.1	173

3. Product Design and Manufacturing Process

In order to make a wound dressing which keep a proper moist environment on a wound for treatment and is transparent that the wound is observable with the dressing on it, a combined product of a transparent and elastic PE film and hydrogel is devised as shown in figure 1. Absorbent (wound side) hydrogel is containing 80% water and absorbs exudate maintain moist wound condition for rapid healing. The Backing is elastic plastic film to control moist condition with vapor permeability and to prevent infection. The release liner is applied to protect the hydrogel surface until use.

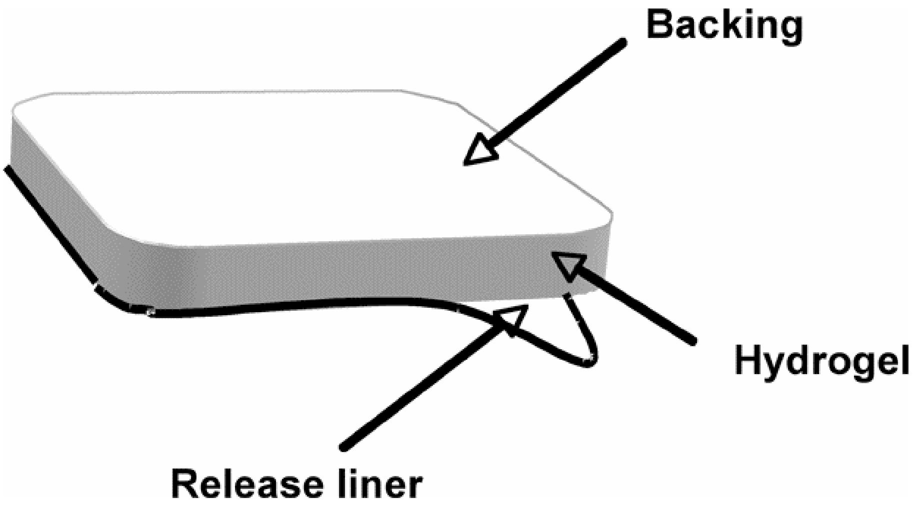


Fig. 1 Composition of Hydrogel Dressing.

In this structure, a series of an in-line production as shown in Figure 2 is possible.

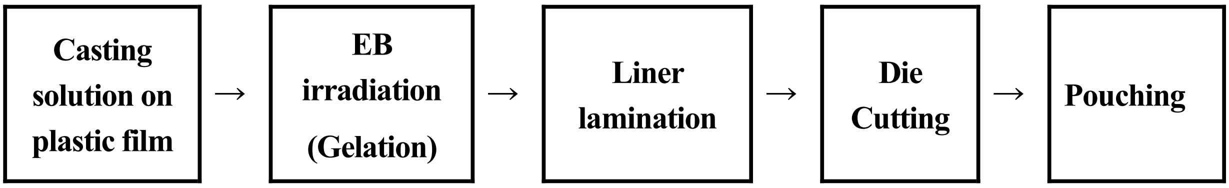


Fig. 2. In-line manufacturing process for Viewgel.

Whereas gelation by a crosslinking agent needs an aging time just like a manufacturing process of a poultice, the crosslinking by electron beam radiation is finished in a very short period and can be proceeded to the next step quickly. Therefore, electron beam crosslinking method has much merit for product itself and manufacturing process.

The electron beam is a kind of ionizing radiation and can be controlled by on-off switch. The absorbed dose can be also controlled by the line speed and the current. The low energy accelerator used in the manufacturing of Viewgel is compact in size and can be installed in a small clean room for the production of medical products. In addition, it is a self-shielding type, therefore regal regulation is easy for a factory.

4. Confirmation of Safety

Generally, when electron beam is irradiated on a polymer, crosslinking and degradation occur together, and a polymer is classified as a crosslinking type or a degradation type depend on which reaction is dominant. PVA is a crosslinking type polymer, but there is small amount of decomposition products in radiation, which may cause side effects such as irritation on the skin and tissues. Therefore, four types of safety tests (cell toxicity test, sensitization test, skin irritation test and intradermal reaction test) were performed by preparing an extract from the composition of this product according to the safety test guideline on medical devices. The test results were all negative and show that PVA hydrogel has enough safety as a wound dressing.

5. Confirmation of Efficacy Based on Animal Wound Model

The target clinical indication of Viewgel is the promotion of a wound healing which damage reaches to the dermis. For example, wound Abrasion, the 2nd degree burn, bedsore and donor sites are indications of Viewgel. Therefore, prior to clinical tests the efficacy of treatment by using Viewgel should be confirmed based on a wound model of rats. A partial thickness wound model (Figure 3) with a width of 25x25mm and a depth of 0.5mm down to dermis is made on the back of a rat using a dermatome.

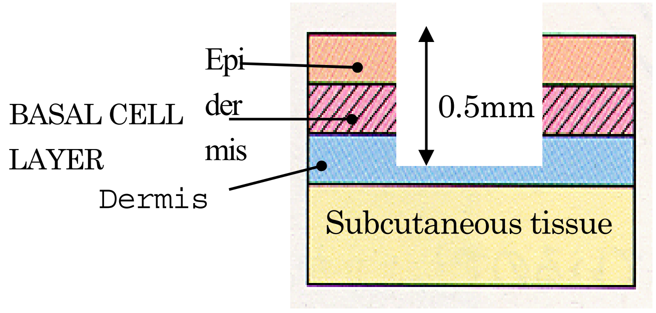


Fig. 3 Partial thickness wound model (size: 25 x 25mm, depth:0.5 mm

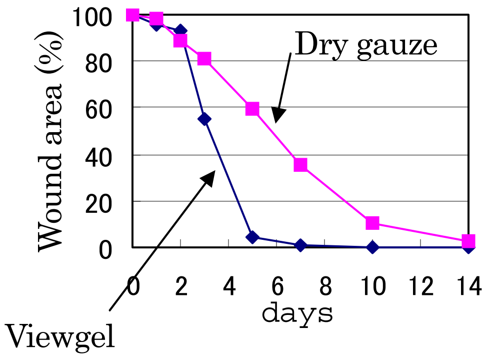


Fig. 4 Healing curve.

The wound was covered with Viewgel or dry gauze for 14 days. The wound area was checked on the 1st, the 2nd , the 3rd, the 5th , the 7th and the 10th day. The results show that the average days for healing is 7 days in Viewgel-treatment group where the moist condition on the wound is maintained. Compared with this, dry gauze-treatment group needed 14days to heal under the dry condition. Therefore, it was confirmed that Viewgel treatment is effective by maintenance of the moist environment (Figure 4).

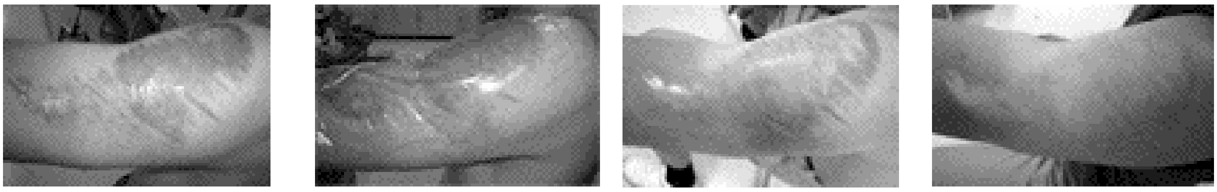
6. Clinical Test Result

In order to confirm the clinical efficacy, the clinical test was done for 23 patients of the 2nd degree burn, abrasion and donor site in three university hospitals. Evident pain relieving effect and fast epithelization were confirmed. The clinical test results are shown in Table 2. In addition, merits in use such as [easy to attach and to be fixed to a wound], [transparent and observation of a wound is possible as attached] and [easy exchange without collapse or dissolution of composition] are proved, and this product will be useful both for the patients and for hospital staffs.

Table 2 Clinical test results in three hospitals

	Total cases	2nd degree burn	Donor site	Abrasion
Number of cases	23	8	14	1
Extremely effective	18	7	10	1
Effective	1	1	0	0
Rather effective	3	0	3	0
No effective	1	0	1	0
Effectiveness	83%	100%	71%	100%

Picture 2 shows the healing process when an abrasion is treated by Viewgel.



(a) (b) (c) (d)

Picture 2. Treatment case by Viewgel.

(a): 2nd day, Abrasion by motor cycle accident
(b): 2nd day, Start of treatment by Viewgel
(c): 5th day, Rapid healing without scab and bleeding
(d): 13th day, Complete healing

7. Conclusion

Hydrogel wound dressing Viewgel was developed by irradiation of electron beam on an aqueous solution of polyvinyl alcohol as a main component. The hydrogel wound dressing can maintain a proper moist environment for a wound healing.

In the near future, this new (no-pain), (rapid healing) wound healing method (=moist healing) by hydrogel is expected to be popular.

This research and development has been done by Nichiban Co., Ltd. with a support of the JAEA (Japan Atomic Energy Agency) by a consigned program of JST (Japan Science and Technology Agency).

3.8 Industrial Applications of Radiation Grafting

Masao Tamada

Quantum Beam Science Directorate, Japan Atomic Energy Agency

Abstract

Radiation grafting can introduce the aiming function to the trunk polymer. This technique gave the separator membrane for a button-shaped battery and the gas adsorbent for fabrication facility as commercial products. This commercialization was realized by the excellent properties which were imparted by graft polymerization into the trunk polymer. As ongoing R &D, the fibrous adsorbent has been synthesized by using fibrous trunk polymer. The metal ion adsorbent is promising materials for removal of toxic metals and the recovery of significant metals from the point of environmental preservation view.

1. Introduction

Radiation graft polymerization is one of radiation processing techniques to modify the general polymers. In Japan the graft polymerization led the industrialization of commercial products such as separator of button battery, air filter for clean room, and etc. This is because the graft polymerization is sophisticated technology which can impart the desired functions to the trunk polymer. This paper deals with the graft polymerization on the point of industrial application view. The belief introduction of grafting, the commercialized products, and possibility of application in current research are mentioned.

2. Graft Polymerization

The processes of grafting in the fruit farm and the radiation processing are very similar to each other as shown in Figure 1. In the fruit farm, the stem of poor fruit tree is cut and then a new fine fruit stem is grafted on it. As a result, the grafted tree can bear many fine fruits. In the case of grafting in the radiation processing, the trunk polymers are irradiated with high energy radiation such as electron beam and γ-ray. After irradiation, the trunk polymer can be reacted with functional monomer. The radicals created by irradiation induce the graft polymerization on the trunk polymer. The imparted graft chain functionalizes the trunk polymer. When polyethylene is used as a trunk polymer, this polymer obtains the properties of electric conductivity and gas adsorption by selecting the grafting functional monomer.

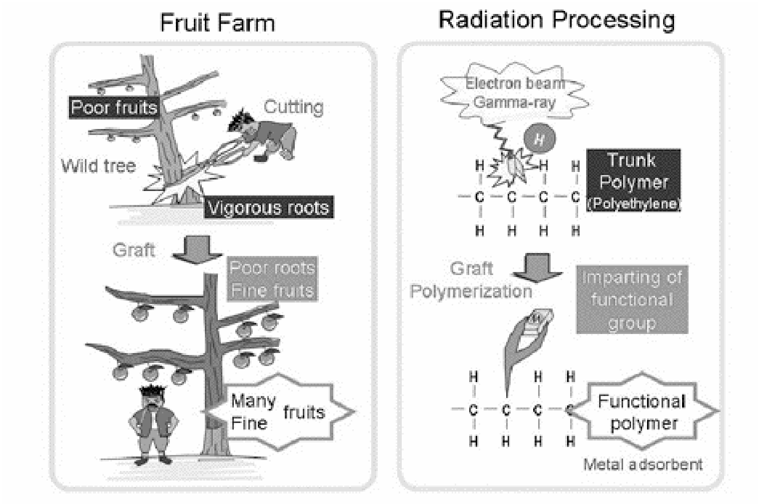


Fig. 1 Grafting in fruit farm and radiation processing.

In the industrial grafting, the pre-irradiation is mainly adopted since the processes of the irradiation and the grafting can be discrete and the creation of homopolymer is depresses in the grafting process. Figure 2 shows the schematic process of the pre-irradiation grafting. First, electron beam and γ-rays are irradiated to the trunk polymer. Then, monomer is reacted with irradiated trunk polymer. Graft chain propagates from the radicals in the irradiated trunk polymer. There are the photographs of trunk polymer in plastic bag in which inside is substituted with N_2 gas, irradiation sample on the conveyer installed beneath EB accelerator, and reaction glass vessel for grafting under the grafting scheme. Chain reaction of functional monomer occurs on the irradiated trunk polymer.

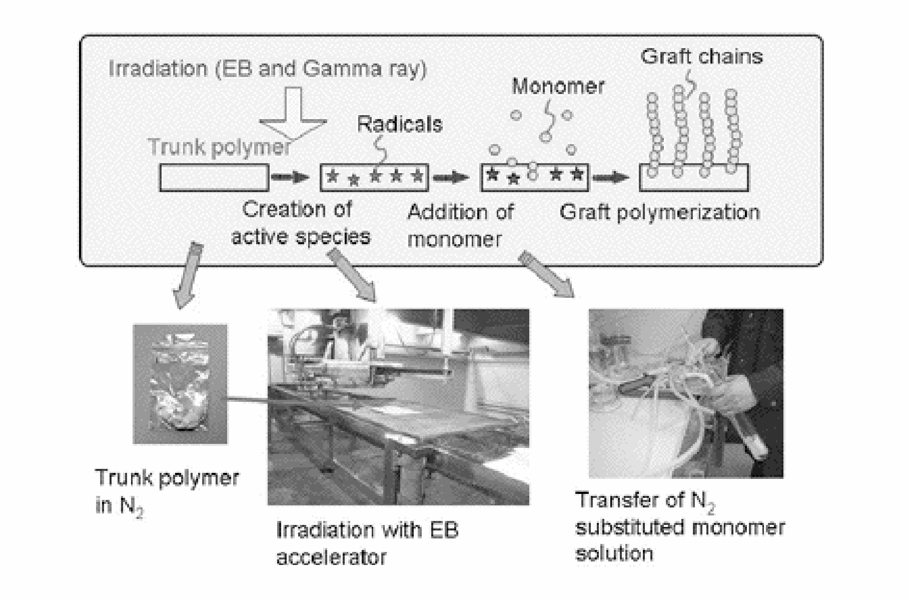


Fig. 2 Process of pre-irradiation grafting.

3. Commercialized Products

3.1 Separator membrane for a button-shaped battery

A separator membrane for a button-shaped battery is the most successful example for the application of graft polymerization. This battery has been a big market in which 1 billion pieces of the battery have been produced for wrist watches and cameras since 1985. Figure 3 shows the separator membrane fabricated by grafting and the structure of button-shaped battery. The separators have been fabricated by electron-beam induced grafting of acrylic acid into polyethylene membrane, 0.25 mm thick [1]. In these button-shaped batteries, anode material (Zn) and cathode material (Ag_2O) were separated by the separator membrane. There was a problem in self-electric discharge which was caused by transfer of $Ag(OH)^{2-}$ to Zn through the separator. As a result, this ion reacted with Zn as follows: $Ag+ZnO+H_2O+e$. This reaction reduces the life of the button-shaped battery. Up to the present, several kinds of separators were developed to improve this self-discharge. Figure 4 shows the effect of storing time on the relative capacity of the developed separator membrane. First, a regenerated cellulose membrane was used only for the cost performance and for the reason of low alkaline resistant. However, this membrane was replaced by a micro-porous polypropylene to overcome less oxidative decomposition. The self-discharge was still observed since the membrane of the micro-porous polyethylene has disadvantage of no exclusive property against ion. Therefore, this disadvantage was improved by radiation grafted polymerization membrane. Development of graft membrane enabled relative capacity of the button-shaped battery to maintain 90 % of the initial level after the storing time at 60ºC. In the pilot plant for preparation of battery separator, the polyethylene membrane is irradiated by passing several times in electron beam. The irradiated membrane was reacted with acrylic monomer and finally dried.

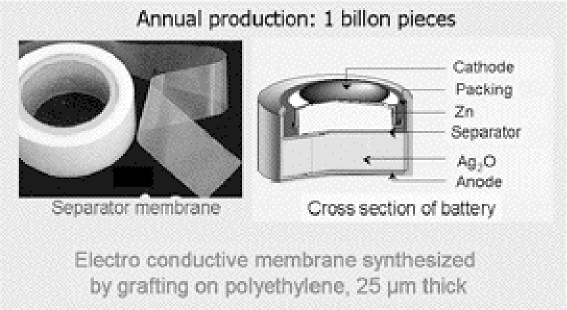


Fig. 3 Separator membrane for button-shaped battery.

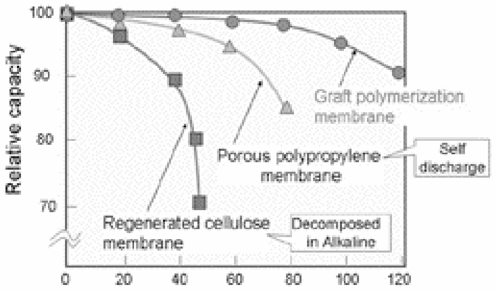


Fig. 4 Storing performance of button-shaped battery.

3.2 Gas adsorbent

There are many kinds of odors in our circumstance. It is very important that functional group for gas adsorbents should be selected from the point of the effective affinity to the objective odor. Acidic adsorbents fit to adsorb alkaline odor like amines and an alkaline ones are effective against acidic odor like aliphatic acid. Another selection is necessary for the trunk polymer. Gas adsorbent should realize the large contact area with gas. In the case of battery separator, the polyethylene membrane was used for the trunk polymer of grafting. However, the fabric polyethylene, nonwoven material, was selected as a trunk polymer. Figure 5 shows the continuous process of radiation grafting for nonwoven fabric 2). The nonwoven fabric irradiated by EB irradiator passes through the monomer reservoir. The grafting proceeds in the following reactor. The grafted nonwoven fabric comes out of the reactor continuously.

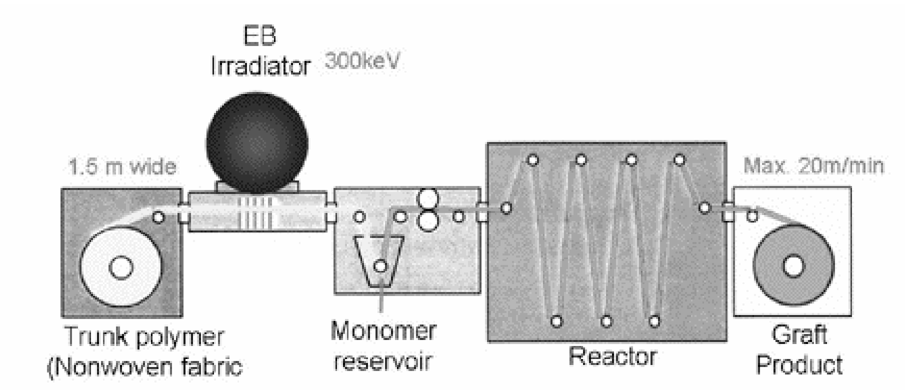


Fig. 5 Continuous process of radiation grafting for nonwoven fabric.

As a grafting monomer, glycidyl methacrylate (GMA) is used to synthesize the precursor adsorbent. The epoxy functions in grafted nonwoven fabric can be into $N^+(CH_3)_3$ and SO_3H by $N^+(CH_3)_3{\cdot}HCl$ and Na_2SO_3, respectively. Figure 6 shows the odor clear using the graft nonwoven fabric commercialized on 1994. Figure 7 shows the adsorption performance of active carbon (charcoal), organic-acid treated charcoal, and graft fiber adsorbent against ammonia gas. The graft fiber performs the highest rate of adsorption of all three kinds of adsorbents. The capacity of adsorption against ammonia reaches 3 mol/g-adsorbent, also. This excellent performance led the application to a chemical filter for a clean room in LSI fabrication facility.

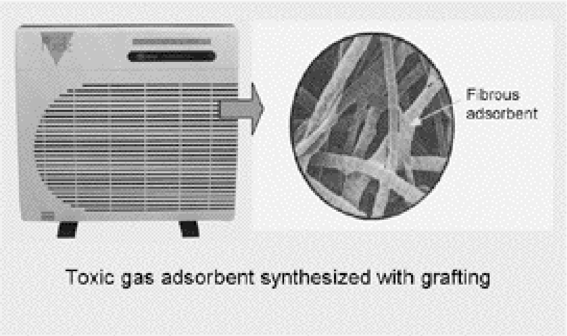


Fig. 6 Odor clear using the graft nonwoven fabric commercialized on 1994.

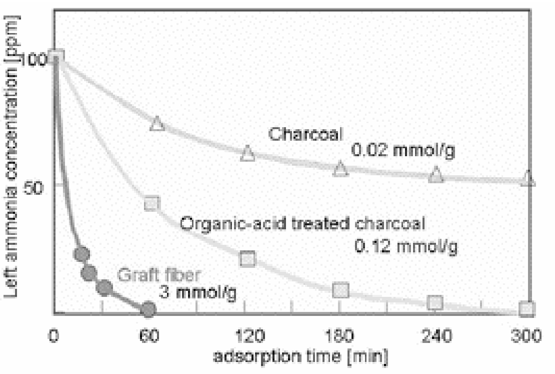


Fig. 7 Adsorption performance of active carbon (charcoal), organic-acid treated charcoal, and graft fiber adsorbent against ammonia gas.

4. Applicable Current Research

Environmental preservation is an essential subject to maintain the health and the prosperity of human beings. When the functional group having the selective affinity against metal ions is introduced into the trunk polymer, the tailored metal adsorbent can be synthesized by the graft polymerization. Such adsorbents for metal ions can be applied to the field in the environmental preservation which removes the toxic metal ions and the collection of significant metal without producing any slag. Hence, the metal ion adsorbent has been extensively synthesized by the radiation-induced graft polymerization. As a trunk polymer for grafting, the polyethylene nonwoven fabric is selected by the rational cost and the convenient handing. When the fibrous adsorbent is put into the solution of metal ion, the adsorbed metal ion on the adsorbent is easy removed by taking the adsorbent from the solution. Additionally, the resulting fibrous adsorbent can perform the swift adsorption of metal ion owing to the large surface area. The adsorption rate becomes more than 100 times faster than that of the commercial resin adsorbent. As applications of graft adsorbent to the removal of toxic metal and the recovery of significant metal are described in this section.

4.1 Removal of toxic metal

Scallop is an edible bivalve which is cultivated in the northern part of Japan. Annual production of the cultured scallops is one hundred thousands tons. After the scallop processing of boiling and packing adductor muscle in cans, one thousand ton of midgut gland was discarded since this midgut gland contained 10 - 40 ppm of toxic cadmium. Midgut gland, however, contained much protein, vitamins, and aliphatic acid such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA). When the cadmium in the midgut gland can be removed, the midgut gland will be used as fertilizer and feeding stuff for livestock and farm-raised fish. To remove the cadmium, the iminodiacetic acid type adsorbent was synthesized by the grafting of glycidyl methacrylate onto the polyethylene nonwoven fabric and the subsequent chemical modification 3). Cadmium in the midgut gland of scallop was extracted by malic acid solution. The released cadmium ions in malic acid solution were pumped into the column packed with the fibrous adsorbent. The concentration of cadmium in the midgut gland was 29 mg/kg. This concentration was reduced to 2.0 mg/kg and 0.7 mg/kg after 24 h and 48 h. Without circulation of malic acid thorough the column the cadmium concentration was 7.6 mg/kg. This circulation system realized the effective removal of cadmium from scallop waste. Figure 8 shows the bench scale equipment for the midgut gland treatment.

This equipment can treat 30 kg of the midgut gland in one batch treatment. In this equipment, the cadmium in the midgut was leached with malic acid solution and then adsorbed by the column packed with the iminodiacetic acid type adsorbent. Column volume was 5 L. Midgut glands of 20 ~ 40 kg can be treated in one batch of 24 h.

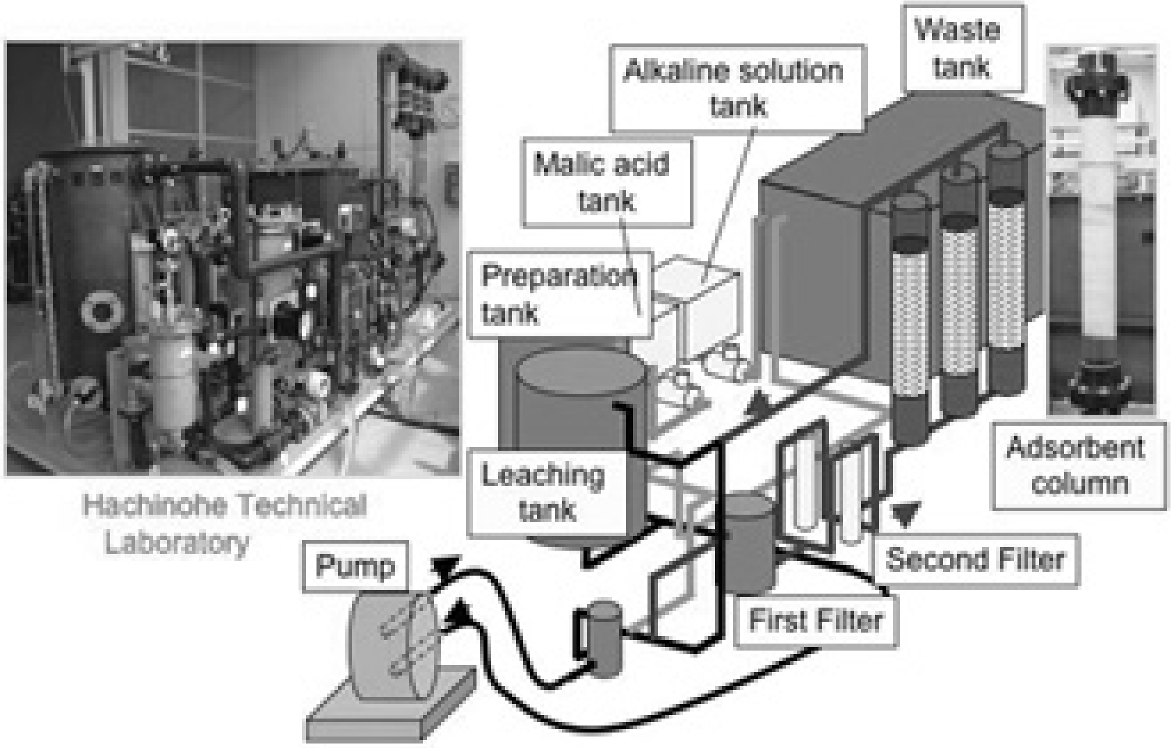


Fig. 8 Bench scale equipment for removal of cadmium from midgut gland of scallop.

The cadmium free midgut gland shown in Figure 9 is considered to fertilizer for carrot, green onion, and Chinese yam and livestock feed.

Fig. 9 Untreated midgut gland, dried cadmium free midgut gland, and after granulation.

4.2 Recovery of significant metals

4.2.1 Uranium in seawater

Abundant amount, 4.5 billion tons, of uranium is dissolved in seawater. The concentration of uranium in seawater, however, is extremely low and its value is 3ppb (3.3mg-U in one ton of seawater). To collect the uranium in seawater with coexistence of numerous sodium and magnesium ions, the amidoxime type adsorbent was synthesized by the co-grafting of acrylonitrile and methacrylic acid onto the polyethylene nonwoven fabric and the subsequent chemical reaction with hydroxylamine. The stacks of fibrous adsorbents (350kg) were soaked in the northern part of sea. Figure 10 shows the marine experiment of the uranium recovery from the seawater. Twelve soaking in three years led the collection of 1kg uranium as yellow cake $^{4)}$. To realize the rational cost for the uranium collection from seawater, the braid type adsorbent was developed. The braid type adsorbent was produced by imparting the amidoxime group into the polyethylene fiber with grafting and chemical modification.

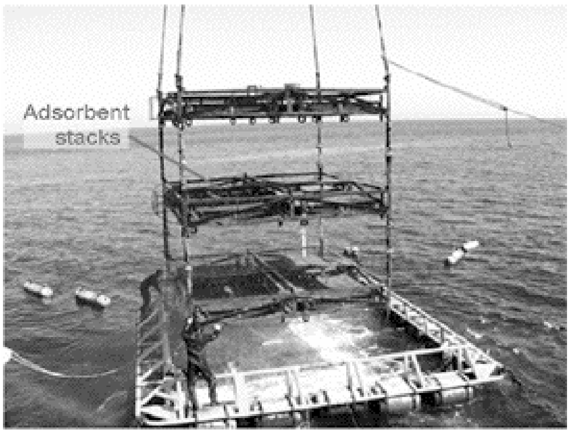


Fig. 10 Marine experiment of uranium recovery from the seawater in Mutsu-Sekine offing.

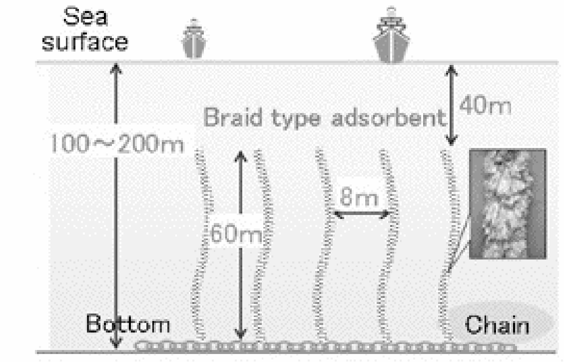


Fig. 11 Recovery system for braid type adsorbent.

Figure 11 shows assemble of braid type adsorbent for mooring on sea bottom. The uranium collection of the braid type adsorbent is three times higher than that of the adsorbent stack when the effect of seawater temperature is included. The collection cost of uranium form seawater was calculated at the present and the expecting level of adsorbent ability. In this estimation, the annual scale of uranium collection was set to 1200 t/y which corresponds to the uranium amount consumed by six nuclear plants. In the adsorbent performance of 2g-U/kg-adsorbent for the soaking of 60 days and the repetition usage of 6 times, the uranium cost was calculated at 88,000 yen/kg-U (750$/kg-U). When performance of 6g-U/kg-adsorbent and repetition usage of 20 times or more will be achieved, the uranium cost reduces to 15,000 /kg-U (130 $/kg-U) 5). This price level is equivalent to that of the highest cost of the minable uranium.

4.2.2 Scandium in hot spring water

Kusatsu hot spring (onsen) is a famous for spa treatment since hot spring water is strongly acidic and contains many kinds of minerals. It was found that scandium was dissolved at the concentration of 20 - 40 ppb. Scandium can be utilized to improve the thermal strength of aluminum alloy and to extend the life time of battery. Recently, the scandium is useful for the solid electrolyte of the fuel buttery. However, the price of scandium is very high and 2 million yen/kg so that the application of scandium is not developed well. The phosphoric adsorbent which was synthesized by graft polymerization could adsorb scandium in the strongly acidic solution, around pH 2 6). The collaborative project was launched in Kusatsu onsen from 2006 to 2007.

Conclusions

Radiation grafting is a powerful tool to modify the property of the polymer. Application of grafting led separator membrane for a button-shaped battery and gas adsorbent are typical commercial products as industrial applications. The imparted properties of electroconductivity in the separator membrane and rapid and large amount of adsorption in the gas adsorbent overcome those of the conventional products. The production cost by means of grafting, however, is relatively higher than that by chemical synthesis since the radiation facility and inert-gas substituted reaction chamber is necessary for grafting process. In this reason, the graft polymerization has been industrially applied in the products which are synthesized only this technique or the product of high cost performance.

The grafting can introduce the aiming functional group to the trunk polymer. This technique can lead the tailored adsorbent for removal of toxic metals and the recovery of significant metals for the purpose of environmental application. The fibrous adsorbent can be easily synthesized by the graft polymerization onto the fibrous trunk polymer. These adsorbent have been applied to the removal of cadmium from scallop waste, the recovery of uranium and scandium. The predominant factors of industrialization are considerer that how the high performance and the rational cost realize in ongoing R &D.

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3.9 Radiation Processing of Starch

Kamaruddin Hashim

Malaysian Nuclear Agency (Nuclear Malaysia)

1. Introduction

Starch is a polysaccharide material and generally, it is non-toxic, biocompatible and biodegradable. It mainly use as foodstuff, food additives, production of sugar and flavouring. Sago palm with scientific name Genus Metroxylon belonging to family Palmae is an important resource in the production of sago starch in Malaysia. Nearly 90% of sago planting areas is found in Sarawak State of Malaysia. It can easily grow under the harsh swampy environment. The sago starch content 4% polyphenol, which is an active compound with antioxidant property that has potential benefit in health and skin care applications. Renewal resources and environmental friendly of natural polymer reason for the researcher to explore the potential of this material in order to improve our quality of live.

2. Sago Starch Hydrogel and its application

Radiation technology has been successfully used to modified synthetic polymer into good performance and quality product. Based on this achievement, one hope that radiation processing could also be use on natural polymers (polysaccharides) in order to replace product based synthetic polymer. However, only polysaccharide of chitosan, starch, cellulose, carrageenan and alginate has been given much attention in radiation processing research activity. The potential of polysaccharide in the medical application can be seen from the blend of this material with synthetic water-soluble polymer, in the production of hydrogel especially for wound burn dressing application. This hydrogel can easily produce by gamma or electron beam irradiation and simultaneously give sterile product. Wound dressing product using polysaccharides currently available in the market such as AQUA GELO 1) by KIK-Gel Company using PVP/Agar, NU-GELO produced by Johnson & Johnson Medical 2) using extracted Alginate and HAZEL 3) made of PVA/carrageenan hydrogel .

Ionizing radiation on polymer material will produce two majors reaction that is crosslinking and degradation. In the case of natural polymer, including also sago starch, degradation is the dominant reaction that taken place during radiation of this material. The viscosity of sago starch aqueous solution reduced to about half after sago starch powder was exposed to 10kGy irradiation dose 4). However, the sago starch is more stable to radiation either gamma or electron beam, base on leaching ability of amylose 5) during gelation process, compare to other starch such as cassava, as shown in Figure 1 below. Amylose of sago starch is much more stable to irradiation than tapioca starch based on existing of amount of amylose in the continuous phase of cooked starch

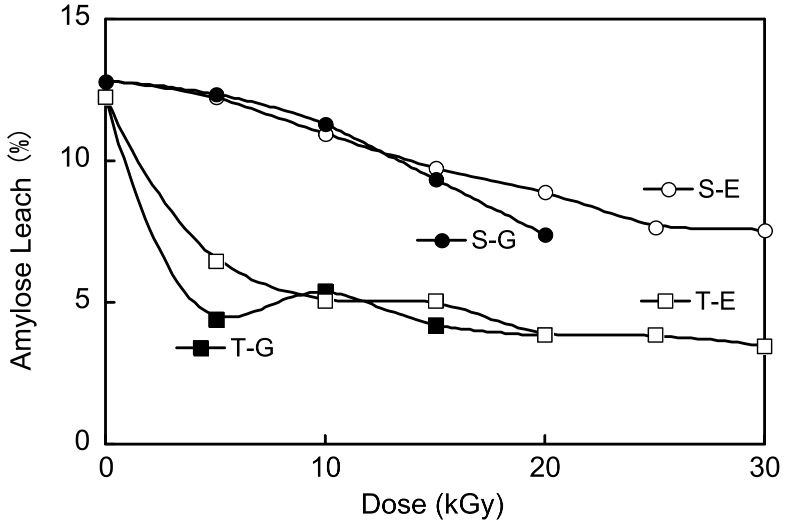
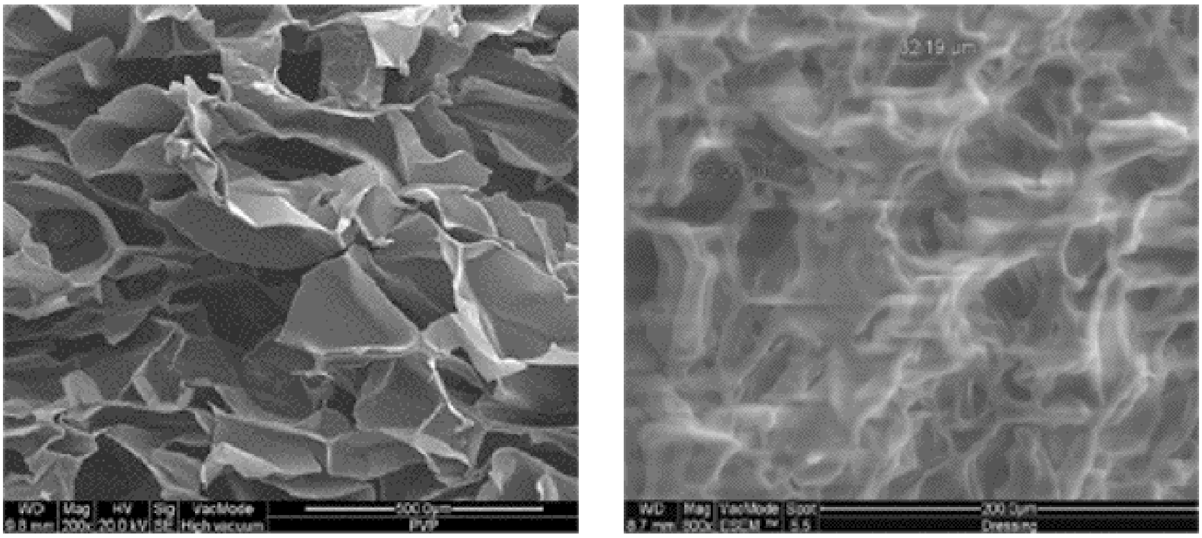


Fig. 1 Leaching of amylose during gelation process of irradiated starch.
S*: sago,* T*: tapioca/cassava,* G*: by gamma.* E*: by electron beam*

In certain condition, radiation can produce copolymer by grafting process where monomer or polymer was grafted onto other polymer chain or backbone. In the process of making sago starch hydrogel where sago starch was blend with PVA and PVP, sago starch molecule will also grafted on the polymers of PVA or PVP on top of degradation during radiation of the blend. Morphology study of sago starch hydrogel reveals the grafting process of sago starch onto inter polymeric network (IPN) of PVP. Figure 2 shown micrographs of PVP and sago starch/PVP hydrogel after freeze dry process. Based on the observation, the rough surface of sago starch/PVP blend (b) is due to grafting of sago starch on the surface of PVP hydrogel compare to PVP hydrogel alone (a). Thermo gravimetric study by Maolin et. al.[6] also reveals some degree of grafting of sago starch on the PVA chain during the radiation process of sago starch/PVA blend.



(a) *(b)*

Fig. 2 Micrograph of PVP (a) and Sago starch/PVP (b) hydrogels.

Radiation process on polysaccharide has produce promising results in turning polysaccharide form foodstuff into much valuable product that could increase it value added. One of the examples, radiation processing of sago starch with water-soluble polymers will transform it into sago hydrogel which could be use as facial mask in skin care cosmetic application for treatment of acne and other skin problem. The sago hydrogel has also been tested and confirm as medical device in wound dressing in medical device application.

Sago starch hydrogel has been licensed to Rumbia Bio-Tech Sdn. Bhd. on September 2003 for commercialization purpose. The company manufactured the sago starch hydrogel facial mask and marketing by multi-level marketing company, EcoFirst Product Sdn. Bhd. under trade name eco-belle hydromiracle mask (Figure 3). Rumbia Bio-Tech is also in the pilot scale stage to manufactured sago starch hydrogel for wound dressing application. For this purpose, the company has been located a grant RM1.7 million from Malaysian Government to produce and carried out clinical test on sago starch hydrogel for wound dressing application (Figure 4).

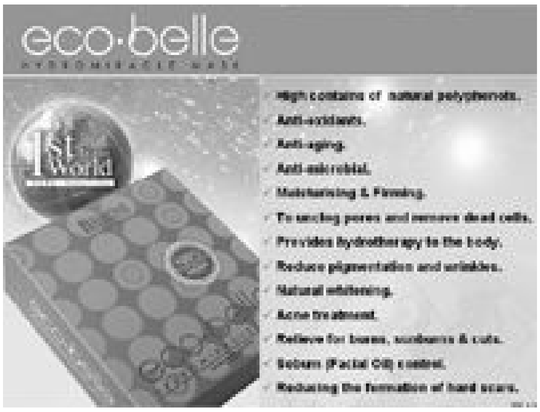


Fig. 3 Eco-bell Sago Hydrogel Facial Mask.

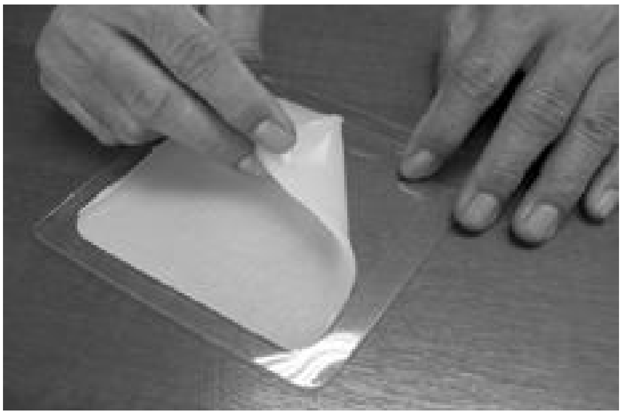


Fig.4 Sago Hydrogel Wound dressing.

3. Carboxymethyl Sago Starch

Radiation and chemical modification of sago starch will enhance and improve its property to be use in various field of application. Etherification process [7, 8, 9] on sago starch will convert it from non water-soluble into water-soluble carboxymethyl sago starch (CMSS), which has thickener or binder properties. This process can also be applied to other polysaccharide and gave same effect on the materials [10]. FTIR and TGA analysis on sago starch and CMSS will indicate the substitution of carboxymethyl group on hydroxyl group of the glucose unit of sago starch. Morphology study on CMSS by Scanning Electron Microscope indicates that substitution is taking place only on the surface of sago starch granule (b) compare to smooth surface of granule sago starch before etherification process, as shown in Figure 5. The degree of substitution (DS) will determine the solubility of CMSS in water where CMSS with DS value 1 will shown complete solubility. Oudhoff et al [11] reported that carboxymethyl cellulose (CMC) with a DS above 0.7 is completely water-soluble. However, the solubility of CMSS in water also depend on it concentration in aqueous solution where at 50% CMSS concentration (b) some of CMSS granule is still remind in granule form compare to the 20% CMSS concentration (a), based on the morphology study of CMSS paste like condition in water, as shown in Figure 6.

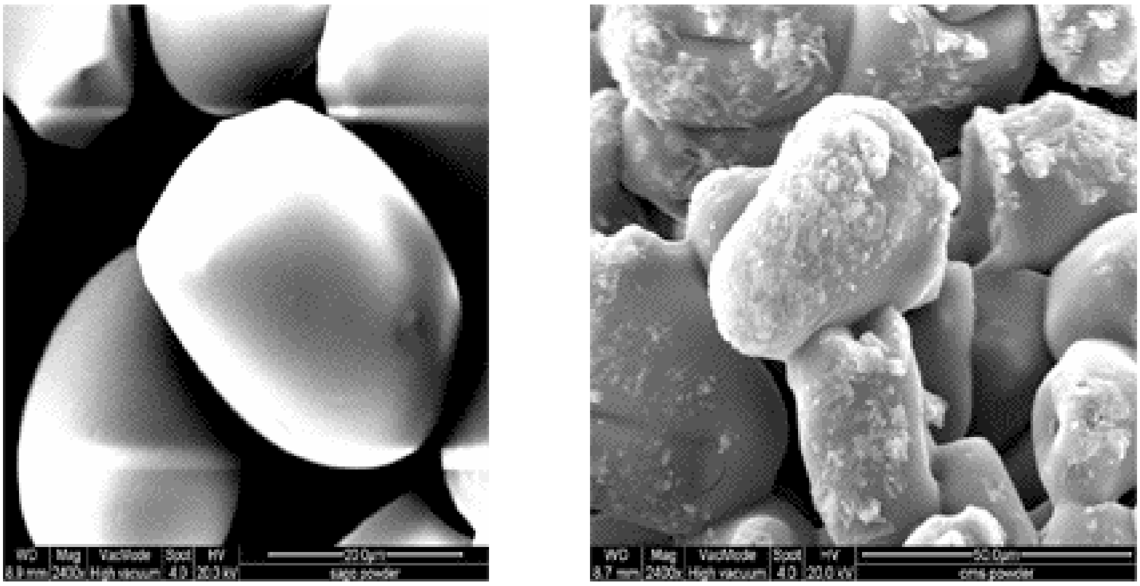

(a) (b)

Fig. 5 Micrograph of granule sago starch (b) before etherification process and granule CMSS after etherification process.

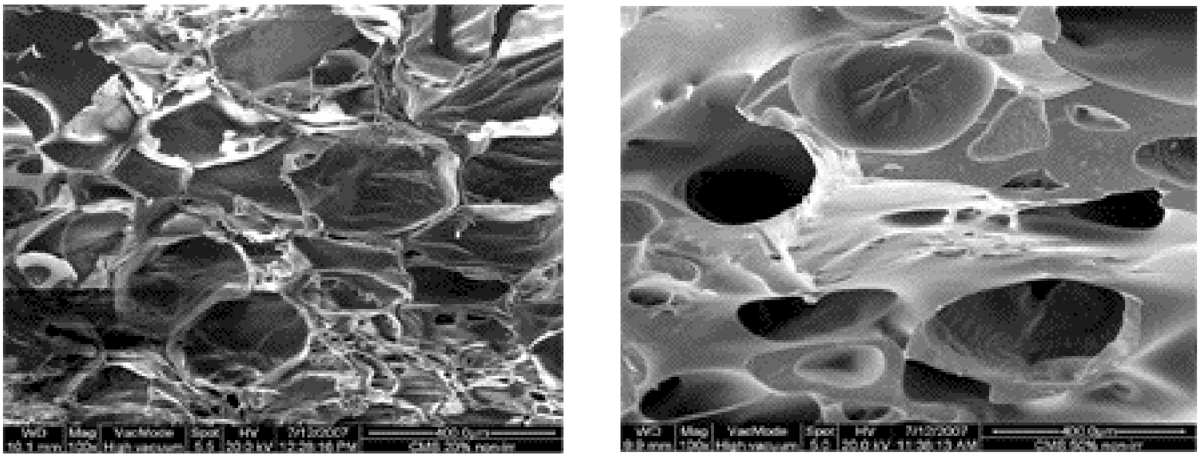
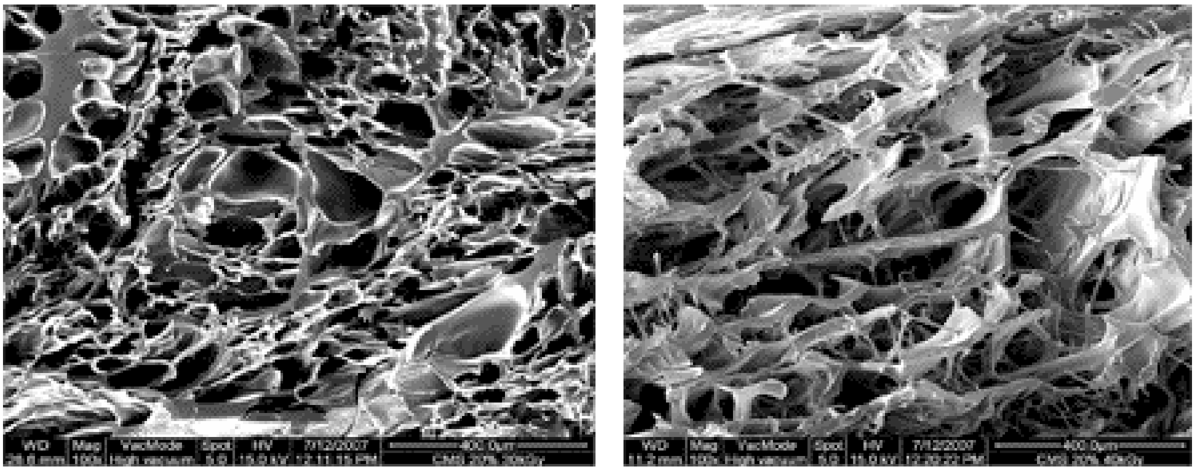

(a) (b)

Fig. 6 Micrograph of the soluble CMSS in water at (a) 20% and (b) 50% concentration in water.

The carboxymethyl group attached on polymer chain, not only make it soluble in water but in paste like condition will crosslink to produce hydrogel when expose to irradiation Yoshii et al. [12] has shown that CMC can only be crosslink by gamma or electron beam irradiation in the paste like condition.. The same situation also applied to CMSS in producing CMSS hydrogel by irradiation process. The degree of crosslink depends on concentration of CMSS and irradiation dose, which determine the inter-polymeric network of CMSS hydrogel. Increase degree of crosslinking will produce hydrogel having much denser network with reduction in pore size, as shown in Figure 7.



(a) (b)

Fig. 7 Micrograph of 20% CMSS hydrogel at (a) 30kGy and (b) 40kGy irradiation dose.

At the same time, these hydrogel will have the swelling property and its swelling capability disproportional to the degree of crosslinking, in other word decrease in swelling with increase irradiation dose and concentration of CMSS in hydrogel. On top of that, its degree of swelling depend on the pH of medium in the following sequent neutral>alkaline/saline>acid. Based on this fact, it has a potential to be use as a carrier in the drug delivery system.

4. Conclusion

Radiation technology has shown it capability to improve and increase value added of natural polymer, in this case sago starch. Radiation processing on blended sago starch with water-soluble polymer produce hydrogel which could be use as facial mask and wound dressing in cosmetic skin care and wound management applications, respectively. Hydrogel from the sago starch derivative (CMSS) has a potential to be use as a carrier in the drug delivery system, based on the swelling ability of this hydrogel at various pH and media conditions such as acid, neutral, alkaline and saline. However, the swelling properties of this hydrogel depend on the homogenous solubility and concentration of CMSS in water, irradiation dose and degree of crosslinking. It need further explore the potential of this material in order to get full benefit of this development.

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3.10 Chitin, Chitosan and Radiation -Relating to Agricultural and Biomedical Applications-

Seiichi Tokura, Hiroshi Tamura, Tetsuya Furuike, Nitar Nwe, Hideaki Nagahama, Yukihiro Maeda, Naotsugu Nagasawa*, Masao Tamada*

Graduate School of Engineering, Kansai University, *Japan Atomic Energy Agency

1. Introduction

Chitin, a natural abundant polysaccharide in cuticles of crustacean and insects, has been investigated as an outstanding biomedical material due to various physiological advantages including biodegradability in animal body. Although chitosan, one of deacetylated chitin derivatives (Figure 1), has been studied in detail due to solubility of chitin-organic acid salts in water, physiological investigation of chitin has recently become popular following the finding of neutral solvent for chitin.

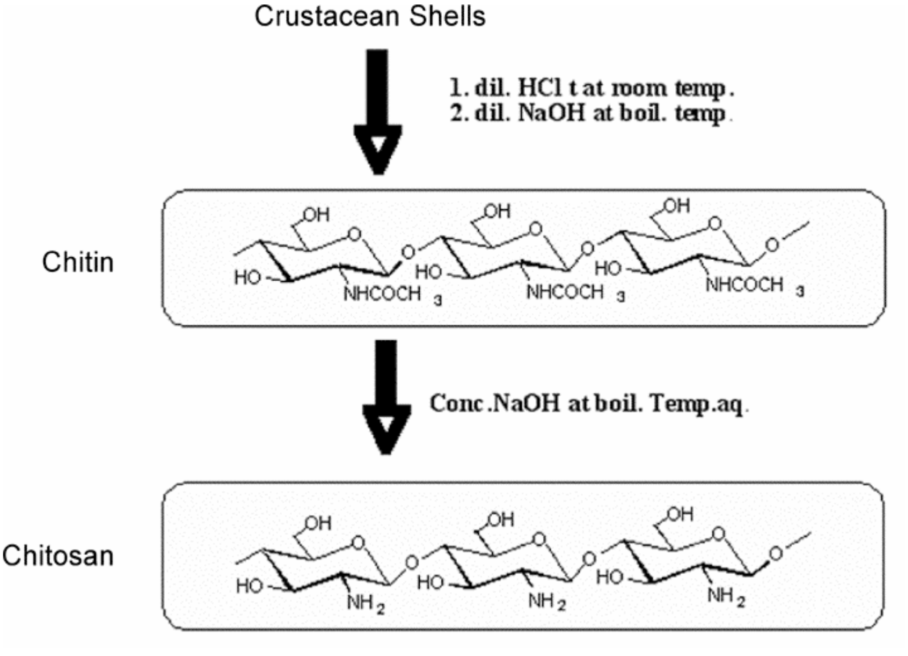


Fig. 1 Chemical structures of chitin and chitosan together with their preparation procedures.

Since there are several differences between chitin and chitosan on the participation for biomedical and agricultural fields, the differences are now requested to make clear for the effective application of them. For example, chitin is reported to induce the epidermal cells recovery in animal and chitosan accelerates to recovery of fibrofrust cell in addition to antimicrobial activity. On the agricultural application, chitin and chitosan have been reported to induce the growth of *Actinomyces sp.* in soil which suppresses the unfavorable activity of *Fusarium sp.* on the growth of plants in addition to antimicrobial activity by chitosan. Chitosan is also reported to induce the secretion of phytoalexins in plants by spraying of chitosan aqueous solution on plant leaves or seed coating. On the slow release of pesticides or drugs has been investigated to prepare beads, film and fiber both in the biomedical and agricultural fields. Chitosan was also found to suppress the virus infection of silkworm effectively when artificial mulberry leaf feed was supplied to the silkworm cultivation mixing with chitosan.

2. Chitin and Chitosan

Chitin, one of natural abundant polysaccharides, is thought to be the most prominent natural polymers due to multi-functions such as biodegradability and low toxicity in animal body, acceleration of skin recovery. But a little of application has been reported owing to sparingly soluble property in general solvents. Chitosan, on the other hand, has been studied on various practical applications due to additive functions over chitin such as antimicrobial activity and acceleration of fibroblast formation in animal body, acceleration blood clotting, good solubility against water following the formation of salts with various organic acids and hydrochloric acid. According to those predominant properties of chitosan, a number of reports have been published including chemical modifications and biomedical applications. Although chitin, a muco-polysaccharides of natural abundant, is hardly found in plant supporting system, it is popular in animal support or tissue of lower evolution such as crustacean, insects and mushrooms. The yield of chitin in nature is said to be second to that of cellulose. Chitin is also known to be biodegradable in nature and in animal body due to close chemical structure of sialic acid which is a component of cell wall supporting materials. Since chitinases and chitosanases are included in animal self defense system to suppress the activity of micro-organism by breaking down the cell wall, chitin is hydrolyzed easily in animal body. The hydrolysate, *N*-acetylglucosamine (GlcNAc) becomes to join into nutrient pathway without any toxicity of chitin hydrolysate. The main function of chitin is acceleration of skin recovery with little of immunological response. The main target of recent research for chitin is regeneration under mild condition to apply for biomedical materials through these predominant functions, although it is tough to find good solvent for chitin. On the other hand, chitosan exists slightly in several mushrooms and is mainly supplied as chemical product of chitin. The predominant functions of chitosan seem to be the antimicrobial activity and inhibitory function toward chitnases in addition to the acceleration of fibroblast formation in animal body. These predominant functions have been applied for biomedical purpose in addition to food preservation field due to high solubility of chitosan into aqueous organic acid solutions and hydrochloric acid aqueous solution which is limited solvent for chitosan among other mineral acid aqueous solutions.

We have succeeded to prepare hydrated chitin1) applying calcium chloride dihydrate saturated methanol for the dissolution of chitin followed by precipitation with large excess of water and extensive rinsing with water. The complete removal of acetate salt from chitosan slurry was carried out by addition of alkaline to precipitate salt free chitosan slurry followed by extensive rinsing with water. The regeneration of chitin non-woven fabrics with rigid crystalline structure was also reported applying hydrated chitin slurry. There are various research reports on chitin and chitosan biomedical materials applying their specific advantages against other polymers including natural polymers. But a number of investigations of chitosan have been achieved due to higher reactivity of amino group than those for chitin due to poor reactivity by rigid crystalline structure. So chitin products have not so much been commercialized except non-woven fabrics for wound dressing from UNITIKA.

3. Antimicrobial Activity of Chitin and Chitosan

On the antimicrobial activity, chitosan was reported to be effective to suppress microbial activities as shown in and Figures 2 and 3 and Table 1 [2)] showing the dependency of molecular weight on the antimicrobial activity against *E. coli* in which chitosan of low molecular weight is rather enhance *E. coli* activity probably due to permeation of oligomer through cell wall of *E. coli*, though the *E. coli* activity is surely suppressed by chitosan oligomer of around 10,000 of molecular weight due to stacking of chitosan onto the surface of *E. coli* cell wall to block nutrition supply.

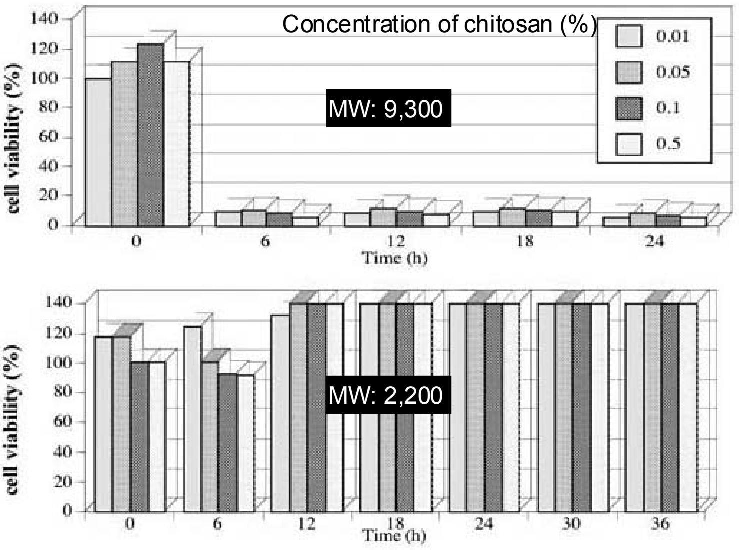


Fig. 2 Dependences of antimicrobial activity on the molecular weight of chitosan.

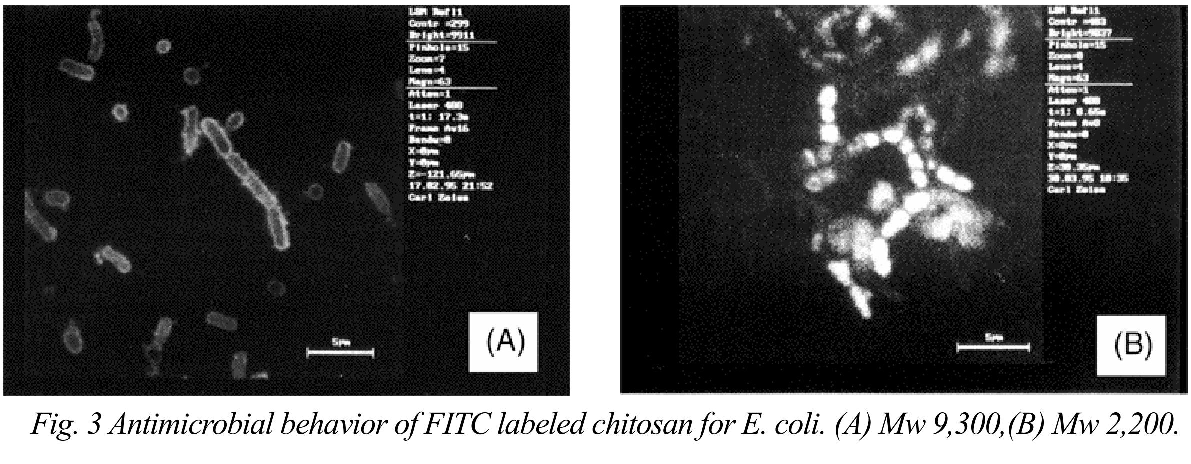


Fig. 3 Antimicrobial behavior of FITC labeled chitosan for E. coli. (A) Mw 9,300,(B) Mw 2,200.

Table 1 Antimicrobial activities by chitosan against various bacteria. Minimal lethal concentration (MLC) of chitosan against microorganisms

	MLC values (ppm.)		
Microorganisms	DAC 95	DAC 75	DAC 47
Bacteria (Gram negative)			
Aeronwnas hydropila	500	1,000	1,500
Escharichia coli	100	100	500
Pseudonwnas auruginosa	200	200	200
Salmonella typhimurium	1,500	1,500	2,000
Shigella dysenteriae	200	200	200
Vibrio cholerae	150	200	200
Vibrio paraha molyticu	100	100	150
Bacteria (gram positive)			
Bacillus cereus	200	200	1,000
Listeria monocy togenes	100	150	150
Staphylococcus aureus	100	50	100
Fungi			
Candida albicam	200	500	800
Fusarium oxysporum	500	800	800
Aspergillus fumigatus	2,000	2,000	2,000
Aspergillus parasiticus	2,000	2,000	2,000

DAC: Degree of deacetylation (DAC 95 = 95 % glucosamine residues and 5% N-acetylglucosamine residues)

4. Radiation effects on Chitin and Chitosan

It is well known that "Crosslinking" and "Degradation" are induced at the same time by irradiation of electron beam or radioactive rays. Though there are many barriers to precise control of these two phenomena, the regulation technology seems to be asked seriously to overcome for the practical application of these binary phenomena, crosslinking and degradation during these beam irradiation. On the irradiation effect for chitin and chitosan, both polysaccharides precede to degrade into oligomers respectively. But chitin hydrogel proceeds to crosslink in the presence of polymers such as polyvinyl alcohol (PVA), carboxymethyl-cellulose (CMC) and so on without degradation under the irradiation of γ-rays between 5 ~ 10 kGy. On the other hand, degradation proceeds predominantly in the case of chitosan even in the presence of polymers as mentioned above. The predominant degradation of chitosan following γ-ray irradiation is interesting phenomena to prepare the matrix of control release of drug, fertilizers, pesticides and so on. Since crosslink of supported polymer starts at the final stage of chitosan degradation, the trapping of chitosan oligomer for the controlled release of the oligomer might easy into polymeric cavities which are formed by crosslinking of supported polymers. The released chitosan oligomer would become effective to form callus and to propagate the roots from callus on tissue culture of plants.

In the case of wound healings by chitin and chitosan, chitin oligomers are effective to the acceleration of epidermal cell regeneration and chitosan oligomers, on the other hand, accelerate the recovery of fibroblast cells on wound healing[3)]. The sustained release of chitin or chitosan oligomers is expected from the crosslinked matrixes of chitin or chitosan gel following radioactive irradiation, when solvated chitin or chitosan is prepared applying non-toxic solvents such as water.

The irradiation of natural polymers seems to be the most prominent process to apply them for life science including waste natural polymers, because application of chemicals is able to reduce to minimum in irradiation method to avoid environmental pollution. Crosslinking of polymeric food wastes could be induced by radiation. The produced gel would be useful to apply for afforest plantation, because the water regain property is expected to the produced gel. The crosslinking process is available to synthesize complicated functional polymers such as star polymers, macromer polymerization, dendorimers and so on. A sustained release of biological materials can also be possible to apply with minimum toxicity, when crosslinking is made by radioactive ray irradiation for natural polymers. On the irradiation studies for polysaccharides (cellulose, chitin and chitosan) have not been studied for commercialization due to uncontrolled degradation processes by irradiation. Tamada et al. revealed that predominant crosslinking was induced by the introduction of carboxymethyl group to cellulose (CMC) following the electron beam irradiation. On the irradiation for chitin and chitosan, we have found crosslinking in the presence of polymers in the case of chitin. But it was hard to find the crosslinking reaction for chitosan until higher irradiation (over 30 kGy) even in the presence of polymers (Figure 4). But chitosan oligomer of low molecular weight fraction was converted to antimicrobial surface when chitosan oligomer of molecular weight lower than 2,200 was immobilized to another polymers such as protein or synthetic polymers. This observation would suggest the conversion of polymeric surface into antimicrobial surface by the immobilization of chitosan oligomers of low molecular weight.

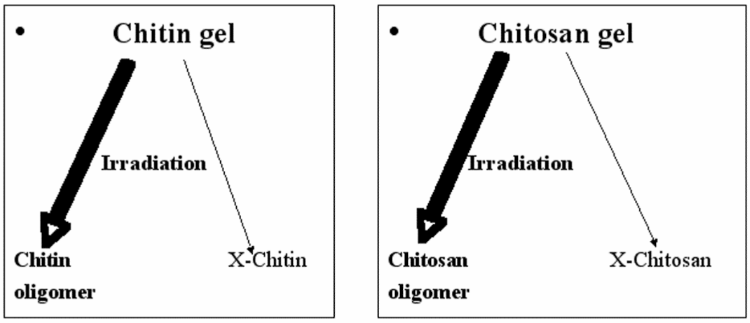
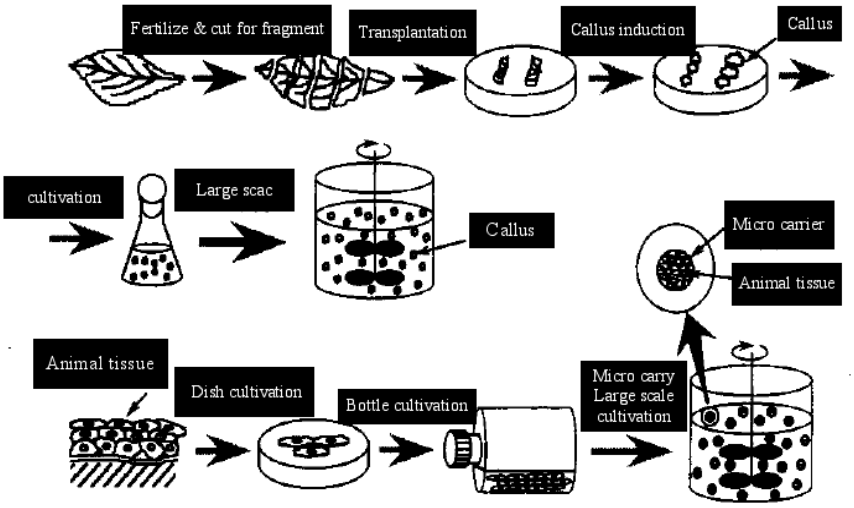


Fig. 4 Predominant routes by irradiation to chitin gel. and chitosan solution respectively.

5. Agricultural Applications of Chitin and Chitosan

On the agricultural applications of chitin and chitosan, chitin was reported to induce *Actinomyces sp.* which suppressed *Fusarium sp.* as a biological pesticides Also chitosan is known widely as a antimicrobial activity against viruses, fungi and molds. A part of antimicrobial activity of chitosan is shown in the Table 1 against various microorganisms. On the silk production, antimicrobial activity of chitosan was applied to silkworm cultivation. An artificial mulberry leave feed containing chitosan was effectively suppressed virus infection of silkworm. Chitosan has been studied to apply for tissue culture of orchid successfully, in which chitosan was applied whole process of orchid cultivation, preferentially to accelerate the propagation of roots. Also advantage of chitosan was found on the tissue culture of plants as shown in Scheme 1 as general scheme.



Scheme 1 General concepts for the tissue culture of plants and animals.

As seen in Figures 5, 6 and 7 axillary bud from orchid was planted in liquid media at 27˚C under gentle stirring after extensive sterilization. There is surely concentration and molecular weight dependency on the growth of orchid callus. Especially, concentration of chitosan oligomer seems to be important factor to accelerate the callus formation. Also the root propagation of plants callus was observed to serve chitosan as an accelerator for the growth of cultured plants.

Fig. 5 Tissue culture of orchid in practice.

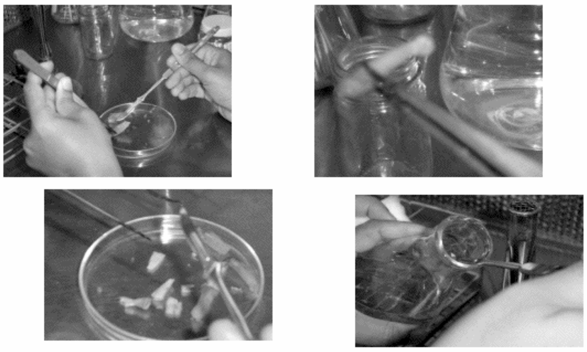


Fig. 6 Preparation of axillary buds from explants.

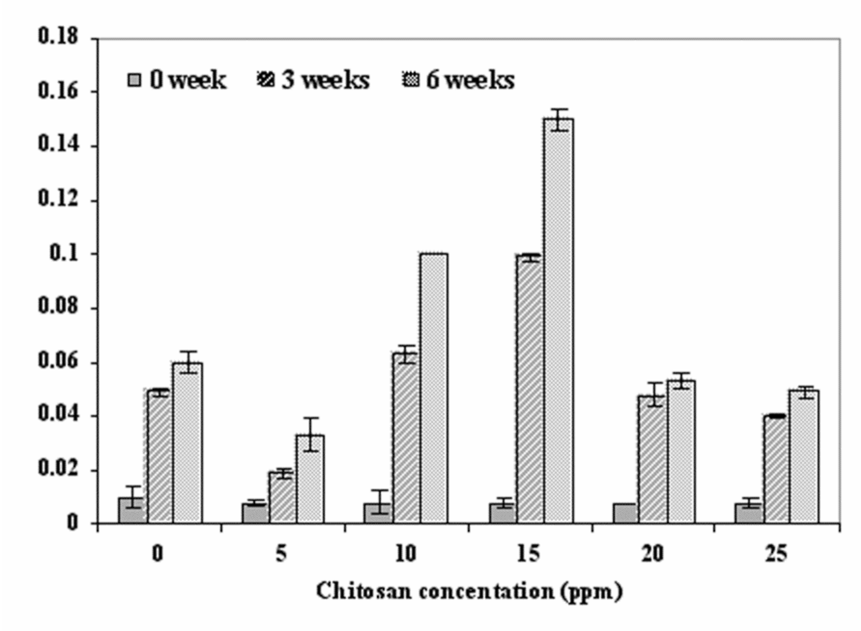


Fig. 7 Dependence of chitosan oligomer concentration on the growth of orchid callus at 27˚C.

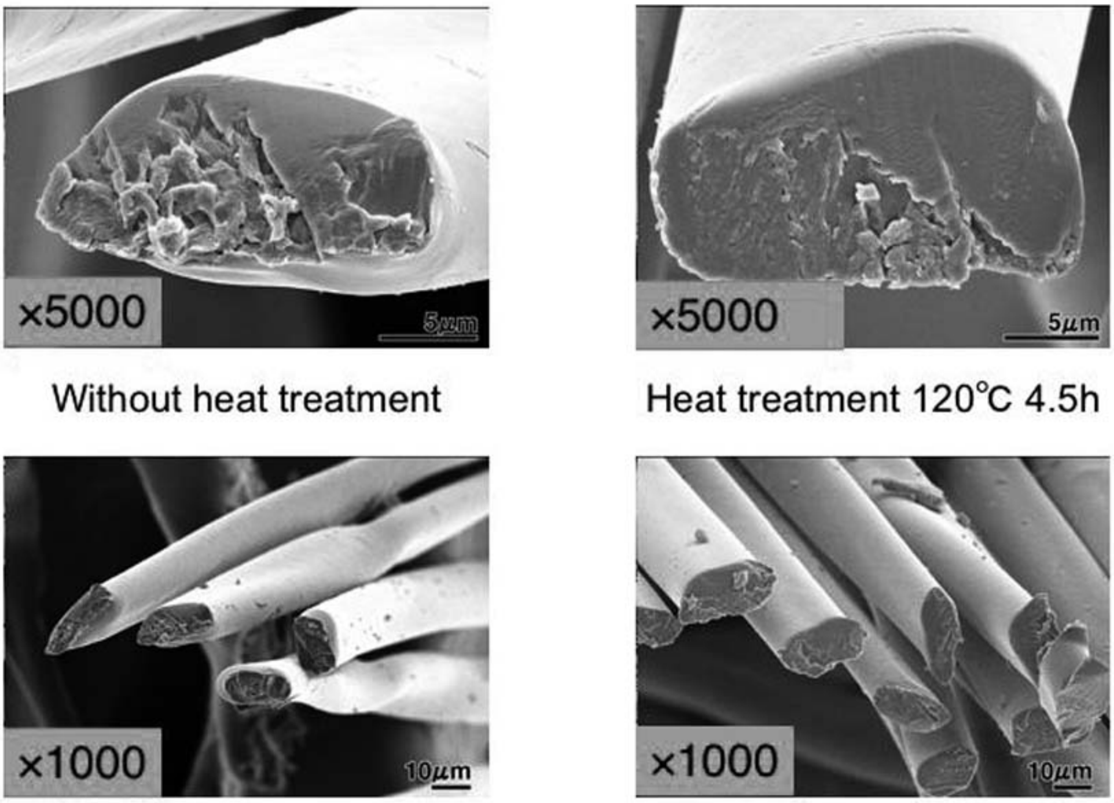
Crosslinked polymeric gel containing chitin or chitosan would be applied for planter of plants or protector for cut flower on transportation. Another possible application of chitin and chitosan on agriculture would be the regeneration of soil which is contaminated by unfavorable microorganisms in agriculture such as *Fusarium sp*. because chitin and chitosan induced *Actinomyces sp.* is reported to suppress *Fusarium sp*. activity effectively. In practice, the spore of *Actinomyces sp.* is fermented at 37 ~ 40˚C for a week under gentle stirring in polluted soil in the presence of fertilizer such as rice scum, beans scum and food waste except hot seasonings. Then fermented soil is diluted by fresh soil repeatedly to increase its volume under similar condition rich by *Actinomyces sp.* gradually.

6. Application to Metal Injection Molding

The electron beam (EB) and γ-ray irradiations seem to also be attractive process to introduce to MIM (Metal Injection Molding) method, because meal powder mold supported by hard polymeric paste is asked to prepare before combustion to produce metallic parts 4). The paste made molding is then applied to combustion at high temperature to produce small parts for aircraft, automobile and so on (mostly parts for engines). We would like to propose starch, agar-agar (one of algae polysaccharides) and other homo-polysaccharides as binder to make metal pastes. The reason why homo-polysaccharides is requested, is environmental factor to maintain environment far from air-pollution. Stainless steel with the 17-4PH composition (SUS630) is one of the most widely used MIM alloys. It is consists of approximately 17% Cr, 4% Ni, 4% Cu, and low concentration of alloying additions of manganese, silicon, niobium, and tantalum. SUS603 is a martensitic precipitate hardening stainless steel. When SUS630 is sintered and heat-treated to the H900 condition (aged at 900˚F or 482˚C), the MIM products typically give yield strength of 1,100 MPa and ultimate tensile strength of 1,200 MPa. The post-sintering heat treatments allow manipulation of the strength and ductility of metals, providing a mean to adjust properties to the application. Because sintering is essentially an annealing process, MIM SUS630 in the as-sintered condition has a lower strength. A typical as-sintered SUS630 parts give yield stress of 730 MPa and ultimate tensile strength of 900 MPa. Avoiding the heat treatment step lowers costs, and in many applications the as-sintered parts provide satisfactory properties. Fatigue strength and fracture toughness are also high for MIM parts. For MIM-processed SUS630 stainless steel delivers fatigue endurance strength just over 500 MPa. This is 42% of the ultimate tensile stress, which is comparable to the wrought alloy. It is therefore important to understand the relationship of sintering conditions and the mechanical properties of stainless steel SUS630 for further commercialization of MIM technology.

7. Application to Gelatin Fine Fibers

EB irradiation for gelatin fine fibers would be the effective process to make gelatin fiber water insoluble as shown in Figure 8, because the gelatin fiber produced by dry spinning of gelatin aqueous solution is water soluble [4)]. The crosslinked gelatin fiber by EB irradiation would be possible to apply for biomedical materials, because biocompatibility and biodegradability of gelatin fiber may be retained even after EB irradiation due to only slight deformation of gelatin molecule after EB irradiation. Also it may possible to apply crosslinked gelatin fiber for safe artificial food.



Without heat treatment

Heat treatment 120℃ 4.5h

Fig. 8 Cut surfaces of fish gelatin fiber prepared dry spinning of aqueous gelatin solution.

8. Conclusion

Chitin and chitosan are asked recycling process for life science due to unexpected increase of waste Crustacean shells. In the case of chitosan which is expected to become multifunctional polymers, though alkaline of high concentration for the preparation of chitosan was concerned to heavy load for environmental condition (9).“Biodegradability” is the most predominant characteristics among general polymers including synthetic polymers and natural polymers have been applied for long time to human life. But natural polymers have a weak point to putrefy or denature under normal condition against synthetic polymers which becomes a bottleneck sometime on the recycling of waste materials from food industries, fisheries and so on. “Gelatin”, for example, has along history on the application for human life as natural glue which is extracted from animal skin or bone. But the striking development of digital camera has induced the remarkable suppression of demand for gelatin. The reuse of animal skin and bone are the most important processes on the prevention of environmental pollution

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3.11 Radiation Processed Polysaccharide for Agricultural Application in Vietnam*

Le Hai

Nuclear Research Institute, VAEC

1. Introduction

Under the Vietnam Atomic Energy Commission there are 5 research and development institutions for radiation processing;□ Nuclear Research Institute (NRI), Institute for Nuclear Science and Technology (INST),□Institute for Technology of Radioactive and Rare Elements (ITRRE); □Center for Nuclear Technique (CNT), □Research and Development Center for Radiation Technology (VINAGAMMA). NRI has Gamma Co-60 cell (2,000 Ci) and Gamma Co-60 chamber (10,500 Ci). Research activities of the Radiation Technology Department of NRI on radiation processing are as follows:

(1) Degradation of natural polymers
(2) Crosslinking
(3) Grafting polymerization

2. Degradation of Natural Polymers

Degradations of natural polymers such as alginate, chitin/chitosan; protein, humic acid have been studied. Radiation degraded natural polymers are produced from sea weal and soled as Plant promoter T&D 4DD (Figure 1) and Plant protector OLICIDE 9DD 4DD (Figure 2).

Fig. 1 Plant promoter T&D 4DD.

Fig. 2 Plant protector OLICIDE 9DD.

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*This text was arranged by the Secretariat of FNCA EB Project, Japan based on a document (Power Point file) presented by the author at the Workshop.

The T&D 4DD is successfully applied in the cabbage farm, sugarcane plantation (Figure 3), tea plantation (Figure 4), coffee plantation, and chrysanthemum. The OLICIDE 9DD is applied on chrysanthemum (Figure 5), orchid plant and sugarcane plantation.

Fig. 3 Application of T&D 4DD on sugarcane plantation (LaNga Sugarcane Joint Stock Co.).

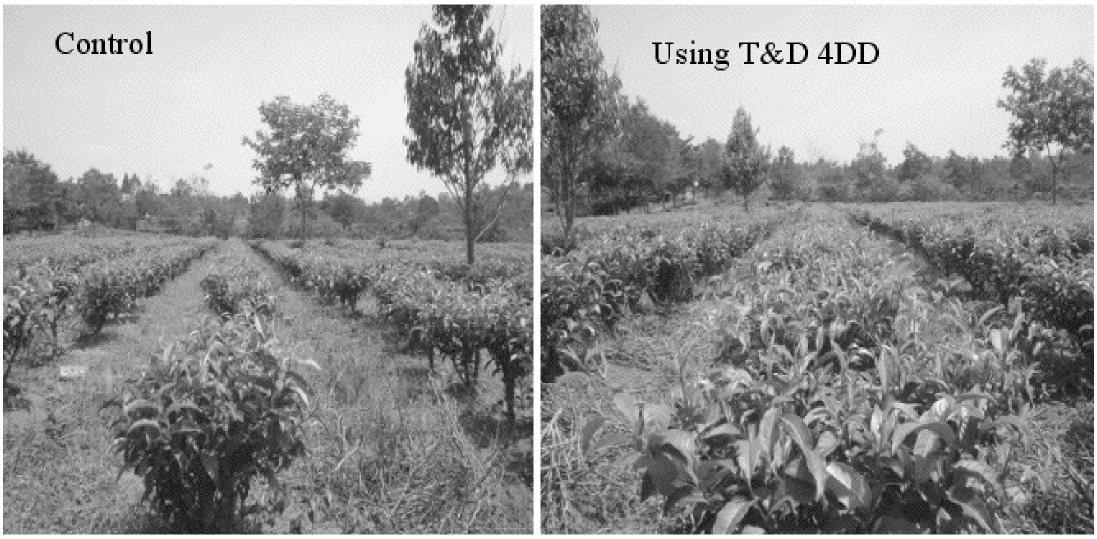


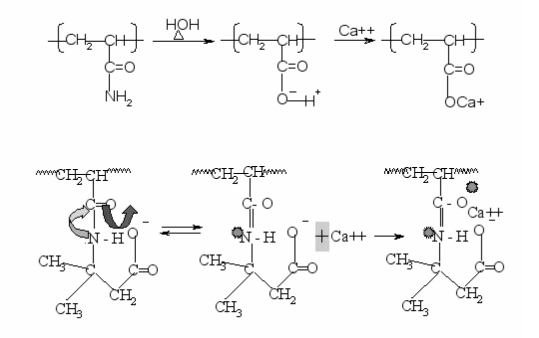
Fig. 4 Application of T&D 4DD on tea plantation.

Fig. 5 Application of OLICIDE 9DD on Chrysanthemum.

The utilization of radiation modified polymers is more effective and prestigious with the end user. Supply OLICIDE 9DD product to Binh Dien Fertilizer Co. is 15 tons/year. Supply T&D 4DD product to La Nga Sugarcane Joint Stock Co. 15 is 20 tons/ year.

3. Modification of Water Soluble Polymer Used for Improvement of Crude Oil Recovery

Water soluble polymers, mainly Poly(acrylamide), have been employed for many years in Enhanced Oil Recovery (EOR) applications to control the viscosity (mobility) of injected water. The required properties of the water soluble polymer for EOR are long-term stability against metal ions in sea water at high temperature. The decomposition of Poly(acrylamide) in the presence of water and Ca^{++} is shown in Figure 6.



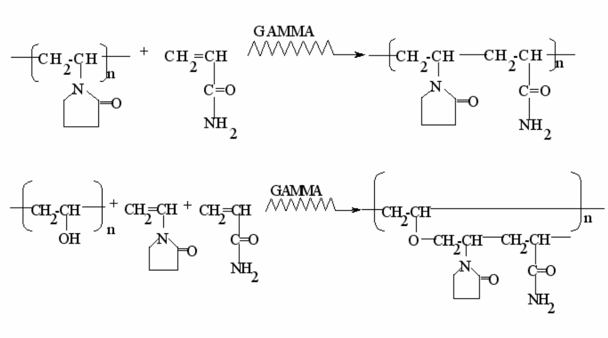


Fig. 6 Mechanism of aging.

Fig.7 Radiation grafting copolymerization.

Radiation modification of Poly(acrylamide) and polyvinyl alcohol (PVA) by graft polymerization has been investigated. Figure 7 shows the graft polymerization of acrylamide and/or *N*-vinyl pyrrolidone onto Poly(acrylamide) and PVA. The studied results (Figures 8 and 9) indicate that rheological property of the modified polymers was stable at high pressure, temperature and salinity conditions. The radiation copolymer enhanced oil recovery more than 10% (in experimental Lab.) as shown in Figure 10.

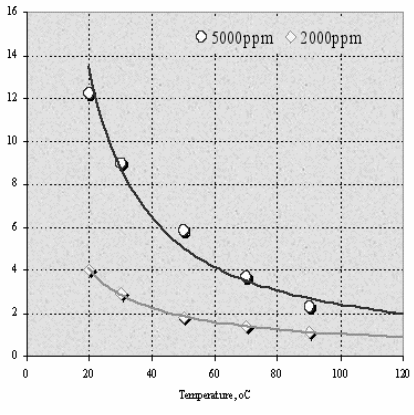


Fig. 8 Temperature effect on the polymer viscosity.

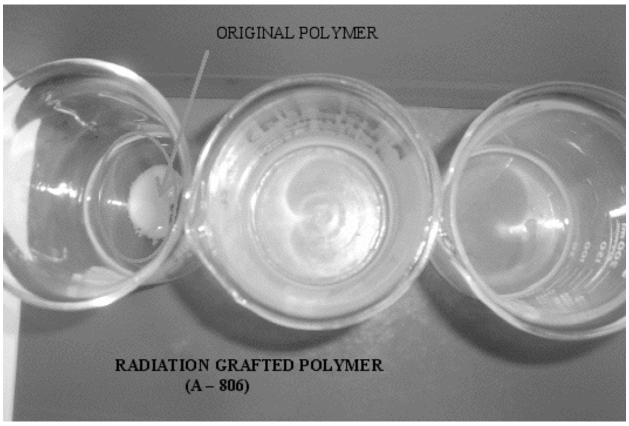


Fig. 9 Radiation grafted polymer after heating for 30 days, at 120°C in seawater.

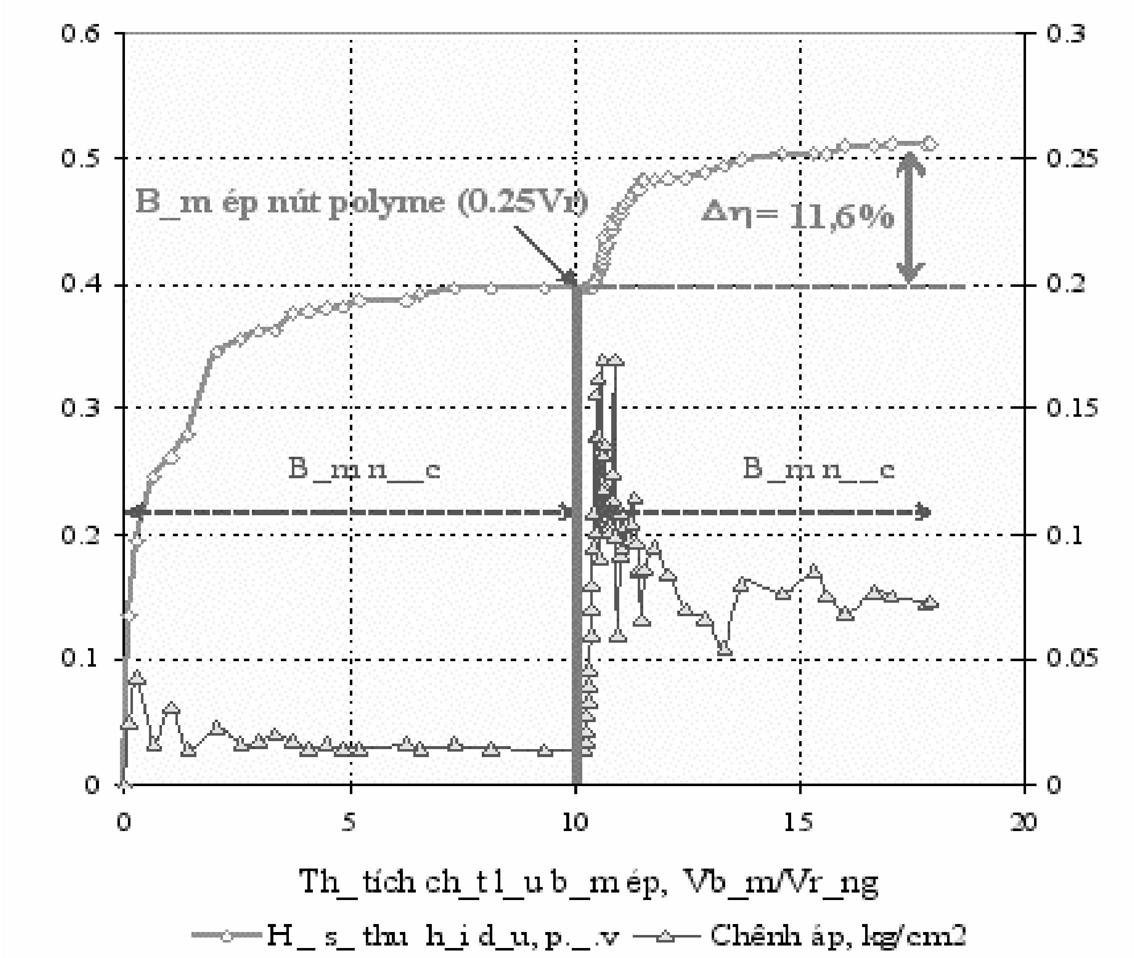


Fig. 10 Injection dynamic of water and polymer button on the bedding reservoir core, miocen sphere of the White Tiger Oilfield.

List of Presenters

Binh Doan ······ 68
Research and Development Center for Radiation Technology, Vietnam Atomic Energy Commission
202A, Str. 11, Linh xuan Ward, Thu duc District, Ho Chi Minh City, Vietnam
Tel: 84-8-8975922, Fax: 84-8-8975921, vinagamma@hcm.vnn.vn

El-Sayed A. Hegazy ······ 49
National Centre for Radiation Research and Technology, Atomic Energy Authority
3 Ahmed El-Zomor, P. O. Box 29, Madinat Nas, Cairo, Egypt
Tel: 00202-26713144&00202-2746791, Fax: 0020-2-22749298, hegazy_ea@hotmail.com

Fumio Yoshii ······ 83, 181
Industrial Cooperation Promotion Department, Japan Atomic Energy Agency
1233 Watanuki, Takasaki, Gunma, 370-1292 Japan
Tel: 81-27-346-9510, Fax: 81-27-346-9480, yoshii.fumio@jaea.go.jp

Gatot Trimulyadi Rekso ······ 97
Center for Application of Isotopes and Radiation Technology, National Nuclear Energy Agency
Jl. Batan No. 1, Lebak Bulus, Jakarta 12440, Indonesia
Tel: 62-21-7690709, Fax: 62-21-7513270, Gatot28@batan.go.id

Guozhong Wu ······ 115, 167
Research Center for Accelerator and Radiation Processing, Shanghai Institute of Applied Physics , Chinese Academy of Science
Jialuo Rd. 2019, Jiading, Shanghai 201800, China
Tel/Fax: 86-21-59558905, Fax: 86-21-59553021, wuguozhong@sinap.ac.cn

Hisaaki Kudo······ 8
Nuclear Professional School, School of Engineering, The Tokyo University
2-22 Shirakata shirane, Tokai, Naka, Ibaraki, 319-1188 Japan
Tel: 029-287-8420, Fax: 029-287-8488, hkudo@nuclear.jp6

Kamaruddin Hashim ······ 198
Radiation Processing Technology Division, Malaysia Nuclear Agency
Tel: 603-89250510, Fax: 603-89202968, kbhashim@nuclearmalaysia.gov.my

Kazuki Isobe ······ 185
Research and Development Department, Nichiban Co., Ltd.
1713 Nomachi, Chikuzen-machi, Asakura, Fukuoka, 838−0815 Japan
Tel: 0946-24-8772, Fax: 0946-24-1096, k-isobe@nichiban.co.jp

Khairul Zaman ······ 23, 169
Radiation Processing Technology Division, Malaysia Nuclear Agency
Bangi, 43000 Kajang, Selangor Darul Ehsan, Malaysia
Tel: 60-3-8925-0510, Fax: 603-8920 2968, khairul@nuclearmalaysia.gov.my

Le Hai ······ 213
Nuclear Research Institute, Vietnam Atomic Energy Commission
01 Nguyen Tu Luc, Dalat, Vietnam
Tel: 84-63-823222, Fax: 84-63-821107, lehaidlvn@vnn.vn, lehaicnbx@yahoo.com

Vibhavadi Rangsit, Chatuchak, Bangkok 10900, Thailand
Tel: 662-5795230 ext 1617, Fax: 662-562010, pihiyatorn@hotmail.com

Tamikazu Kume 3, 159
Takasaki Advanced Radiation Research Institute, Japan Atomic Energy Agency
1233 Watanuki, Takasaki, Gunma, 370-1292 Japan
Tel: 81-27-346-9520, Fax: 81-27-347-2561, kume.tamikazu@jaea.go.jp

Tariq Yasin 148
Pakistan Institute of Engineering and Applied Sciences
P.O. Box Nilore, Islamabad 45650, Pakistan
Tel: 92-51-2207382, Fax: 92-51-2207215, yasintariq@yahoo.com

Young-Chang Nho 15
Radiation Industrial & Environmental Research Center, Korea Atomic Energy Research Institute
1266 Singeong, Jeongeup, Jellabuk-do, 580-185, Korea
Tel: 82-63-570-3060, Fax: 82-63-570-3069, ycnho@kaeri.re.kr

国際単位系（SI）

表１．SI 基本単位

基本量	SI 基本単位	
	名称	記号
長さ	メートル	m
質量	キログラム	kg
時間	秒	s
電流	アンペア	A
熱力学温度	ケルビン	K
物質量	モル	mol
光度	カンデラ	cd

表２．基本単位を用いて表されるSI組立単位の例

組立量	SI 基本単位	
	名称	記号
面積	平方メートル	m^2
体積	立法メートル	m^3
速さ，速度	メートル毎秒	m/s
加速度	メートル毎秒毎秒	m/s^2
波数	毎メートル	m-1
密度（質量密度）	キログラム毎立法メートル	kg/m^3
質量体積（比体積）	立法メートル毎キログラム	m^3/kg
電流密度	アンペア毎平方メートル	A/m^2
磁界の強さ	アンペア毎メートル	A/m
（物質量の）濃度	モル毎立方メートル	mol/m^3
輝度	カンデラ毎平方メートル	cd/m^2
屈折率	（数の）　１	1

表５．SI 接頭語

乗数	接頭語	記号	乗数	接頭語	記号
10^{24}	ヨタ	Y	10^{-1}	デシ	d
10^{21}	ゼタ	Z	10^{-2}	センチ	c
10^{18}	エクサ	E	10^{-3}	ミリ	m
10^{15}	ペタ	P	10^{-6}	マイクロ	μ
10^{12}	テラ	T	10^{-9}	ナノ	n
10^{9}	ギガ	G	10^{-12}	ピコ	p
10^{6}	メガ	M	10^{-15}	フェムト	f
10^{3}	キロ	k	10^{-18}	アト	a
10^{2}	ヘクト	h	10^{-21}	ゼプト	z
10^{1}	デカ	da	10^{-24}	ヨクト	y

表３．固有の名称とその独自の記号で表されるSI組立単位

組立量	SI 組立単位			
	名称	記号	他のSI単位による表し方	SI基本単位による表し方
平面角	ラジアン (a)	rad		$m\cdot m^{-1}=1$ (b)
立体角	ステラジアン (a)	sr (c)		$m^2\cdot m^{-2}=1$ (b)
周波数	ヘルツ	Hz		s^{-1}
力	ニュートン	N		$m\cdot kg\cdot s^{-2}$
圧力，応力	パスカル	Pa	N/m^2	$m^{-1}\cdot kg\cdot s^{-2}$
エネルギー，仕事，熱量	ジュール	J	N・m	$m^2\cdot kg\cdot s^{-2}$
工率，放射束	ワット	W	J/s	$m^2\cdot kg\cdot s^{-3}$
電荷，電気量	クーロン	C		s・A
電位差（電圧），起電力	ボルト	V	W/A	$m^2\cdot kg\cdot s^{-3}\cdot A^{-1}$
静電容量	ファラド	F	C/V	$m^{-2}\cdot kg^{-1}\cdot s^4\cdot A^2$
電気抵抗	オーム	Ω	V/A	$m^2\cdot kg\cdot s^{-3}\cdot A^{-2}$
コンダクタンス	ジーメンス	S	A/V	$m^{-2}\cdot kg^{-1}\cdot s^3\cdot A^2$
磁束	ウエーバ	Wb	V・s	$m^2\cdot kg\cdot s^{-2}\cdot A^{-1}$
磁束密度	テスラ	T	Wb/m^2	$kg\cdot s^{-2}\cdot A^{-1}$
インダクタンス	ヘンリー	H	Wb/A	$m^2\cdot kg\cdot s^{-2}\cdot A^{-2}$
セルシウス温度	セルシウス度 (d)	℃		K
光束	ルーメン	lm	cd・sr (c)	$m^2\cdot m^{-2}\cdot cd=cd$
照度	ルクス	lx	lm/m^2	$m^2\cdot m^{-4}\cdot cd=m^{-2}\cdot cd$
（放射性核種の）放射能	ベクレル	Bq		s^{-1}
吸収線量，質量エネルギー分与，カーマ	グレイ	Gy	J/kg	$m^2\cdot s^{-2}$
線量当量，周辺線量当量，方向性線量当量，個人線量当量，組織線量当	シーベルト	Sv	J/kg	$m^2\cdot s^{-2}$

(a) ラジアン及びステラジアンの使用は、同じ次元であっても異なった性質をもった量を区別するときの組立単位の表し方として利点がある。組立単位を形作るときのいくつかの用例は表４に示されている。

(b) 実際には、使用する時には記号rad及びsrが用いられるが、習慣として組立単位としての記号“１”は明示されない。

(c) 測光学では、ステラジアンの名称と記号srを単位の表し方の中にそのまま維持している。

(d) この単位は、例としてミリセルシウス度m℃のようにSI接頭語を伴って用いても良い。

表４．単位の中に固有の名称とその独自の記号を含むSI組立単位の例

組立量	SI 組立単位		
	名称	記号	SI 基本単位による表し方
粘度	パスカル秒	Pa・s	$m^{-1}\cdot kg\cdot s^{-1}$
力のモーメント	ニュートンメートル	N・m	$m^2\cdot kg\cdot s^{-2}$
表面張力	ニュートン毎メートル	N/m	$kg\cdot s^{-2}$
角速度	ラジアン毎秒	rad/s	$m\cdot m^{-1}\cdot s^{-1}=s^{-1}$
角加速度	ラジアン毎平方秒	rad/s^2	$m\cdot m^{-1}\cdot s^{-2}=s^{-2}$
熱流密度，放射照度	ワット毎平方メートル	W/m^2	$kg\cdot s^{-3}$
熱容量，エントロピー	ジュール毎ケルビン	J/K	$m^2\cdot kg\cdot s^{-2}\cdot K^{-1}$
質量熱容量（比熱容量），質量エントロピー	ジュール毎キログラム毎ケルビン	J/(kg・K)	$m^2\cdot s^{-2}\cdot K^{-1}$
質量エネルギー（比エネルギー）	ジュール毎キログラム	J/kg	$m^2\cdot s^{-2}\cdot K^{-1}$
熱伝導率	ワット毎メートル毎ケルビン	W/(m・K)	$m\cdot kg\cdot s^{-3}\cdot K^{-1}$
体積エネルギー	ジュール毎立方メートル	J/m^3	$m^{-1}\cdot kg\cdot s^{-2}$
電界の強さ	ボルト毎メートル	V/m	$m\cdot kg\cdot s^{-3}\cdot A^{-1}$
体積電荷	クーロン毎立方メートル	C/m^3	$m^{-3}\cdot s\cdot A$
電気変位	クーロン毎平方メートル	C/m^2	$m^{-2}\cdot s\cdot A$
誘電率	ファラド毎メートル	F/m	$m^{-3}\cdot kg^{-1}\cdot s^4\cdot A^2$
透磁率	ヘンリー毎メートル	H/m	$m\cdot kg\cdot s^{-2}\cdot A^{-2}$
モルエネルギー	ジュール毎モル	J/mol	$m^2\cdot kg\cdot s^{-2}\cdot mol^{-1}$
モルエントロピー，モル熱容量	ジュール毎モル毎ケルビン	J/(mol・K)	$m^2\cdot kg\cdot s^{-2}\cdot K^{-1}\cdot mol^{-1}$
照射線量（Ｘ線及びγ線）	クーロン毎キログラム	C/kg	$kg^{-1}\cdot s\cdot A$
吸収線量率	グレイ毎秒	Gy/s	$m^2\cdot s^{-3}$
放射強度	ワット毎ステラジアン	W/sr	$m^4\cdot m^{-2}\cdot kg\cdot s^{-3}=m^2\cdot kg\cdot s^{-3}$
放射輝度	ワット毎平方メートル毎ステラジアン	$W/(m^2\cdot sr)$	$m^2\cdot m^{-2}\cdot kg\cdot s^{-3}=kg\cdot s^{-3}$

表６．国際単位系と併用されるが国際単位系に属さない単位

名称	記号	SI 単位による値
分	min	1 min=60s
時	h	1h =60 min=3600 s
日	d	1 d=24 h=86400 s
度	°	1° =（π/180） rad
分	’	1’ =(1/60)° =（π/10800） rad
秒	”	1” =(1/60)’ =（π/648000） rad
リットル	l、 L	$1l=1\ dm^3=10^{-3}m^3$
トン	t	$1t=10^3$ kg
ネーパ	Np	1Np=1
ベル	B	1B=(1/2)ln10(Np)

表７．国際単位系と併用されこれに属さない単位で
SI単位で表される数値が実験的に得られるもの

名称	記号	SI 単位であらわされる数値
電子ボルト	eV	$1eV=1.60217733(49)\times10^{-19}J$
統一原子質量単位	u	$1u=1.6605402(10)\times10^{-27}kg$
天文単位	ua	$1ua=1.49597870691(30)\times10^{11}m$

表８．国際単位系に属さないが国際単位系と
併用されるその他の単位

名称	記号	SI 単位であらわされる数値
海里		１海里=1852m
ノット		１ノット=１海里毎時=(1852/3600)m/s
アール	a	$1\,a=1\ dam^2=10^2m^2$
ヘクタール	ha	$1\,ha=1\ hm^2=10^4m^2$
バール	bar	$1\,bar=0.1MPa=100kPa=1000hPa=10^5Pa$
オングストローム	Å	$1\,Å=0.1nm=10^{-10}m$
バーン	b	$1\,b=100fm^2=10^{-28}m^2$

表９．固有の名称を含むCGS組立単位

名称	記号	SI 単位であらわされる数値
エルグ	erg	$1\ erg=10^{-7}\ J$
ダイン	dyn	$1\ dyn=10^{-5}N$
ポアズ	P	$1\ P=1\ dyn\cdot s/cm^2=0.1Pa\cdot s$
ストークス	St	$1\ St=1cm^2/s=10^{-4}m^2/s$
ガウス	G	$1\ G \triangleq 10^{-4}T$
エルステッド	Oe	$1\ Oe \triangleq (1000/4\pi)A/m$
マクスウェル	Mx	$1\ Mx \triangleq 10^{-8}Wb$
スチルブ	sb	$1\ sb=1cd/cm^2=10^4cd/m^2$
ホト	ph	$1\ ph=10^4lx$
ガル	Gal	$1\ Gal=1cm/s^2=10^{-2}m/s^2$

表10．国際単位に属さないその他の単位の例

名称	記号	SI 単位であらわされる数値
キュリー	Ci	$1\ Ci=3.7\times10^{10}Bq$
レントゲン	R	$1\ R=2.58\times10^{-4}C/kg$
ラド	rad	$1\ rad=1cGy=10^{-2}Gy$
レム	rem	$1\ rem=1\ cSv=10^{-2}Sv$
X線単位		$1X\ unit=1.002\times10^{-4}nm$
ガンマ	γ	$1\gamma=1\ nT=10^{-9}T$
ジャンスキー	Jy	$1\ Jy=10^{-26}W\cdot m^{-2}\cdot Hz^{-1}$
フェルミ		$1\ fermi=1\ fm=10^{-15}m$
メートル系カラット		$1\ metric\ carat = 200\ mg = 2\times10^{-4}kg$
トル	Torr	1 Torr = (101 325/760) Pa
標準大気圧	atm	1 atm = 101 325 Pa
カロリー	cal	
ミクロン	μ	$1\ \mu=1\mu m=10^{-6}m$

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