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Proceedings of the FNCA 2006 Workshop on Application of Electron Accelerator

– Radiation Processing of Natural Polymer –

12～16 December 2006, Kuala Lumpur, Malaysia

(Eds.) Masao TAMADA and Tamikazu KUME

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（Eds.） Masao TAMADA and Tamikazu KUME+

Environment and Industrial Materials Research Division,
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This workshop was co-sponsored by the Ministry of Education, Culture, Sports, Science and Technology, Japan and the Ministry of Science, Technology and Innovation, Malaysia and jointly organized by the Japan Atomic Energy Agency and the Malaysian Nuclear Agency. The main objectives of the workshop were to discuss the commercial status of radiation processing of natural polymer in the participating countries and to prepare the work plan for the Forum for Nuclear Cooperation in Asia (FNCA) activities on radiation processing of natural polymer. The workshop was attended by experts on radiation processing from China, Indonesia, Japan, Korea, Malaysia, Philippines, Thailand and Vietnam.

The radiation processing of natural polymer is divided into radiation crosslinking and degradation of polysaccharides. The radiation crosslinking of polysaccharides is mainly used to prepare hydrogel for healthcare and environment. Several hydrogels were commercialized in Korea, Japan and Malaysia, respectively. Hydrogels containing chitosan and carrageenan are currently in trial in China, Indonesia, Philippines and Vietnam. Cassava hydrogel is developing in Thailand. Radiation degraded chitosan is actually used in Vietnam and China in agriculture and aquaculture, respectively. Indonesia, Philippines and Thailand are trying in laboratory and pilot scale as plant growth promoter.

All manuscripts submitted by every speaker were included in the proceedings.

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

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+*Takasaki Advanced Radiation Research Institute*

FNCA2006 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-
2006 年 12 月 12 日～12 月 16 日、マレーシア、クアラルンプール

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[+]

（2007 年 5 月 21 日受理）

本ワークショップは文科省及びマレーシア科学技術革新省の後援のもと、日本原子力研究開発機構及びマレーシア原子力庁の共同で開催された。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。会議には、中国、インドネシア、日本、韓国、マレーシア、フィリピン、タイ及びベトナムの放射線加工の専門家が参加した。

天然高分子の放射線加工は、 多糖類の放射線架橋及び分解に分けられる。多糖類の放射線架橋は、主に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。キトサン等を含むハイドロゲルが、韓国、日本及びマレーシアで実用化された。中国、インドネシア、フィリピン及びベトナムでは、キトサン及びカラギーナンを含むハイドロゲルが臨床試験中にある。キャッサバのハイドロゲルはタイで開発されつつある。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実際に農業及び水産養殖で使用されている。インドネシア、フィリピン及びタイでは、放射線分解多糖類の植物生長促進剤効果が実証試験されている。

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。

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1. Outline of Project

1.1 Progress in Phase 1 and Outline of Phase 2 of FNCA Industrial Application Project

Tamikazu Kume
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Takasaki Advanced Radiation Research Institute, Japan Atomic Energy Agency

1. Review of the Activities on Application of Electron Accelerator in Phase 1

1.1 Name of the project:

Application of Electron Accelerator

1.2 Objective of the project:

Objective of the project is to develop new technology of EB irradiation system that has a variety of applications and good safety features, and to demonstrate its application. A self-shielded low energy accelerator system needs an initial investment much lower than a Co-60 facility. Its operation is simple and safe. The system can be applied in various fields such as radiation processing, environmental conservation, etc. The first project in the field of industry aims at wider application of electron accelerator and also aims at implementation of practical application that brings benefit for participating countries through not only the information exchange but also joint study by taking experimental data.

1.3 Achievement from FY 2001 through FY 2005

a. Specific results and outcomes

a-1) Through the workshop, the experience, data and technical information on the applications of low energy electron accelerators derived from this project are shared with other members of the FNCA countries.

a-2) Research collaboration for radiation processing of natural polymers using electron beam was conducted at JAERI-Takasaki under MEXT program (5) and bilateral cooperation (3).

a-3) The demonstration on liquid sample (degradation of natural polymer), solid (crosslinking of thin film), gas (flue gas) and wastewater were successfully implemented at JAERI-Takasaki (2002), MINT (2003), CAEP/Tsinghua University (2004) and KAERI (2005), respectively.

a-4) Development of new technology:

1) Application of radiation degraded natural polymers such as alginate, chitosan and carrageenan as plant promoter has been carried out in Indonesia, Japan, Philippines, Thailand and Vietnam.
2) EB crosslinking of thin film/sheet of agar hydrogel and sago starch hydrogel for wound dressing and facemask, respectively have been commercialized in Malaysia. In Japan, EB crosslinked hydrogel has been commercialized using CMC for bed sore and PVA for wound dressing.
3) EB treatment of flue gases is being commercialized in China and developed at semi-pilot scale in Malaysia and Korea. Radiation treatment of VOC has been developed at laboratory scale in Japan, China and Korea.

4) EB treatment of textile wastewater is being commercialized in Korea.

a-5) Publications:

1) Four proceedings of workshop were published as JAERI-Conf 2002-013, 2003-016, 2004-007, 2005-005, and another proceeding will be published.

2) More than ten papers were published in the international journal.

b. Specific social and economic impacts

b-1) Open Seminar attended by a large number of participants from industry, university and research institutes was an important activity in promoting the technology to end users.

b-2) To some countries, this project has resulted in the establishment of a national committee on the application of electron accelerator. It has also created awareness among the top management of the atomic energy commission. Efforts are being made by Vietnam, Thailand and Philippines, who do not have electron accelerators, to acquire the machine for R&D and commercial use in the near future.

b-3) List of the irradiation facilities (electron accelerator and Co-60 gamma-ray irradiator) was prepared and can be found on the website of FNCA.

2. Project on Industrial application (Electron accelerator) Proposed at EB WS 2005, November 2005, Daejeon, Korea

2.1 Backgrounds

- 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 needs an initial investment much lower than a Co-60 facility. Its operation is simple and safe.
- The current project in the field of industry aims at wider application of electron accelerator and also aims at implementation of practical application to bring benefit to the participating countries through not only the information exchange but also joint study by taking experimental data.
- This project should be market driven whereby direct linkage with end user is recommended.

2.2 Project period

From FY 2006 to FY 2008 (3 years)

2.3 Subjects and participating countries

2.3.1 Radiation degradation of natural polymers

*Agriculture (plant growth promoter):

alginate (Vietnam), chitosan (China, Indonesia, Thailand, Vietnam), carrageenan (Philippines), etc.

*Medicine and healthcare (anti-cancer, anti-microbial):

chitosan (China, Indonesia, Korea, Malaysia, Thailand, Vietnam), etc.

2.3.2 Radiation modification of polysaccharide and its derivatives

*Hydrogel for wound dressing:

chitosan (China, Vietnam), carrageenan (Indonesia, Philippines), starch (Malaysia,

Thailand), etc.
*Hydrogel for medical, sanitary use:
CMC (Japan), chitosan with PVA/PVP (Korea, Malaysia)

2.3.3 Radiation treatment of wastewater
China, Japan, Korea, Malaysia, Philippines, Vietnam

2.4 Objectives of project

1) To conduct joint comparative study on the proposed activities with regard to EB and gamma-rays
2) To analyze the advantages of the products and processing
3) To evaluate cost benefit of radiation technology in collaboration with end users

2.5 Work plan

1) Comparison of the effect on natural polymers and evaluation of the data obtained with γ-rays, high energy electron beams (HEB) and low energy electron beams (LEB)
2) Study on wastewater treatment for interested chemicals
3) Cost estimation and evaluation of the process and products
4) Establishment of working group in each member country
5) Technology transfer to the end users

2.6 Available electron beam facilities

1) Electron Accelerator in Japan (250 keV, 10 mA and 2 MeV, 25 mA)
2) Electron Accelerator in Malaysia (200 keV, 20 mA, 3 MeV, 30 mA and 1 MeV, 40 mA)
3) Electron Accelerator in Korea (10 MeV, 1 mA, 1 MeV, 400 mA and 1 MeV, 50 mA)
4) Electron Accelerator in Indonesia (300 keV, 50 mA, 350 keV, 10 mA and 2 MeV, 10 mA)

2.7 Expected output

1) Specify the benefit of EB treatment and processing of natural polymer and wastewater
2) Increase the number of the EB equipments in each member country
3) Develop new value added products for commercial application using EB
4) Transfer the technology to end user

3. Conclusion of the 7th FNCA Coordinators Meeting on Industrial application (Electron Accelerator), March 2006, Tokyo, Japan

a. Dr. Tamikazu Kume, Project Leader of Japan, made a presentation on the progress and achievements of the project. He reported on the successful workshops and demonstrations on the application of low energy electron accelerator for liquid natural polymers (Japan), thin films (Malaysia), flue gas treatment (China) and wastewater treatment (Korea) and major outcomes of the project in the participating countries.

b. He also reported that based on the good results of the project, it is proposed that it will be continued for three more years under the second phase (2006 ~ 2008) with the emphasis on radiation degradation of natural polymers, radiation crosslinking of natural polymers and radiation treatment of wastewater.

c. Dr. Machi made his presentation on the evaluation of the project. He noted that the project had made great achievements, and proposed to extend it for two more years only. He proposed that the feasibility study on economic aspects should be carried out in the second year. He also commented that it is important to make linkage with end-users in order to achieve the desired goal for industrial and commercial applications of the project.

d. He also mentioned that for the next phase of the project, it is not limited only to the application of low energy electron accelerator as it will include also high energy EB as well as gamma rays. It is also expected that economic comparison studies between gamma ray facility and EB facility will also be carried out.

e. All the participating countries had expressed their satisfaction on the achievements and supported the continuation of the project for two more years.

4. Proposal for Phase 2 and Work Plan in 2006 and 2007

4.1 Name of the project

Application of Electron Accelerator (Phase 2)-Radiation Processing of Natural Polymers-

4.2 Objective of the project

- To specify the advantage of radiation processing of natural polymers
- To promote its application for end-users
- To develop new technology on radiation processing of natural polymers

4.3 Project period

From FY 2006 to FY 2007 (2 years)

4.4 Subjects and participating countries (<u>Lead country</u>)

4.4.1 Radiation degradation of natural polymers
  *Agriculture:
    alginate (<u>Vietnam</u>),
    chitosan (Indonesia, Thailand, Vietnam),
    carrageenan (<u>Philippines</u>), etc.
  *Medicine and healthcare:
    chitosan (<u>China</u>, Indonesia, Korea, Malaysia, Thailand, Vietnam)

4.4.2 Radiation modification of polysaccharide and its derivatives
  *Hydrogel for wound dressing:
    chitosan (China, Vietnam),
    carrageenan (<u>Indonesia</u>, Philippines)
    starch (<u>Malaysia</u>, <u>Thailand</u>)
  *Hydrogel for medical, sanitary use:
    CMC (<u>Japan</u>)
    chitosan with PVA/PVP (<u>Korea</u>, Malaysia)

4.4.3 Other activities
  Mission for peer review
  Cooperation and allocation of roles between FNCA and RCA

2. Invited Paper

2.1 Review of Radiation Processing of Natural Polymer

Khairul Zaman
Malaysian Nuclear Agency

Abstract

In recent years, natural polymers are being investigated with renewed interest because of their abundant quantity and unique characteristics such as inherent biocompatibility, biodegradability and renewable. It is also known as green polymer. Natural polymers such as carrageen, alginate, chitin/chitosan and starch are traditionally used in food-based industry. But now, the applications of natural polymers are being sought in knowledge-driven areas such as healthcare, agro-technology and industry. Radiation degraded alginates, carrageenan and chitosan as plant growth promoter and protector have been developed. Radiation degraded chitosan, carrageenan and starch have also been used together with synthetic polymers for hydrogel production to be used for wound dressing, skin moisturization and for biodegradable packaging films and foams. Radiation crosslinking of natural polymer derivatives such as carboxymethyl chitosan, carboxymethyl starch have been successfully developed in Japan and used for various applications such as removal of pollutants, removal of waters from livestock excrete as well as for bedsores protection mat.

1. Introduction

Radiation processing has been extensively used in industry since 50's. The main sources of radiation are the electron beam generated from electron accelerator and gamma radiation from radioactive source, Co-60. Electron accelerators come with a wide range of energy from 80 keV to 10 MeV. Radiation processing is known as clean and green process that uses neither chemical initiator, catalyses nor solvent. They are used for variety applications such as curing of thin layer coatings, crosslinking of polymeric products, to degrade polymer compounds and sterilization of medical items in big boxes. The thickness and density of the products will determine the type of energy of the electron accelerator required to perform the process. On the other hand, due to high penetration of gamma radiation, it is mainly used for the sterilization of medical products and irradiation of food items that are bulky and packed with high-density products. Currently there are about 123 gamma irradiation units around the world and 85 % of them are for sterilization purposes 1). In Malaysia, we have 4 gamma irradiation industrial plants for sterilization services. On the other hand, there are more than 900 units electron accelerators around the world and about 6 units are in Malaysia 2).

When polymer material is exposed to radiation at any temperature, under any pressure, and in any phase (gas, liquid or solid), chemical reaction will occur even in the absence of catalyst or initiator. Reactive intermediates will be formed either in the form of radicals, or positive/negatively charge species that subsequently undergo chemical reaction at the molecular level. The ultimate effects of these reactions can be the formation of oxidized products, grafts, scission of main chains or crosslinking. The degree of these transformations depends on the structure of the polymer and the conditions of treatment before, during and after irradiation. Good controls of all of these processing factors facilitate the modification of polymers by radiation processing.

Natural polymer such as polysaccharide (cellulose, chitosan, carrageenan, alginate) is largely available in nature well known radiation degraded. In recent years, natural polymers are being investigated with renewed interest because of their abundant quantity and unique characteristics such as inherent biocompatibility, biodegradability and renewable. It is also known as green polymer. Natural polymers such as carrageen, alginate, chitin/chitosan and starch are traditionally used in food-based and few in healthcare industries. But now, the applications of natural polymers in knowledge-driven areas such as healthcare, agro-technology and industry are increasing.

2. Radiation Effects on Polysaccharides

Excitation and ionization are the primary events that occur when polymer molecules are directly exposed to high-energy radiation. That leads to the formation of reactive species called radicals within the molecular chains of the polymer. Subsequently, these free radicals will undergo rearrangement or formation of new bonds structure depending on the molecular structure and conditions of the reactions and irradiation. The ultimate effect of these reactions is the formation of oxidized products, grafts, crosslinking and scission of main or side chains which is called degradation. Gamma irradiation of polysaccharide powder leads to the degradation of these compounds accompanied by decomposition of the pyranose ring and formation of compounds with carbonyl and carboxy groups, as well as formation of hydrogen, carbon dioxide, and carbon monoxide 3). The efficiency of degradation increases considerably with temperature and depends on the structure of the polysaccharide and the nature of its constituents.

High energy radiation has been shown to be effective in reducing the molecular weight of starch, alginate, chitosan and carrageenan 4 ~ 6). In aqueous solution of polysaccharides and its derivatives (conc, <10 %), hydroxyl radicals have been shown to react predominantly with the polysaccharides by H abstraction at a rate of reaction ~ 10^8 $M^{-1}s^{-1}$ and to cause the breakdown at the glucosidic chain. Hydrated electron has been shown to react with CM-chitin and CM-chitosan but at lower rate, ~ 10^7 $M^{-1}s^{-1}$ 7~10) . In the radiation chemistry of polysaccharides, the scission of glycosidic linkage is the most dominant process as it leads to the reduction of their molecular weight as shown in Figures 1 and 2. In disaccharides and polymeric carbohydrates, the ether type radicals such as 1 and 2 have the radical site proximate to the glycosidic linkage and therefore play a major role in scission.

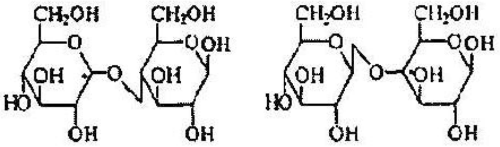

Fig. 1 Formation of glucosidic radicals

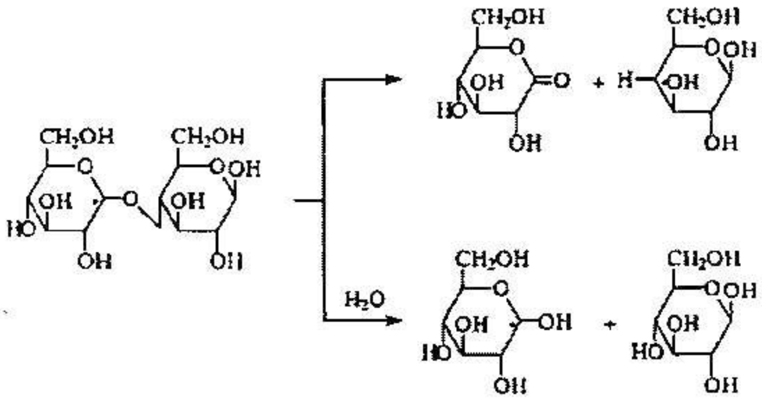

Fig. 2 Basic transformations of glucosidic bond-scission

Radiation degradation of polysaccharides and its derivatives occurs at solid states and in aqueous solution with concentration less than 10 % as shown in Figures 3 and 4. However, it was found that at paste-like form, at the concentration above 10 % and up to 50 %, polysaccharide derivatives of carboxymethyl (CM) starch or CM-cellulose will undergo radiation crosslinking to form hydrogel 12 ~ 14).

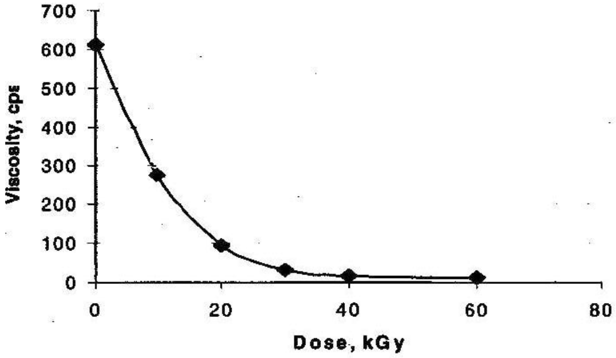

Fig. 3 Effect of irradiation dose on viscosity of 10 % starch gelation in aqueous 4)

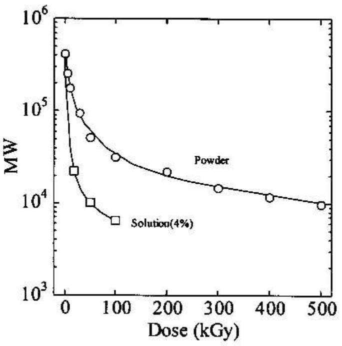

Fig. 4 Molecular weight reduction of irradiated chitosan in solid state and in aqueous solution and 4 % conc. 11)

Gel strength that indicates radiation crosslinking density of the hydrogel will increase as the concentration of CMS and CMC increases as shown in Figures 5 and 6. The degree of substitution (DS) of water-soluble polymer, CMS or CMC has influenced on radiation crosslinking of the hydrogel. Radiation crosslinking will enhance when the DS is high.

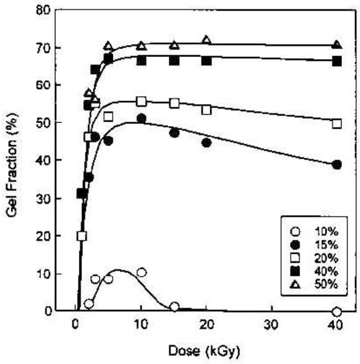

Fig. 5 Effect of concentration on crosslinking of CMS irradiated in vacuum 12)

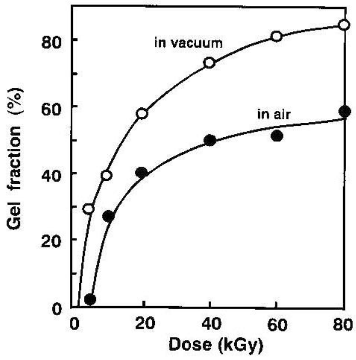

Fig. 6 Crosslinking of CMC(30 %) irradiated in air and vacuum 14)

With this finding, radiation crosslinking hydrogel can be prepared from polysaccharide derivatives (carboxymethyl polysaccharides) without having to blend with other water-soluble polymer. Polysaccharide has disadvantages over CM-polysaccharide whereby it degrades upon irradiation and it has to be blended with other radiation crosslinkable water soluble polymer such as poly(vinyl alcohol) (PVA), poly(N-vinylpyrrolidone) (PVP) or poly(ethylene oxide) (PEO) to form hydrogel. However, radiation degraded polysaccharides have direct applications that will be described later in this paper.

3. Applications of Radiation Processing of Polysaccharides in Agriculture

The oligosaccharides derived from depolymerization of polysaccharides through enzymatic hydrolysis have been reported to exhibit growth-stimulating activity like phytohormones that induce the promotion in germination, shoot and root elongation in variety of plants [15~17]. Radiation degraded polysaccharides also show similar effects as plant growth promoter. Radiation degraded alginate solution (4 %) at 100 kGy has been shown to significantly enhance the growth of rice in hydrophonic system [18]. They showed that the suitable range of concentration of degraded alginate was between 20 ~ 100 ppm to impact 15 ~ 60 % weight gain of rice and peanuts respectively. On the other hand, Tomoda et al. showed that higher concentration, 1,000 ppm of degraded alginate prepared by degradation of enzymatic lyases was required to obtain the optimum growth-promotion of barley roots.

A similar study has been conducted by Relleve et al., [19] using irradiated carrageenan for rice seedlings under non-circulating hydrophonic condition. The study showed that kappa carrageenan irradiated at 100 kGy gave maximum weight gained. However, iota carrageenan exhibited less growth promoting properties than kappa carrageenan and required higher irradiation dose to degrade at approximately the same molecular weight as kappa carrageenan. Both of irradiated iota and kappa carrageenan have caused the disappearance of fungi growth on the roots of rice. In the case of irradiated chitosan (oligochitosan), it has been shown not only exhibit as plant growth promoter, but also exhibit highly anti-microbial activity. Irradiated chitosan either in solid state of in aqueous solutions are able to suppress the growth of various fungi strains and showed higher fungicidal effect than that of non-irradiated chitosan [20]. It has been recognized as potent phytoalexin inducer (elicitor) to resist infection of diseases for plants.

Oligochitosan has also been shown to be able to form chelate complexes with metal in solution such as vanadium (V) that is well known to cause stress to plant. The addition of irradiated chitosan solution to plant seedlings of rice, wheat, soybean and barley contained VCl_3 has able to suppress the absorption and transportation of Vanadium to the leaf from root of the plants [21]. The effects of radiation degraded polysaccharide on the growth promotion of plant is not well understood. However, radiation degraded polysaccharide can be control to certain size of molecular weight to produce oligosaccharides that are mobile and easy for uptake by the plant. Radiation has also been shown does not affect the functional groups of carrageenan ($-OSO_3^-$) and chitosan ($-NH_2$) but instead enhance the anti-microbial activity of the oligosaccharides that improved the plant resistively towards fungi attacked.

4. Application of Radiation Processing of Polysaccharide for Healthcare

Hydrogels are three dimensional network structures of hydrophilic polymers that swell but do not dissolve in water. Many materials, both naturally occurring and synthetic can be radiation crosslinked to form three dimensional network as hydrogels. Hydrogels based on synthetic polymers include poly(hydroxyalkylmetharylate), poly(acrylamide), PEO, PVP and PVA. Polysaccharides derivatives such as carboxymethyl (CM) starch, CM-cellulose, CM-chitosan are some of the examples of natural based polymers that can be radiation crosslinked to form hydrogels.

Hydrogels have found wide range of bio-medical applications that include wound and burn dressing, control drug delivery systems, tissue scaffold etc. Hydrogels based on synthetic polymer, that is radiation crosslinked PVP has been successful developed and used for wound and burn dressing by Rosiak [22] and it has now been commercialized. Since then, several countries in the Asia and Pacific Region such as India, Vietnam, China, Philippines, Indonesia and Malaysia have developed the blend of natural polymers with synthetic water soluble polymers that radiation crosslinked to form hydrogel for wound dressing applications. Japan has developed radiation crosslinked synthetic hydrogel made of polyvinyl alcohol as well as radiation crosslinked natural polymer hydrogel made of CM-starch and CM-cellulose.

In Malaysia, the Malaysian Institute for Nuclear Technology Research (MINT) has developed radiation crosslinked starch-PVA hydrogel for biogel face mask as well as for wound dressing. Starch hydrogel for biogel facemask has been commercialized. Figures 7 and 8 showed the gel strength of hydrogels starch-PVA and starch-PVP respectively. Both results showed increase in gel strengths with increase in starch and PVA/PVP content up to 10 %. Sufficient gel strength is required for easy handling of the hydrogel. However, it has to be balanced with the water content of the hydrogel since the water absorption capacity of hydrogel will drop with the increasing content of starch as shown in Figures 9 and 10.

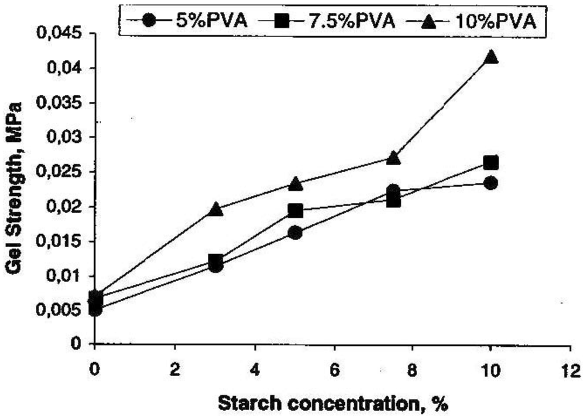

Fig. 7 Gel strength of starch-PVA blend at different blend ratio irradiated at 20 kGy [4)]

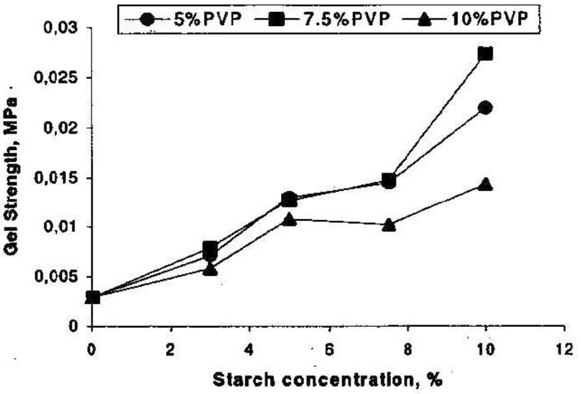

Fig. 8 Gel strength of starch-PVP blend at different blend ratio irradiated at 20 kGy [4)]

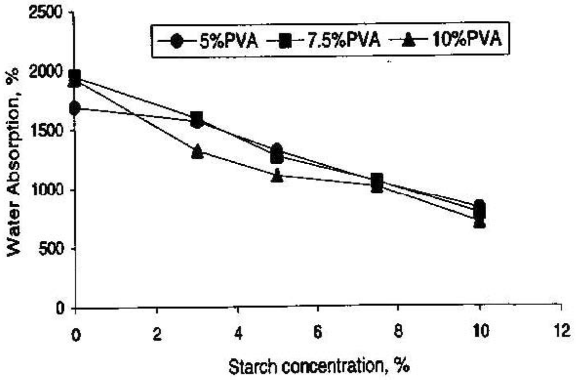

Fig. 9 Water absorption of starch-PVA blend at different blend ratio irradiated at 20 kGy [4)]

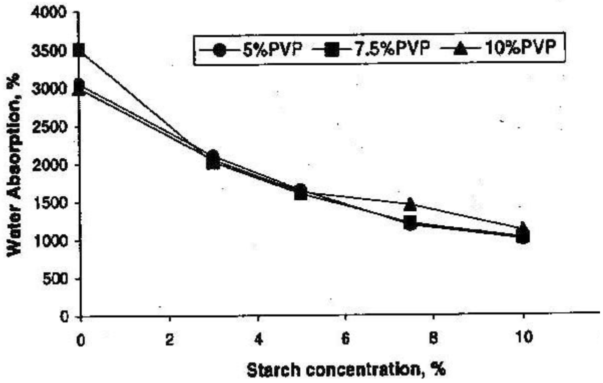

Fig. 10 Water absorption of starch-PVP blend at different blend ratio irradiated at 20 kGy [4)]

5. Other Applications of Radiation Processing of Natural Polymers

In addition to the above applications, radiation crosslinked hydrogels such as radiation crosslinked CMS and CMC is now being used for bedsore prevention mat. The bed mat is filled with soft crosslinked CMC hydrogel. This bed mat is useful for preventing bedsore in particular for bed-ridden patient and for surgical operation mat [23)]. On the other hand, the CMC hydrogel waste can be converted into fertilizer by degradation of bacteria in soil. CMC dry gel has also been used to reduce water content in livestock excrete that contains water up to 85 ~ 90% [23)]. In conventional process, saw dust is mixed with the excrete at a volume ratio of 1.0 to 1.5 to reduce water content up to 65 ~ 70 % which subsequently undergo fermentation process. In Japan, dumping and outdoor storage of livestock excretes are prohibited. The use of CMC gel together with saw dust has significantly reduce water content in the excretes and provide easy handling of the waste for further fermentation process. Biodegradable CMC gel disappears by degradation of bacteria and water evaporation during fermentation.

To date, convergence of technology is a way forward. Previously, in the viscose process, radiation processing was used to reduce the molecular weight of the cellulose pulp and followed by dissolving the cellulose pulp using low concentration of carbon disulphide. Integrating the radiation technology and biotechnology, cellulose pulp can now be dissolved even without using toxic carbon disulphide 24). After electron beam degradation of the cellulose pulp to a desired level, enzymatic modification is introduced to produce alkali soluble cellulose. Radiation processing of cellulosic agro-waste materials into substrate for growing mushroom and subsequently using it as an animal feed is another example of convergence radiation technology with biotechnology.

6. Conclusion

Radiation processing of natural polymers has been the subject of research by countries in this region in the past several years. Radiation technology is used to induce modification of natural polymer and its derivatives either for the reduction of the molecular weight or for crosslinking to produce three dimensional networks called hydrogels. Radiation technology itself is a green process and no additional chemical initiator or solvent is used. Products that are produced have found many applications in agriculture, healthcare and for environment protection. The challenge now is to fully utilize the technology at the commercial scale in particular for the environment protection. On the other hand, many new and emerging areas for applications of radiation processed natural polymer can be developed for pharmaceuticals, biotechnology and medical industry.

Acknowledgements

The program on the application of electron accelerator for modification of natural polymer is an on-going program under the Forum for Nuclear Cooperation Agency (FNCA). Similar project on radiation processing of natural polymer was also conducted earlier under the IAEA/Regional Cooperation Agreement (RCA) for the Asia and Pacific Region.

References

1) IAEA Directory of Gamma Processing Facilities in Member States, *IAEA-DGPF/CD*, February (2004).
2) S. Tagawa, M. Kashiwagi, T. Kamada, M. Sekiguchi, K. Hosobushi, H. Tominaga, N. Ooka, K. Makuuchi, “Economic scale of utilization of radiation (I): Industry, Comparison between Japan and USA”, *J. Nucl. Sci. Technol.*, **39**, 1002 (2002)..
3) B. G. Ershov, "Radiation-chemical degradation of cellulose and other polysaccharides", *Russ. Chem. Rev.*, **67**, 315 (1998).
4) K. Hashim, N. Mohid, K. Bahari, K. Zaman, “Radiation crosslinking of starch/water soluble polymer blends for hydrogel”, *JAERI-Conf 2000-003*, (2000).
5) N. Nagasawa, H. Mitomo, F. Yoshii, T. Kume, “Radiation-induced degradation of sodium alginate”, *Polym. Degradat. Stabil.*, **69**, 279 (2000).
6) Le Hai, Tran Bang Diep, N. Nagasawa, F. Yoshii, T. Kume, “Radiation depolymerization of chitosan to prepare oligomers”, *Nucl. Instrum. Methods Phys. Res., B,* **208**, 466 (2003).
7) T. Kume, M. Takehisa, “Effect of gamma-irradiation on sodium alginate and carrageenan powder”, *Argic. Biol. Chem.*, 47, 889 (1983).

8) P. Ulanski, J. M. Rosiak, “Preliminary studies on radiation-induced changes in chitosan”, *Radiat. Phys. Chem.,* **39**, 53 (1992).
9) M. Zhai, H. Kudoh, G. Wu, R. A. Wach, Y. Muroya, Y., Katsumura, N. Nagasawa, L. Zhao, F. Yoshii, “Laser photolysis of carboxymethylated chitin derivatives in aqueous solution. Part I. Formation of hydrated electron and a long-lived radical”. *Biomacromolecules*, **5**, 453 (2004).
10) M. Zhai, H. Kudoh, R. A. Wach, G. Wu, M. Lin, Y. Muroya, Y. Katsumura, L. Zhao, N. Nagasawa, F. Yoshii, “Laser photolysis of carboxymethylated chitin derivatives in aqueous solution. Part 2. Reaction of OH• and SO4•- radicals with carboxymethylated chitin derivatives”. *Biomacromolecules*, **5**, 458 (2004).
11) T. Kume, “Radiation Processing of Polysaccharide for agriculture”, *IAEA-SM-365/22*, p. 90 (2000).
12) N. Nagasawa, T. Yagi, T. Kume, F. Yoshii, “Radiation crosslinking of carboxymethyl starch”, *Carbohydrate Polym*., **58**, 109 (2004).
13) F. Yoshii, L. Zhao, R. A. Wach, N. Nagasawa, H. Mitomo, T. Kume, “Hydrogel of polysaccharide derivatives crosslinked with irradiation at paste-like condition”, *Nucl. Instrum. Methods Phys. Res. B,* **208**, 320 (2003).
14) B. Fei, R. A. Wach, H. Mitomo, F. Yoshii, T. Kume, “Hydrogel of Biodegradable Cellulose Derivatives. l. Radiation-Induced Crosslinking of CMC”, *J. Appl. Polym. Sci*., **78**, 278 (2000).
15) H. Akiyama, T. Endo, R. Nakakita, K. Murata, Y. Yonemoto, K. Okayama, “Effect of depolymerization alginates on the growth of Bifidobacteria”, *Biosci. Biotech. Biochem*., **56**, 335 (1992).
16) M. Natsume, Y. Kamo, M. Hirayama, J. Adachi, “ Isolation and characterization of alginate-derived oligosaccharides with root growth-promoting activities”, *Carbohydrate Res*., **256**, 187 (1994).
17) Y. Tomoda, K. Umemura, T. Adachi, “Promotion of barley root elongation under hypoxic conditions by alginate lyase-lysate (A.L.L)”, *Biosci. Biotech. Biochem*, **58**, 203 (1994).
18) N. Q. Hien, N. Nagasawa, X. T. Le, F. Yoshii, V. H. Dang, H. Mitomo, K. Makuuchi, T. Kume, “Growth promotion of plants with depolymerization alginates by irradiation”, *Radiat. Phys Chem*., **59**, 97 (2000).
19) L. Relleve, L. Abad, C. Aranilla, A. Aliganga, A. Dela Rosa, F. Yoshii, T. Kume, N. Nagasawa, “Biological activities of radiation degraded carrageenan”, *IAEA-SM-365/22*, p. 98 (2000).
20) N. Q. Hien, “Radiation degradation of chitosan and some biological effects”, *IAEA-TECDOC-1422*, p. 67, (2004).
21) L. X. Tham, N. Nagasawa, S. Matsuhashi, N. S. Ishioka, T. Ito, T. Kume, “Effect of radiation-degraded chitosan on plants stressed with vanadium”, *Radiat. Phys Chem.*, **61**, 171 (2001).
22) J. M. Rosiak, “Hydrogel dressing”, *Radiation Effects on Polymers* (*ACS Book Ser.* 475), p. 271, (1991).
23) F. Yoshii, Application of functional polysaccharide derivatives modified by radiation crosslinking techniques, IAEA Report of the Consultants Meeting on Irradiation of Natural Resources for Marketable Products, Houffalize, Belgium, Sept 30 ~ Oct. 3, p. 26 (2004).
24) H. Struszczyk, D. Ciechanska, D. Wawro, A. Niekraszewicz, G. Strobin, “Review of alternative methods applying to cellulose and chitosan structure modification”, *IAEA-TECDOC-1422*, p. 55 (2004).

2.2 Potentiality of processed natural polymers

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1. Introduction

“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 a 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.

Chitin and chitosan, one of most abundant natural polysaccharides, are also asked to find 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 1). It is well known that “Crosslinking” and “Degradation” are induced by irradiation of electron beam or radioactive rays at the same time. 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 beam irradiation.

2. Antimicrobial Activity of Chitosan

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 2). The sustained release of chitin or chitosan oligomers is expected from the crosslinked chitin or chitosan gel following radioactive irradiation, when solvated chitin or chitosan is prepared applying non-toxic solvents such as water. We have succeeded to prepare hydrated chitin 3) and chitosan slurries applying calcium chloride dehydrate saturated methanol for the dissolution of chitin followed by extensive rinsing with water and thee complete removal of acetate salt from chitosan by strong alkaline followed by extensive rinsing with water. The regeneration of chitin non-woven fabrics with rigid crystalline structure was also reported applying hydrated chitin slurry. On the antimicrobial activity, chitosan was reported to be effective to suppress microbial activities 4).

Antimicrobial activity of chitosan seems to be independent on the cell surface nature. The antimicrobial activity by chitosan was suggested that there is molecular weight dependency on the suppression of microbial activity in the case of E. coli. Thus relatively high molecular weight chitosan oligomer (higher than 9,000) is effective to suppress the bacterial and the lower molecular weight fraction (less than 2,200) seems to accelerate the bacterial activity probably due to accumulate chitosan oligomer inside of bacterial cell as nutrition. This hypothesis was confirmed by application of fluorescent labeled chitosan oligomers. But chitosan oligomer of low molecular weight fraction was converted to antimicrobial material when chitosan oligomer 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 through the radioactive or electron beam irradiation.

Chitosan molecule was reported to adsorb hemato-porphyrin-IX (HP) attached by binary carboxyl residues and then becomes to produce O-radicals on the surface of chitosan molecule following visible light irradiation [5]. EB irradiation for the HP-chitosan complex film may be useful to produce chitosan oligomers of designed size under visible light irradiation as shown in Figure 1. As di-allyl-chitin was also reported to produce C-radicals by visible light irradiation, EB irradiation may induce the rigid chitin gel and chitin oligomer with vinyl compounds which are expected to produce variously branched gel or dendorimers [6].

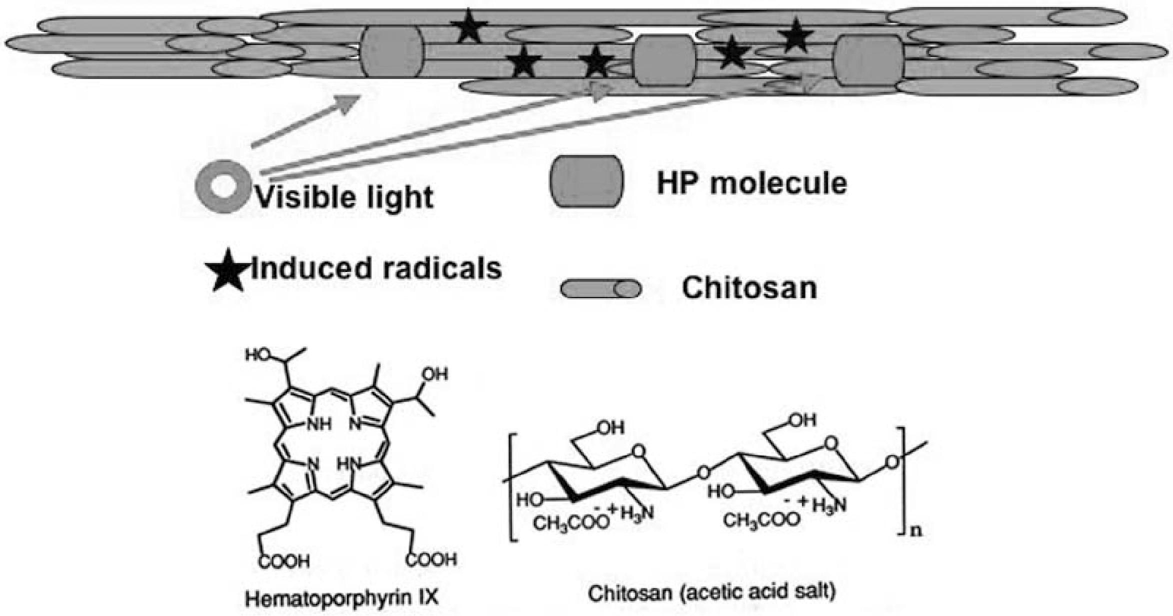

Fig. 1 Binding of hemato-porphyrin-IX on chitosan

3. Metal Injection Molding

The electron beam (EB) irradiation seems to be attractive to introduce to Metal Injection Molding (MIM) method, because meal powder mold supported by hard polymeric paste is asked to prepare before combustion to produce metallic parts [7]. 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 a 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.

4. Bacterial Cellulose

On the recycle of cellulosic wastes, the production of bacterial cellulose (BC) seems to be one of major technology applying specific bacteria or enzyme system, though BC is high cost due to specific substrate and specific condition. But the high cost might become negotiable when BC membrane or fiber is able to harvest directly from fermentation medium. A shallow pan incubator was designed to harvest BC membrane and fiber directly from the surface of fermentation medium as shown in Figure 2 and Figure 3. As seen in these Figures, BC fiber and membrane were prepared smoothly by wind up roller. EB irradiation might be effective to enforcement of BC membrane and BC fiber during direct harvest [8].

EB irradiation for gelatin fine fibers would be the effective process to make gelatin fiber water insoluble as shown in Figure 4, because the gelatin fiber produced by dry spinning of gelatin aqueous solution is water soluble [9]. 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.

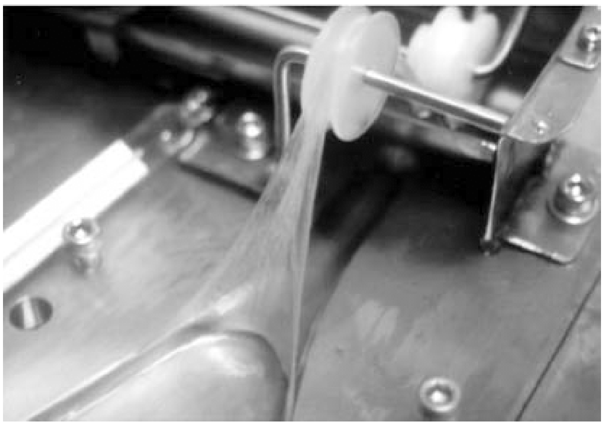

Fig. 2 The wind up of BC fiber bundle directly from medium surface

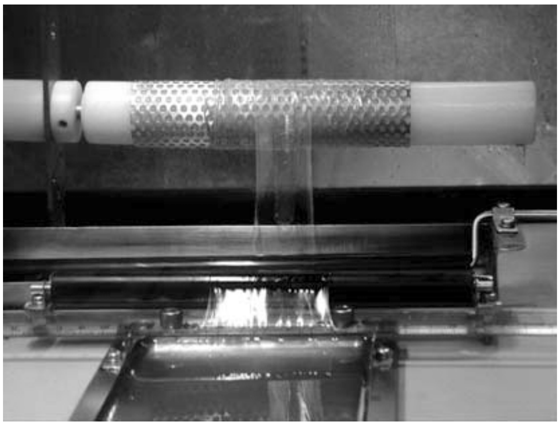

Fig. 3 Direct wind up of BC membrane from medium surface

As the crosslinking for polymeric food wastes is possible to induce, produced gel would be useful to apply for afforest plantation, because the water regain property is expected to the produced gel.

5. Conclusion

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. 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.

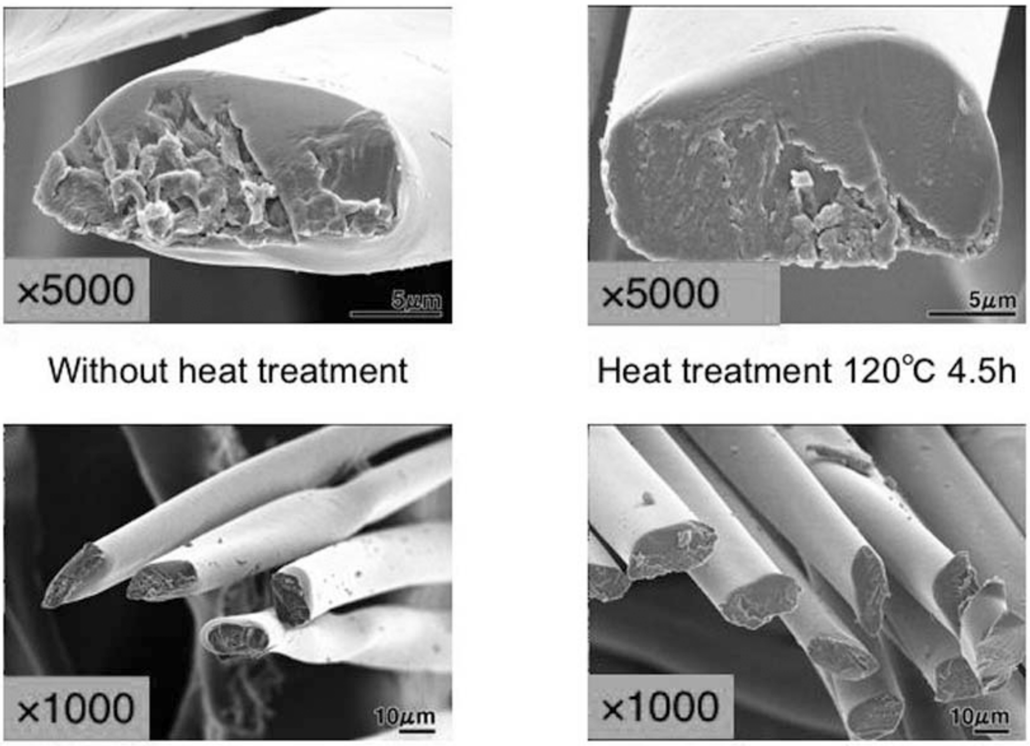

Fig. 4 Cut surfaces of fish gelatin fiber prepared dry spinning of aqueous gelatin solution

References

1) G. L. Clark, A. F. Smith, *J. Phys. Chem.*, **40**, 863 (1936).
2) S. Minami, Y. Okamoto, K. Hamada, Y. Fukumoto, Y. Shigemasa, *"Chitin and Chitinases"* ed. by P. Jelles, R. A. A. Muzzarelli, Birkhauser, Basel, Boston, Berlin, p. 265 (1999).
3) H. Tamura, S. Tokura, "*Advances in Chitin and Chitosan*" ed. by H. Struszczyk, A. Domard, M. G. Peter, H. Pospieszny, Poznan, p. 26 (2005, 2004).
4) S. Tokura, K. Ueno, S. Miyazaki, N. Nishi, *Macromol. Symp.*, **120**, 1 (1997).
5) H. Kaneko, A. Shirai, K. Takahashi, Y. Miura, K. Nitta, S-I. Nishimura, N. Nishi, S. Tokura, *Polym. Inter.*, **36**, 365 (1995).
6) S. Tokura, Y. Uraki, K. Ohmiya, A. Tsutsumi, H. Sashiwa, *Carbohydrate Polym.*, **13**, 363 (1990)
7) J. C. LaSalle, R. Bellows, *Advance in P/M & Particular Materials*, **6**, 19 (1999).
8) S. Tokura, H. Asano, N. Sakairi, N. Nishi, *Macromol. Symp.*, **127**, 23 (1998).
9) H. Tamura, H. Nagahama, S. Tokura, in preparation.

2.3 Operational & Safety Requirement of Radiation Facility

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1. Introduction

Gamma and electron irradiation facilities are the most common industrial sources of ionizing radiation. They have been used for medical, industrial and research purposes since the 1950s. Currently there are more than 160 gamma irradiation facilities and over 600 electron beam facilities in operation worldwide. These facilities are either used for the sterilization of medical and pharmaceutical products, the preservation of foodstuffs, polymer synthesis and modification, or the eradication of insect infestation. Irradiation with electron beam, gamma ray or ultra violet light can also destroy complex organic contaminants in both liquid and gaseous waste. EB systems are replacing traditional chemical sterilization methods in the medical supply industry. The ultra-violet curing facility, however, has found more industrial application in printing and furniture industries.

Gamma and electron beam facilities produce very high dose rates during irradiation, and thus there is a potential of accidental exposure in the irradiation chamber which can be lethal within minutes. Although, the safety record of this industry has been relatively very good, there have been fatalities recorded in Italy (1975), Norway (1982), El Salvador (1989) and Israel (1990). Precautions against uncontrolled entry into irradiation chamber must therefore be taken. This is especially so in the case of gamma irradiation facilities those contain large amounts of radioactivity. If the mechanism for retracting the source is damaged, the source may remain exposed. This paper will, to certain extent, describe safety procedure and system being installed at ALURTRON, Nuclear Malaysia to eliminate accidental exposure of electron beam irradiation.

2. Basic Safety Requirement

Construction of shielding of gamma and electron irradiation facilities has to ensure that during normal operation radiation exposure of workers will be negligible. It has to also ensure there is no significant exposure to members of the public. A properly design and constructed facility can minimize the potential and risk of accidental exposures. Adequate biological shielding especially the irradiation bunker and entrance interlocks for the facilities are of paramount important. Equally important is a good radiation protection program with special emphasis on training and access control such that the one emphasized in The IAEA Basic Safety Standards for Radiation Protection (BSS).

The operator of the irradiation facilities has to be highly trained and a skillful worker. These workers should keep themselves updated with new knowledge and advancement of radiation processing as well as safety matters. At ALURTRON, the operation of the accelerator is managed by operation unit that is also responsible for the maintenance of the machine. Quality and product development unit supplement the management and overall operation of the e-beam irradiator. Poorly paid and non-dedicated operators can pose serious problems to the safe operation of the irradiators. A motivational program should be introduced to minimize this factor. Figure 1 shows the organizational structure of ALURTRON. At ALURTRON, a refreshing course is conducted annually to keep operator updated with regard to safety as well the need to improve the delivery of services as stipulated in our quality management system.

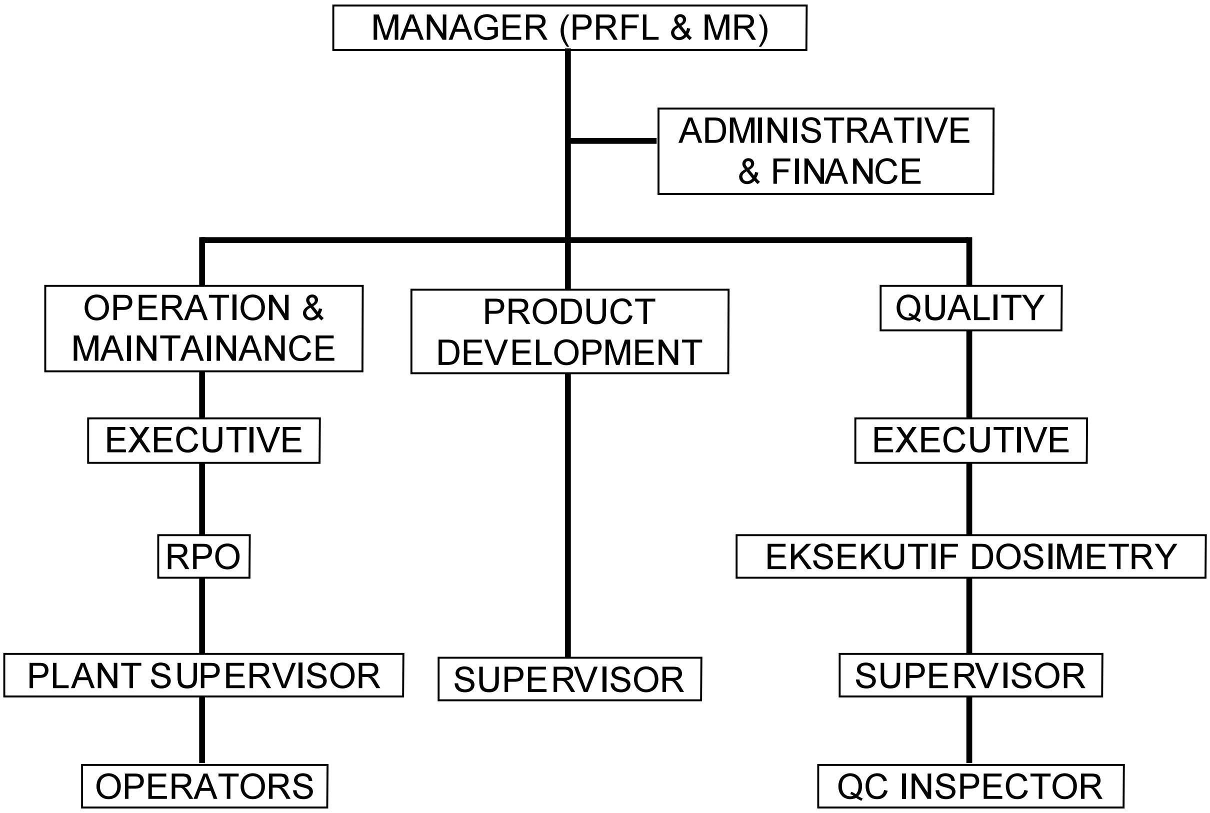

Fig. 1 Organizational structure of ALURTRON

3. Maintenance and Continuous Upgrading of Irradiator

Another important factor that needs consideration in order to ensure safe operation of irradiation centre is maintenance. Corrective and preventive maintenance programs should be implemented, as poor or inadequate maintenance of critical components will significantly increase potential of radiation exposure. As in the case of gamma irradiator, radiation exposure may result from loss of control over or damage to the radiation source as a result of neglect in the maintenance. In extreme cases the exposures may be sufficient to cause serious injury or even fatalities in the short term. Damage to the source can also lead to widespread contamination. In the case of electron beam accelerator, poor maintenance of the machine will result in frequent machine breakdown and therefore loss of irradiation time and customer confidence. At ALURTRON, routine and regular as well as annual maintenance are carried out according to the manufacturer's instructions and recommendations. Besides, many improvements and modifications were carried out to upgrade safety features to further enhance safety measures such as access control and interlocks. Figures 2, 3 and 4 show the upgraded radiation monitors at ALURTRON.

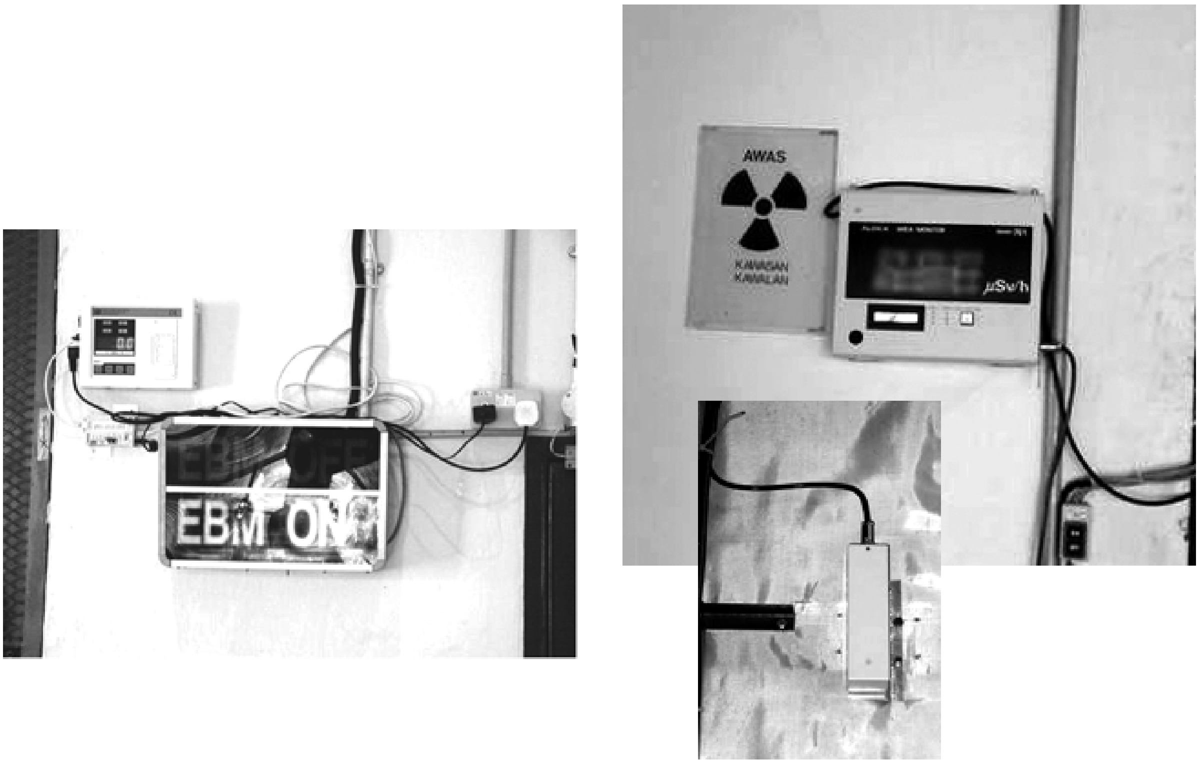

Fig. 2 Upgrading of radiation monitors at ALURTRON, (on-line area radiation monitor and X-ray detectors)

Fig. 3 Pneumatic shutter doors (access control for product and workers)

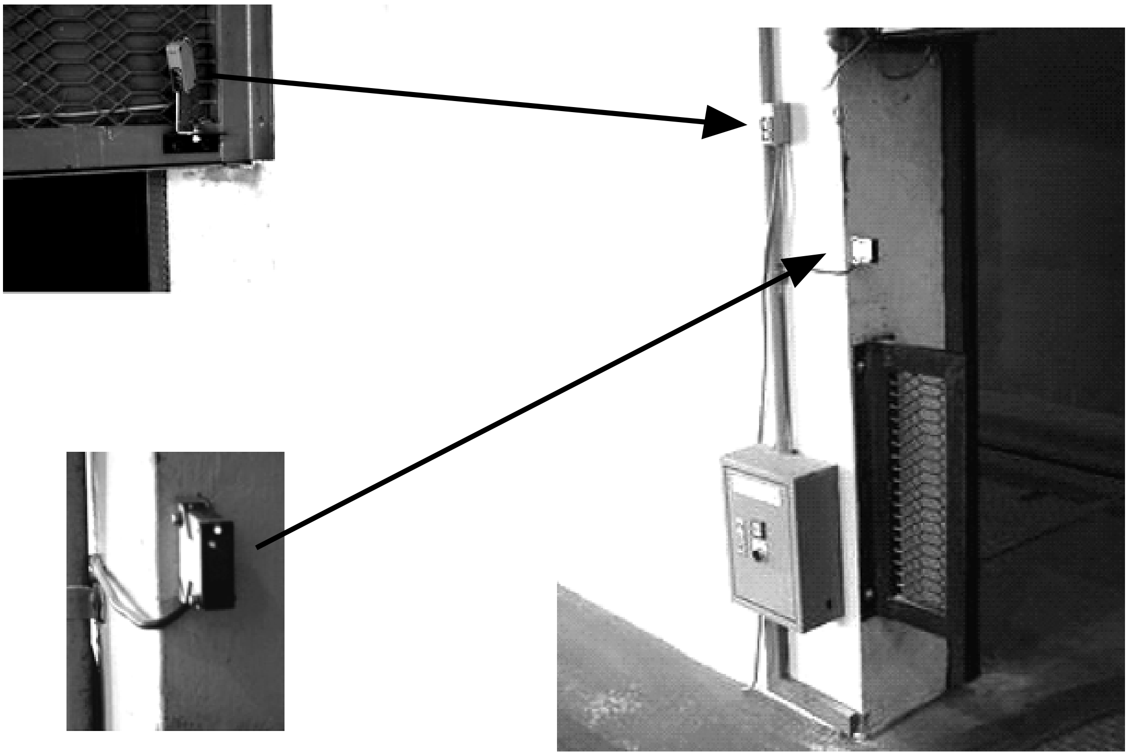

Fig. 4 Entrance checker installed at ALURTRON to monitor product entry and movement of workers

Electron beam irradiator plant should be mindful on the need to have ready stock of spare-parts. These parts normally take lengthy processes to procure them. Beside a long lead time required by the manufacturer to fabricate and supply them, bureaucracy in purchasing process and budget approval can prolong the delivery of essential parts. Delay in getting these critical components can affect availability of machine time and thus irradiation time.

Having competent technical staff will be an added advantage to electron beam accelerator facilities. These workers need to carry out routine and daily maintenance as well as visual inspection to ensure machine is in good working condition. These competent workers together with ready spare-parts can minimized the cost of getting an engineer from the machine manufacturer to carry out annual maintenance and machine overhaul if the need arises. Our ALURTRON operators cum technical staff have achieved the level of knowledge, experience and competency needed to overhaul the NHV-3000 accelerator as shown in Figures 5 and 6.

4. Safety Requirement for Irradiator

All irradiation centers must ensure that during normal operation, maintenance and in emergency situations the radiation exposure of both workers and the public is kept as low as reasonably achievable (ALARA) and follow that limit set-out and recommended in the IAEA basic safety standard (BSS). Table 1 lists the issues need to be considered to safely operate either gamma plant or electron beam accelerator.

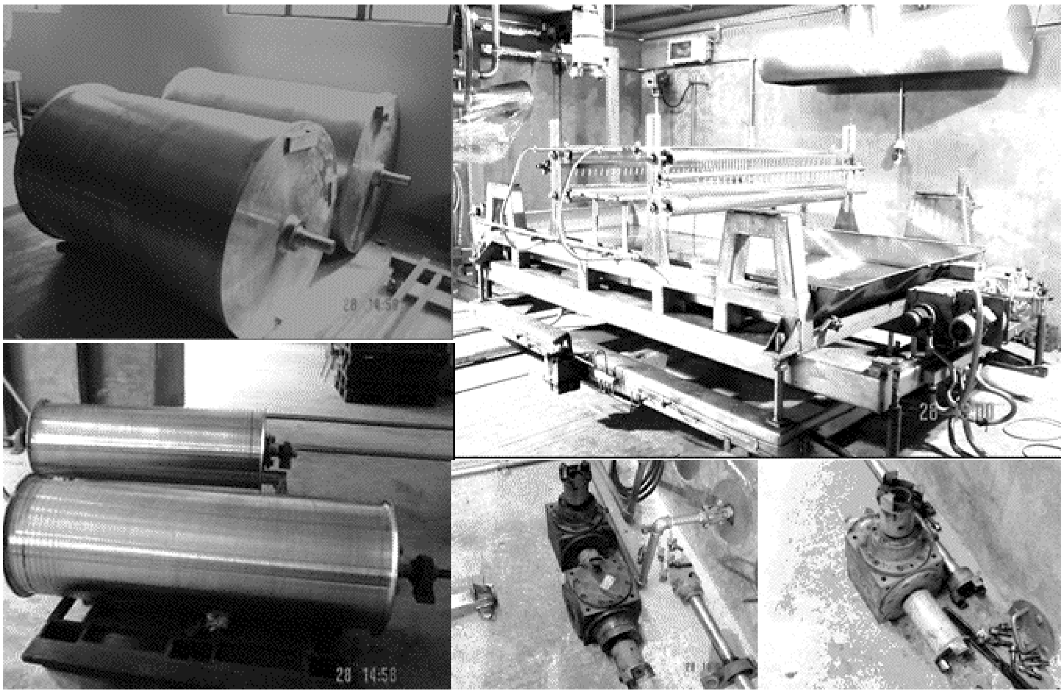

Fig. 5 Maintenance of electron beam handling equipment at ALURTRON

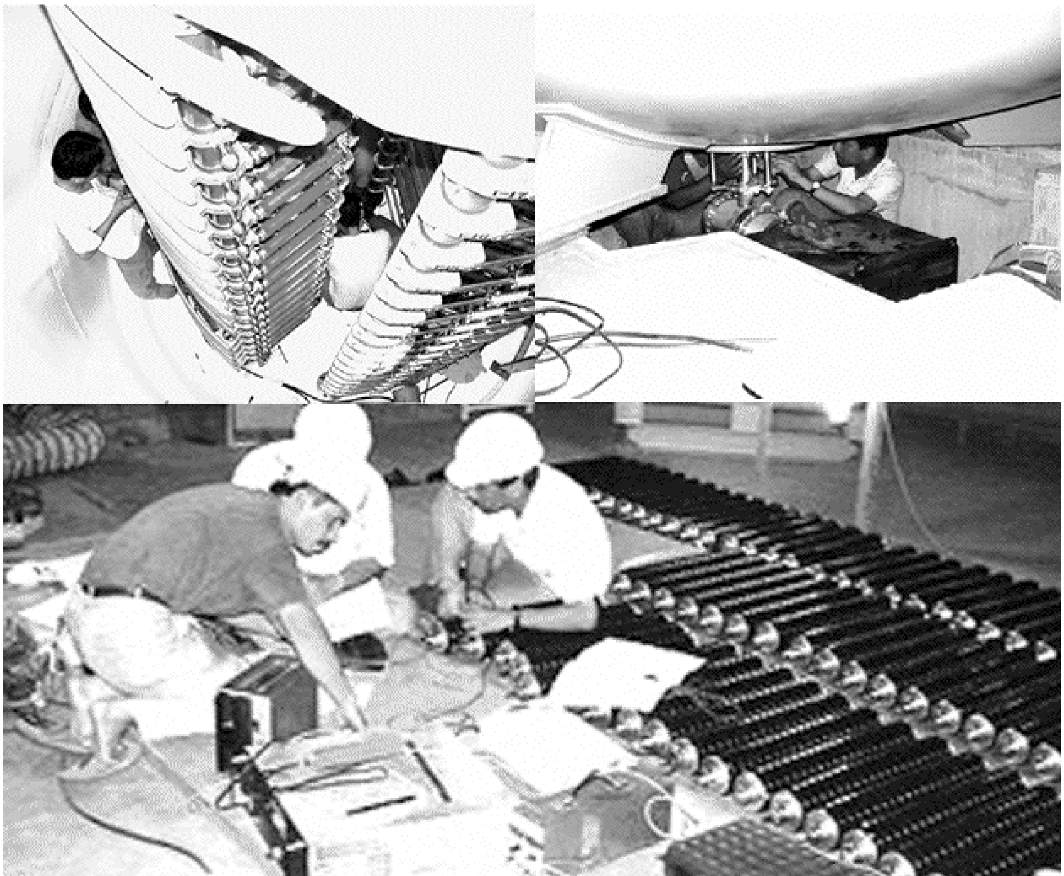

Fig. 6 Maintenance of electron beam accelerator at ALURTRON

Table 1 Requirements for safely operation of gamma irradiator and electron beam accelerator

Gamma Irradiator	Electron Beam Irradiator
Requirements for source - Design of sealed source (ISO 2919) - Source accountancy records - Source holder and rack - Source guard - Design of source capsule - Integrity of pool - Control of water level - Water conditioning	Power supply control systems - Continuous monitoring of operating parameters - Shielding - Bremsstrahlung dominates requirements -Low atomic number materials used - Spurious X-rays - Backscattered electrons - Dark currents

Other requirements are related to shielding, access rules and procedures to enter irradiation room as summarized in Table 2.

Table 2 Requirements for irradiator

Requirements for shielding (designed to keep radiation doses ALARA)	Prevention of access to irradiation room	Master control console	Requirements for irradiation room
•Use of maze entrances •Movable shielding interlocked •All leakage paths assessed •Use of radiation monitor	•Interlocks •Personnel access monitoring (CCTV, entrance checker) •Product entry and exit monitoring (product sensor) •CCTV	•Prevention of unauthorised operation •Access keys •Emergency stop provided	•Safety delay timer •Emergency exit or shielding •Emergency stop •Fire protection •Ventilation •CCTV •Buzzer/siren

The annual safety audit should be carried out by irradiation centres. This is to ensure that all related components needed to safely operate the plant are in good shape and functional. The audit report will reveal shortcomings in critical component, hardware and standard operating procedures (SOP). Any potential hazard and faulty hardware would surface from the audit exercise. The comprehensive safety checklist must include a comprehensive inspection and examination of the following areas:

- Safety control systems
- Warning systems
- Safe operation – management
- Safe operation – technical
- Quality assurance records
- Classification of areas
- Local rules
- Monitoring
- Control of visitors
- Sources of exposure
- Waste disposal
- Monitoring of public exposure
- Emergency plans
- Training and exercises
- Records

5. Conclusion

Radiation is a very powerful form of energy that, when properly used, produces profound economic benefits in industries. In many instances, radiation technology is much superior compared to alternative conventional technology in term of cost and advantages. However, since ionizing radiation is also harmful, operating irradiators such as gamma plant and electron beam accelerator need special safety consideration with regard to standard and safe operating procedure. This is to ensure that during normal operation, radiation exposure of workers will be very low and there is no significant exposure to members of the public. Most manufacturer and supplier of irradiators design their system to minimize the risk of exposure and subsequently make recommendation to facility owner on how to install and fix the necessary radiation protection measures. However, the safe operation of the irradiator remains in the hand of the operators and how these safety features were installed and maintained by the owners.

References

1) Lecture Note of RCA Regional Workshop On Radiation Safety At Industrial Irradiation Facilities Bangkok, Thailand 19 – 23 November 2001.
2) *Radiological Safety in the Design and Operation of Particle Accelerators*, ANSI-N43.1, American National Standards Institute, New York (1969).
3) *IAEA Radiological Safety Aspects of the Operation of Electron Linear Accelerators*, Technical Reports Series No. 188, IAEA, Vienna (1979).
4) *Sealed Radioactive Sources: General Classification, ISO/TC 85/SC 2/WG UN 31E*, ISO, International Organization for Standardization, Geneva (1990).
5) *Safety Assessment Plans For Authorization And Inspection Of Radiation Sources, IAEA-TECDOC-1113,* IAEA, VIENNA (1999).
6) Nuclear Malaysia Report on Safety Assessment of ALURTRON E-Beam Irradiation Facility.
7) *The IAEA Basic Safety Standards for Radiation Protection (BSS),* Safety Series 115, IAEA Vienna, (1996).

3. Country Report

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3.1 A Brief Introduction of Application of Chitosan in Agriculture of China

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Abstract

As one of the largest agricultural country in the world, China pays great attention to boost the turnout and quality of crops. Thus the well-known biological product, chitosan, has a huge potential market. Chitosan is one of the second most abundant natural resources, mainly derived from the shell of crab and shrimp, fungi, etc. Owing to its many unique properties such as biocompatibility, biodegradability, bioactivity, non-toxicity and sterilization, chitosan is extensively investigated and used in agriculture, e.g. as seed coating to improve physiological properties of the vegetables, as plant regulator to accelerate plant growth, as feed additive to promote fish immunity.

1. Current Status of Chitosan Application in Agriculture of China

At present, the theoretic output of chitosan is 0.3 million tons in China, but the practical yield is merely 30,000 tons and more than 90 % of chitosan is exported abroad. However, this situation will gradually be improved since more and more research institutes and companies are making arduous efforts into developing high add-value products based on chitosan. For instance, the symposium on chitosan is held every 2 years by the Chinese Society of Chitin Research. Currently, chitosan is mostly utilized as food preservative, seed coating, plant regulator and feed additive in the agriculture of China. The preservation effect of chitosan from housefly larvae on tomato, pepper and eggplant was studied and it was found that the three kinds of vegetables treated with chitosan were better than vacant treatment in indexes such as loss rate of water, rate of decay, intensity of respiration and content of vitamin C. It was also indicated that the preservation effect of tomato (less than 12 days) and pepper (less than 4 to 6 days) were better than eggplant 1). Lin at GuangXi University of China applied chitosan in preservative of lychee and also gained positive effect (Figure 1).

Fig. 1 chitosan as preservative of lychee

Chitosan as seed coating has not been in the market of China by so far, but there are a lot of published papers. Zhou, et al. treated seed of maize with different concentrations of chitosan, e. g. 0.1 %, 0.2 % and 0.3 %. The results showed that chitosan could increase seed germination percentage, germination index, seedling height, the content of soluble sugar and chlorophyll. Among the three concentrations, the concentration of 0.2 % was the best [2]. Chitosan is extensively studied as plant regulator in China. For example, Chen represented that chitosan improved nutrition quality and horticulture properties of plant. Simultaneously, it rapidly stimulated plant defense responses [3]. The use of chitosan as plant growth promoter has been commercialized by Hangzhou Derek Chemical Co., Ltd. Chitosan can stimulate plant growth and increase production. Meanwhile, it also can improve disease resistance of plants, immunize plants to kill many kinds of fungus, bacteria and virus. Zhang, et al. studied the effect of chitosan on chicken growing development. The experiment showed that the addition of chitosan (200 ppm) had an obvious effect on improving chicken weight [4]. Nantong Xincheng Biological industrial Ltd Co. researched and produced chitosan feed additive (Figure 2). The results testified that this kind of chitosan feed additive solution could supply nutrition for chicken and increase its weight, boost stability of fish feedstuff to improve its utilization rate in water.

Fig. 2 Chitosan feed additive

2. 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. However, environmental pollution caused by the production of chitosan is a big problem in chitosan industry of China, it is essential to take steps to solve this problem.

References

1) J. W. Huang, X. M. Zhou, et al., “Freshing effect of chitosan on several vegetable”, *Natural Enemies of Insects*, **27**, 10 (2005).
2) T. Zhou, Y. J. Hu, K. Jiang, et al., “Effect of chitosan on seed germination and seeding growth of maize”, *J. Jillian Agr. Sci.*, **29**, 8 (2004).
3) H. P. Chen, L. L. Xu, “Progress of study on chitosan in regulating plants’ growth and eliciting plants’ defense responses”, *Acta Botanica Yunnanica*, **27**, 613 (2005).
4) K. S. Zhang, Q. H. Guan, H. Q. Wu, et al., “Effect of chitosan on chicken growing development”, *J. AnHui Agr. Sci.*, **33**, 856 (2005).

3.2 Research and Development of Radiation Processing of Polysaccharide in Indonesia

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Abstract

The research activities on natural polymer in Indonesia, especially chitosan as growth promoters and carrageenan for hydrogel are summarized. Isolation processes of chitin from shrimp shell were developed and the technology was transferred to fishing villages in north and south seaside Java Island. Chitosan with 80.5 % degree of deacetylation was irradiated in dry solid, wet and aqueous solution at a dose of 50 kGy by gamma ray from Co-60 source. Irradiation of chitosan in aqueous solution gives the highest decreasing of molecule weight from 1.6×10^4 become 1.1×10^4. A large field experiment was carried out at a field of red chili in cooperation with farmer in the village. The irradiated chitosan were dissolved in water and 300 mL of water that contains concentration of 50 ppm chitosan was sprayed to red chili plant three times a week for each plant. Irradiation of chitosan in dry solid condition gives the highest degree of height growth of plant to 50.2 % and the degree of growth promotion to 92.6 %. The production yield was around 60 % higher than without using irradiated chitosan. Modification of kappa carrageenan (κC) has been carried out by radiation co-crosslinking with poly(N-vinylpyrrolidone) (PVP) to prepare a new material. Solution of κC was mixed with PVP solution at various concentrations. PVP- κC hydrogel was obtained by irradiation of the solution with electron beams. The best condition for co-crosslinking of κC with PVP was established. The PVP- κC hydrogel can be used as a matrix for immobilization of bioactive materials and wound dressing

1. Introduction

Indonesia is the world's largest archipelago with around 13,000 islands and occupies a 5,100 km stretch from the Indian to the Pacific Ocean. Shell seafood waste such as prawn shell, crabs shells are abundantly found in Indonesia. Utilization of the fishery waste to the useful product is suggested not only to recycle the fishery waste but also to reduce the environmental pollution and to improve the economic situation by preparing the field employee occupation and by bringing socio-economic benefit. The remarkable rapid and successful expansion of prawn processing industry in Indonesia suggests the possibility of utilizing prawn-processing waste as raw material for the manufacture of many valuable products such as chitin and chitosan for industrial and health care product. According to the Directorate General of Fishery Affairs. Indonesia's shrimp production in 2006 had been projected at 350,000 tons. The shrimp producing areas are located in 27 provinces. Chitosan is a linier polysaccharide derived from chitin, which is a major component of the shell of the crustacean organisms and the second most abundant biopolymer in nature next to cellulose. It is known that the radiation-degraded chitosan can induce various kinds of bioactivities such as growth promotion of plant, suppression of heavy metal stress in plant and antimicrobial activities. Radiation processing provides a simple and fast method for degradation of chitosan for a specific application. Carrageenan is the name to a family of linier sulfated polysaccharide obtained from the red seaweed. Product of seaweed in Indonesia on the Asian country is not so much compare with Philippine or Thailand. Radiation modification of carrageenan is also promising in Indonesia. Current status of the R&D carried out by BATAN in the field of natural polymer is summarized in this report, especially emphasized in chitosan as growth promoters and carrageenan for hydrogel.

2. Application of Irradiated Chitosan for Growth Promoters

2.1 Isolation of chitin

Chitin extracted from prawn shell (Penaeus Monodon), it was got from Desa Gebang, Cirebon. The prawn shells were initially washed by water then dried on the sunshine. In the beginning of our research, advisability of the natural of resource for chitin and chitosan was investigated from various kind of prawn and crab shell. The survey was done in side beach of north Java Island. We found that prawn and crabs shells are easily collected from the frozen prawn processing plant. Shell was ground using a blender. Then served to obtain particle size of (40 ~ 60) mesh. The schematic diagram of isolation chitin is shown in Figure 1.

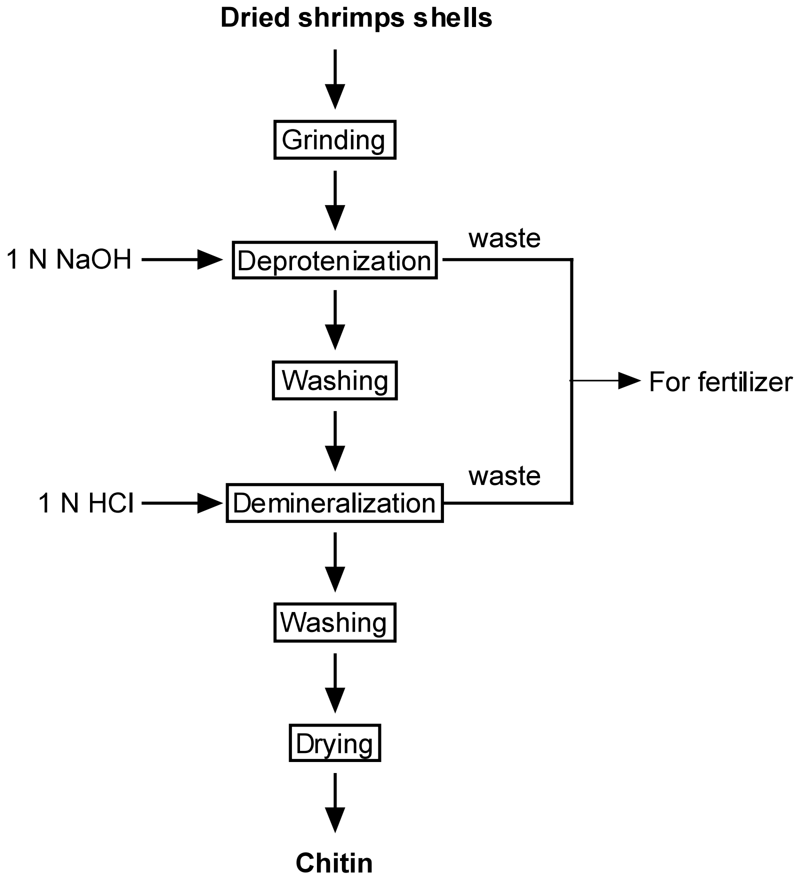

Fig. 1 Flow diagram of isolation of chitin

The average yield of isolation chitin from shrimp's shell is shown in Table 1. The number of extraction affected the yield of chitin. It was reported that the number of stage of extraction affected the mineral removal significantly. From the table it was seen that by single stage extraction the average yield of chitin was 28.7 % and the solids obtained were brown-light and still have a weak odor. This unexpected color and odor was caused by the presence of some protein mineral and pigment such as carotene. The double extraction gave an average 24.8 % and no odor, the color was white. So it is obvious that the number of extraction affected the protein and mineral removal. However for three times extraction yield of the solid was not giving significantly different compare with double extraction. It was meaning that double stage extraction was enough for isolation of chitin from shrimp's shell. This method for isolation of chitin already transferred to the fishery for developing of rural people in north and south seaside

Java Island where rich with shell shrimp or crab waste. We introduce and teach them how to make chitin from that waste after that they can make by themselves and sells the product to private company and use the waste from that process for fertilizer.

Table 1 Yield of chitin at various numbers of extractions

	Number of extraction		
	Single	Double	Triple
Yield (%)	28.7	24.8	23.2
Visual appliance			
Color	Brown light	White	White
Odor	Weak	No	No

2.2 Preparation of chitosan

The conversion of chitin to chitosan was achieved by extracting chitin in 50 percent sodium hydroxide with solid:liquid ratio = 1:20 at temperature of 100˚C for 120, 240, and 300 minutes. The data obtained gave an average yield of chitosan from chitin were 78,4 %, 75,6 % and 72,6 %. The degree of deacetylation was determined by means of FTIR spectrophotometer. It is determined by the base line method shown in Table 2. It can be seen in Table 2 that the deacetylation time gave significant effect of deacetylation. After 120 minutes degree of deacetylation reaches 78.2 %, it is gradually increased as the time increased. The highest degree of the deacetylation was achieved for 300 minutes.

Table 2 Yield and degree of deacetylation at various times of reaction

	Deacetylation time (min)		
	120	240	300
Yield of chitosan from chitin	78.4	75.6	72.6
Degree of deacetylation	65.4	78.2	79.8

2.3. Preparation of irradiated chitosan

The irradiation of chitosan was carried out in a Co-60 Gamma irradiation source. The irradiation conditions of chitosan were (1) dry solid, wet and solution (5 % chitosan in 1 % acetic acid). The irradiation dose used was 50 kGy with a dose rate of 5.1 kGy/h. Molecular weight and solubility were measured after irradiation.

2.3.1 Effect of irradiation condition of chitosan on the molecular weight and the solubility

Gamma-irradiated chitosan showed a rapid decrease in molecular weight with a concomitant increase of the solubility of the chitosan in 1 % acetic acid. Table 3 shows the effect of irradiation conditions of chitosan on the average molecule weight. Chitosan in the solution phase give a lowest molecular weight than solid and wet conditions. It is clear that radicals produced by irradiation of water could benefit to depolymerization of chain of chitosan. It was found that upon irradiation, chitosan is actually degradation of any polymer by means of irradiation causes the chain length of chitosan to become shooter with the formation of shooter fragment the molecular size, depend on the condition of chitosan used during irradiation. It was because the radiolysis of water occurs during irradiation.

Table 3 Effect of irradiation condition on average molecular weight of chitosan

	Average molecular weight (× 10^4)		
	Irradiation condition		
Dose (kGy)	Dry	Wet	Solution
0	1.574	1.574	1.574
50	1.105	0.921	0.745

Furthermore, Table 4 shows the effect of different condition of irradiation chitosan on the solubility properties (in 1 % acetic acid). The irradiation condition of chitosan gave a significant effect on the solubility of chitosan. The wet chitosan give a higher of solubility value than dry chitosan. This would tend that low molecular weight of chitosan give a better solubility.

Table 4 Effect of irradiation condition of chitosan on solubility properties in 1 % acetic acid

Dose (kGy)	Solubility (g/mL)	
	Irradiation condition	
	Dry	Wet
0	0.045	0.045
50	0.120	0.144

2.3.2 Effect of irradiated chitosan on the growth of the red chili plant

A large field experiment was carried out at a field of red chili in cooperation with farmer in the village (Figure 2). Five series with 2 replicated each were done, the experiment was carried out in 10 plots, the area of the plots was 10 m^2 (10 plants). The irradiated chitosan were dissolved in water and 300 mL of water that contains concentration of 50 ppm chitosan was sprayed to red chili plant three times a week for each plant. The growth promotion degree of the plant was calculated based on untreated one.

Fig. 2 Preparation of plots for experiment of red chili plants

Figure 3 and the data shows in Table 5 clearly demonstrated that the irradiated chitosan could effectively help developing of height of the plants faster than that of without irradiation (0 kGy) and control (without chitosan). In this experiment, chitosan with condition of dry solid state when irradiated was the most effective as red chili plant growth compare with wet and solution chitosan. It was because when chitosan irradiated in solution or wet state radical occurs from radiolysis of water damaged the active side of chitosan.

Control-without chitosan   + Irradiated chitosan

Fig. 3 Effect of irradiated chitosan on red chili

Table 5 Effect of irradiated chitosan on height of red chili plant after 3 months

Chitosan	Height of plant (cm)										Average	Growth promotion degree (%)
	Plant number											
	1	2	3	4	5	6	7	8	9	10		
Non irradiated	34	36	35	37	33	34	35	39	34	34	35.1 ± 1.34	18.2
Dry 50 kGy	50	56	58	60	52	53	52	55	52	53	54.1 ± 2.72	82.1
Wet 50 kGy	42	48	50	56	57	58	55	52	59	40	51.7 ± 5.96	74,0
Solution 50 kGy	48	42	44	50	42	43	44	40	42	40	43.5 ± 2.40	46,4
Control	32	28	33	29	27	29	29	28	32	30	29.7 ± 1.12	0

*without chitosan

Table 6 shows the effect of irradiation condition of chitosan on growth promoter for red chili plants. The chitosan irradiated at dry condition attained the highest increase of growth promotion degree (146.4 %). The lower degree of growth promotion of chitosan irradiated in solution or wet indicates that radiolysis products of water could damage the bioactive site of chitosan.

Table 6 Growth promotion degree of irradiation chitosan on red chili plants

	Average weight of red chili plant (g)	Growth promotion degree (%)
Non irradiated	21.2	69.6
Dry 50 kGy	30.8	146.4
Wet 50 kGy	27.2	117.6
Solution 50 kGy	24.5	96.0
Control*	12.5	0.0

*without chitosan

Table 7 summarizes the effect of the growth promotion of the irradiated of dry chitosan on red chili plants 40 days age. The irradiated of dry solid chitosan showed strong effect of the growth promotion on red chili plant at all and roots and leaves were found to develop at a faster rate than that of without chitosan. Results of field test showed that by spraying water contents of dry state irradiated chitosan made the productivity increase around of 60 %.

Table 7 Growth promotion effect of irradiated dry chitosan

Characteristics of plant	Control (Without chitosan)	Irradiated dry chitosan
Height (cm)	7	12
Amount of root	8	19
Length of root (cm)	3	8
Amounts of leaves	4	7

Similar plant growth promotion effects were observed in cabbage, potatoes, carrot and corn.

3. Application of Carrageenan as Hydrogel Material

The Eucheuma seaweed, which produced carrageenan, is grown in cultivation farms located mostly in North Java and in South Celebes. The carrageen family has three main branches named Kappa, Iota and Lambda, which are well differentiated in term of their gelling properties and protein reactivity. Kappa carrageenan (κC) produces strong rigid gel while those made with Iota products are flaccid and compliant. Although Lambda carrageenan does not gel in water. Modification of κC with PVP has been carried out by radiation to prepare a new material.

3.1 Effect of the composition of PVP and κC

Aqueous solution of κC with the concentrations ranged of 0 ~ 2 wt % was mixed with aqueous solution PVP in the concentration of 0~2 wt % and then homogenized at 80°C. The samples were packed in the polypropylene (PP) plastic film then irradiated to doses from 10 to 40 kGy by electron beam machine at the doses of 10 kGy/pass. Table 8 shows of the physical appearance of the hydrogels which were made by the various concentrations of PVP and κC. The best condition for co-crosslinking of κC with PVP was that in the composition of 2/2 (g/g) and the other compositions relatively did not good (fragile).

Table 8 Physical appearance of PVP- κC hydrogel by various concentrations of PVP and κC

PVP (wt %)	κC (wt %)	Physical appearance
0.5	0.5, 1.0, 1.5, 2.0	Soft and Brittle
1.0	1, 1.5, 2.0	Soft and Brittle
2.0	0.5, 1.0, 2.0, 3.0	Soft and Brittle
3.0	3.0	Tough, Brittle

3.2 Properties of PVP and κC hydrogel

The effect of irradiation on the percentage of gel content is presented in Figure 4. It can be seen that the percentage of the gel content increases by increasing of total dose, this means more crosslinking occurs. The relationship between total dose and tensile strength of hydrogel shows in Figure 5. Tensile strength increases with increasing dose.

4. Cooperation

For promoting the application of chitosan irradiated to the farmer as the users, we cooperate with local government in West Java and Center Java. Also we promote by poster in some exhibition. Also we do cooperation with Unibraw University for trial of irradiated chitosan to the farmer land and compare the results by treatments that the usually use. Study on oligo chitosan as additive for food preservation is a Joint Research with National Agency of Drug and Food Control, Indonesia.

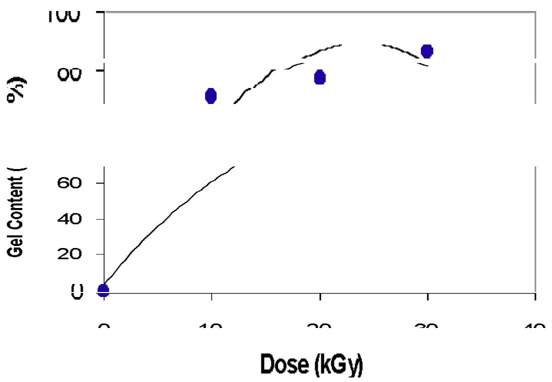

Fig. 4 Dose and gel content

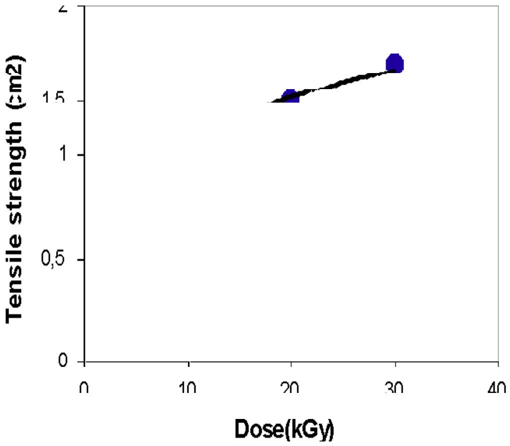

Fig. 5 Dose and tensile strength

5. Conclusions

It is clear that the irradiation treatment was applicable on modification of chitosan for growth promoters and carrageenan for hydrogel. The field data of using irradiated chitosan for red chili plant shows of the increase in production yield was around 60 % higher than without using irradiated chitosan. The best condition for co-crosslinking of κC with PVP was that in the composition of 2/2 (g/g) and the other compositions relatively did not good (fragile). The gel content hydrogel and tensile strength of hydrogel increases with increasing irradiation dose.

References

1) M. F. A. Goosen, "*Application of Chitin and Chitosan*", Technomic Publishing Company, Inc, Lancaster, Pennsylvania, USA. p. 297 (1997).
2) K. Kurita, Y. Koyama, A. Taniguchi, *J. Appl. Poly. Sci.*, **31**,1169 (1986).
3) K. N. O. Hong, S. P. Mayer, K. S. Lee, *J. Agric. Food Chem.*, **37**, 575 (1989).
4) G. T. Rekso, A. Sunarni, Kadarijah, I. Marliyanti, R. Chosdu, "Preliminary Studies of Chitin Sterilized by Irradiation," *Proceeding book of 4th Scientific Conference of The Asian Societies of Cosmetic Scientists*, Bali, Indonesia, 7-9 April, (1999).
5) G. T. Rekso, N. M. Surdia, "The Effect of Total Irradiation Dose on Graft Co polymerization of Acrylic Acid onto Chitin by pre-irradiation Technique", *Proceeding of The 4th ITB-UKM Joint Seminar on Chemistry*, Jogyakarta, 12-13 April, (2000).
6) N. Q. Hien, N. Nagasawa, L. X. Tham, F. Yoshii, V. H. Dang, H. Mitomo, K. Makuuchi, T. Kume, "Growth promotion of plants with depolymerization alginates by irradiation", *Radiat. Phys Chem.*, **59**, 97 (2000).
7) G. T. Rekso, A. Sunarni, Kadariah, I. Marliyanti, "The influence of irradiation dose for the preparation of bioplastic materials from shrimp shell", *Proceeding National Seminar* V, JASA-KAI, Mar, (2002).
8) Erizal, et al., *Technical Report, PATIR-BATAN*, 2005.

3.3 Technology Transfer on Radiation Processing of Natural Polymer in Japan

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Abstract

Carboxymethyl cellulose (CMC) crosslinked at paste-like condition forms hydrogel. The hydrogel was applied as a coolant to keep flesh of vegetables and fish at low temperature. Shochu (Japanese liquor of 25% alcohol content) residue produced by fermentation of rice and sweet potato was rapidly converted to animal feed by water absorption of CMC dry gel. Poly(lactic acid) crosslinked by irradiation in the presence of triallyl isocyanurate, TAIC was soaked in plasticizer to give softness. A maximum of 60 wt% plasticizer was incorporated in PLA resin and flexible PLA sheet was obtained. Growth of flowers was accelerated when sprayed with radiation degraded alginate and shipment schedule of the flowers was advanced to one week.

1. Introduction

Synthetic polymer materials such as polyethylene, polypropylene and rubber modified by radiation were used in various fields. FNCA member states actively carried out modification of natural polymers by degradation and crosslinking techniques. As results, plant growth promoter, wound dressing and bioform were commercialized. In Japan, radiation modification of carbon neutral materials such as polysaccharide derivatives and poly(lactic acid) (PLA) are carried out by crosslinking techniques, and practical test and preparation of test sample for marketing is done [1,2]. In this country report, current status of technical transfer of carboxymethyl cellulose (CMC) hydrogel, crosslinked PLA and radiation degraded alginate [3] are reported.

2. Application of CMC hydrogel

2.1 Radiation synthesis of CMC hydrogel

It is well known that CMC irradiated in solid phase and in dilute aqueous solution (below 10%) undergoes degradation but we found that CMC undergoes crosslinking in irradiation at paste-like condition of high concentration. High concentration is better for crosslinking of CMC. Furthermore, it was found that crosslinking is affected greatly by degree of substitution (DS) of CMC. The crosslinked CMC hydrogel absorbed much water.

2.2 Hydrogel coolant

CMC hydrogel was applied as coolant, as shown in Figure 1. The CMC gel coolant formed high quality product to cool fishes and vegetables. This coolant consists of 2 % CMC dry crosslinked gel (swollen) and other components.

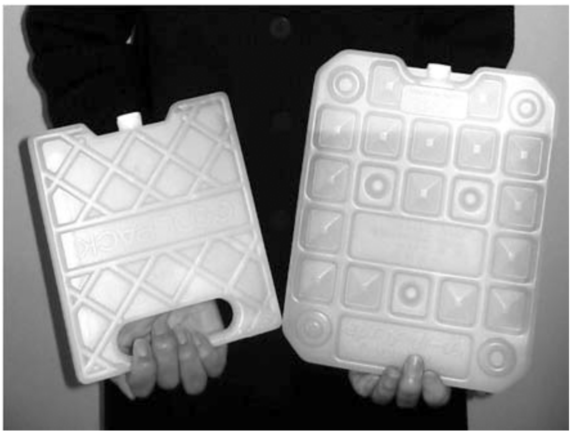

Fig. 1 CMC hydrogel coolant

2.3 Treatment of Japanese shochu residue

Japanese liquor, shochu (alcohol content, 25 %) is produce by fermentation of rice and sweet potato. After production of shochu, a lot of shochu residues are formed. These residues, which contain 90% water, are thrown away in the deep sea and rapidly gather molds. But, throwing of shochu residues on the sea will be prohibited from end of March 2007. Thus, it is desired to find new technology for reuse of shochu residue. A technology to utilize shochu residue for animal feeds was proposed, as shown in Figure 2. Practical plant for processing of animal feeds from shochu residue was installed at Kumamoto prefecture (Kyushu). Corncob is added into rotary oven to absorb water in shochu residues. After that, the mixture is dried for 2 hours at 120℃ and dry powder animal feed is obtained. In this case, corncob of 650 kg was required for one ton shochu reside treatment. So, CMC gel was added to reduce corncob. Required corncob was reduced to 200 kg by addition of 0.2 % (2 kg) CMC dry gel per one ton shochu residue. It was confirmed that water absorption by CMC dry gel is effective to convert shochu residue into animal feed.

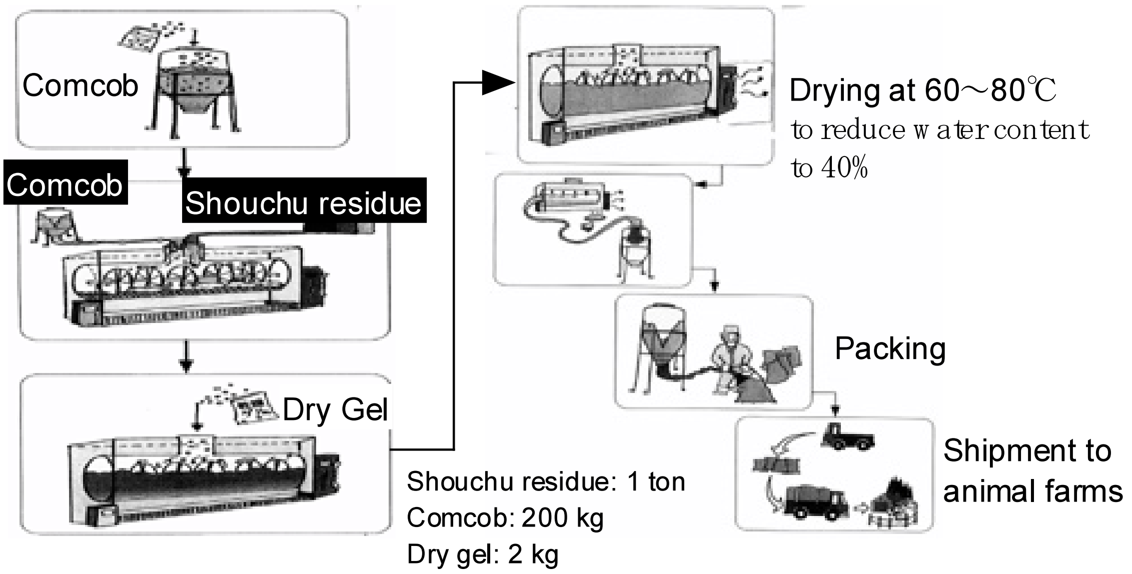

Fig. 2 Treatment of shochu residue by CMC dry gel and corncob for animal feed

2.4 Livestock excrement treatment

In Japan, release of excrement and urine from domestic animals, such as cattle and pigs, in 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 undergo fermentation smoothly. Thus, present method consists of mixing sawdust from 1.0 - 1.5 times (volume) with the excrement and urine to reduce 65 % to 70 % water content and enhancing fermentation. Addition of 0.2 % CMC dry gel to the process can reduce consumption of sawdust by 1/3 in comparison with the present method (Figure 3). This novel technology give following advantages; 1) reduction of saw dusts, small storage area for saw dust, 3) decrease in heavy work, reduction of odor diffusion in environment.

3. Application of Crosslinked PLA

3.1 Radiation crosslinking of PLA

PLA predominantly undergoes degradation under direct irradiation. When the polymer is exposed to gamma rays or electron beam, the mechanical and physical properties of the polymer decrease due to reduction of the molecular weight of the polymer. We employed polyfunctional monomers (PFM) to induce crosslinking of this degradable type polymer during irradiation. PFMs have been widely used as crosslinking agents for polyolefins. Six kinds of PFMs were incorporated to induce crosslinking of PLA. It was found that TAIC was the most effective to lead crosslinking of PLA. TAIC concentration of 3 ~ 5% in PLA gave gel fraction of 80%. Crosslinking due to presence of TAI C improved heat stability of PLA.

(a) CMC dry gel *(b) Excrement from cattle*

(c) Mixing with dry gel and saw dust *(d) Fermentation*

Fig. 3. Acceleration of fermentation in excrement composting by CMC dry gel

3.2 Marketing of crosslinked PLA

PLA has high transparency and hardness property. As mentioned earlier, heat stability of PLA was improved by crosslinking in EB irradiation in presence of TAIC. Further modification was carried out by adding plasticizer to give softness to PLA. After irradiation, crosslinked PLA was soaked in plasticizer at more than Tg to enhance concentration of plasticizer in PLA resin. Bleed (migration) test for PLA resin containing 40 wt% plasticizer was carried out at 80℃. Bleeding of plasticizer from PLA resin is hardly observed even after 2 weeks. From these facts, it was deduced that plasticizer is strongly fixated in the network structure due to crosslinking. It was also deduced that softness and flexibility of crosslinked PLA could be controlled by the concentration of plasticizer. Sheets of PLA with 40 wt% plasticizer were prepared by injection molding (Figure 4). It is confirmed that these sheets have flexibility and do not break even for bending many times. Accordingly, it is concluded that soaking method, in order to incorporate plasticizer in crosslinked PLA resin, is effective to give flexibility for thin film and sheet.

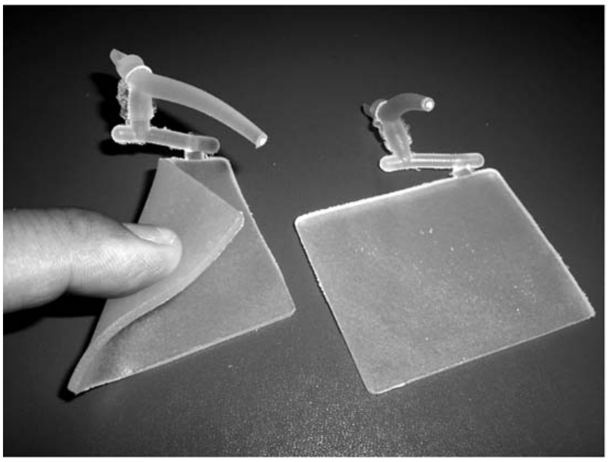

Fig. 4 Injection molding sample of PLA including plasticizer

4. Commercialized Hydrogel Wound Dressing

The hydrogel wound dressing covered on the wound accelerates its healing in a moist environment. Hydrogel wound dressings have several advantages compared to a dry type dressing, which are faster healing, no pain during pealing and no residue on the skin after peeling4). The wound dressing hydrogel synthesized by EB irradiation has been on sale since July 2004. The registered name is "VIEW GEL". VIEW GEL are used in the hospital for healing of burns, bedsores and scratches. The GEL PROTECTOR to prevent shoe sore was also developed by the same radiation processing and is available in drugstores. Hydrogel based on polysaccharides such as methylcellulosel cellulose and hydroxypropylcelluse have high gel strength and are very safe for use. In near future, applications in medical and cosmetic field of such hydrogels are foreseen.

5. Field Test of Plant Growth Promoter for Practical Application

Alginate in aqueous solution formed oligo-alginate at lower irradiation dose compared solid phase irradiation. Vietnam Atomic Energy Commission has commercialized oligo-alginate obtained by radiation degradation as a plant growth promoter. Japanese farmer (Tochigi prefecture) carried out field tests using the oligo-alginate prepared by VAEC, as shown in Figure 5. Oligo-alginate was sprayed every 2 weeks. The results revealed several advantages: (1) number of flower is rich, (2) whole volume is larger, and (3) shipment is one week earlier. From fact (3), fuel for warm heater to keep desired temperature is save.

Control (without oligo-alginate) *With oligo-alginate*

Fig. 5 Effect of plant growth promoter (oligo-alginate) on flower growth

References

1) F. Yoshii, R. A. Wach, N. Nagasawa, L. Zhao, H. Mitomo, T. Kume, "Hydrogels of polysaccharide derivatives crosslinked with irradiation at paste-like condition", *Nucl. Instrum. Methods Phys. Res. B,* **208,** 320 (2003).
2) N. Nagasawa, A. Kaneda, S. Kanazawa, T. Yagi, H. Mitomo, F. Yoshii, M. Tamada, "Application of poly(lactic acid) modified by radiation crosslinking", *Nucl. Instrum. Methods Phys. Res. B*, **236**, 611 (2005).
3) N. Q. Hien, N. Nagasawa, L. X. Tham, F. Yoshii, V. H. Dang, H. Mitomo. K. Makuuchi, T. Kume, "Growth-promotion of plants with depolymerized alginates by irradiation", *Radiat. Phys. Chem.*, **59**, 97 (2000).
4) F. Yoshii, K. Makuuchi, D. Darwis, M. T. Razzak, J. M. Rosiak, "Heat resistance poly(vinyl alcohol)", *Radiat. Phys. Chem.*, **46**, 169 (1995).

3.4 Progress in R&D on Radiation Processing of Natural Polymers in Korea

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1. Progress in the R&D on a Radiation Processing of Natural Polymers

1.2. Hydrogel based dressing "Cligel"

Dr. Nho's research members at KAERI invented a treatment dressing (commercial name; Cligel) for a patient whose skin is widely damaged by a burn, car accident etc. Compared with the petrolatum gauze that is currently used in Korea, this reduces the treatment term and improves the treatment effect without any side effect. The dressing is made of poly(N-vinylpyrrolidone) (PVP) and carrageenan, biocompatible hydrophilic polymers that can hold excess water. Since Cligel provides an appropriate moisture to a burn, wound, bedsore etc, it reduces the scars and scab formation. KAERI formed a technology transfer agreement with HUGEL Co. Ltd in September of 2001, on a gauze alternative for the treatment of a wound and burn as a government project. HUGEL Co. Ltd., a bio venture company found in December of 2002, started developing the manufacturing process of Cligel through a technical tie-up with KAERI. Cligel was approved by KFDA (Korea Food & Drug Administration) on February 11 of 2004 and is currently sold by Hyundai Pharm. Ind. Co. Ltd. Figure 1 shows the Cligel and its example of its use of) for treatment.

Fig. 1 Hydrogel based dressing (Cligel) for wound and burn treatments

1.2. R&D of a gelatin based hydrogel for healthcare.

Recently hydrogels have been increasingly studied for tissue engineering purpose since hydrogels are considered as excellent matrices for repairing and regenerating various tissues and organs. To successfully prepare hydrogels with the desired biological and physical properties, several factors such as a biocompatibility, biodegradability, sterilizability, mechanical strength, drug loading capacity, water content (degree of swelling), and the components of the hydrogels etc, must be considered carefully.

Figure 2 illustrates the procedure for the gelatin hydrogel. Gelatin, a derivative of collagen obtained through a partial hydrolysis of a collagen has been widely used in the food, pharmaceutical, and photo industries etc. For the biomedical applications, Recently, we utilized a radiation generated from a Co-60 source or electron accelerator for the preparation of crosslinked gelatin hydrogels and tested them as tissue scaffold materials.

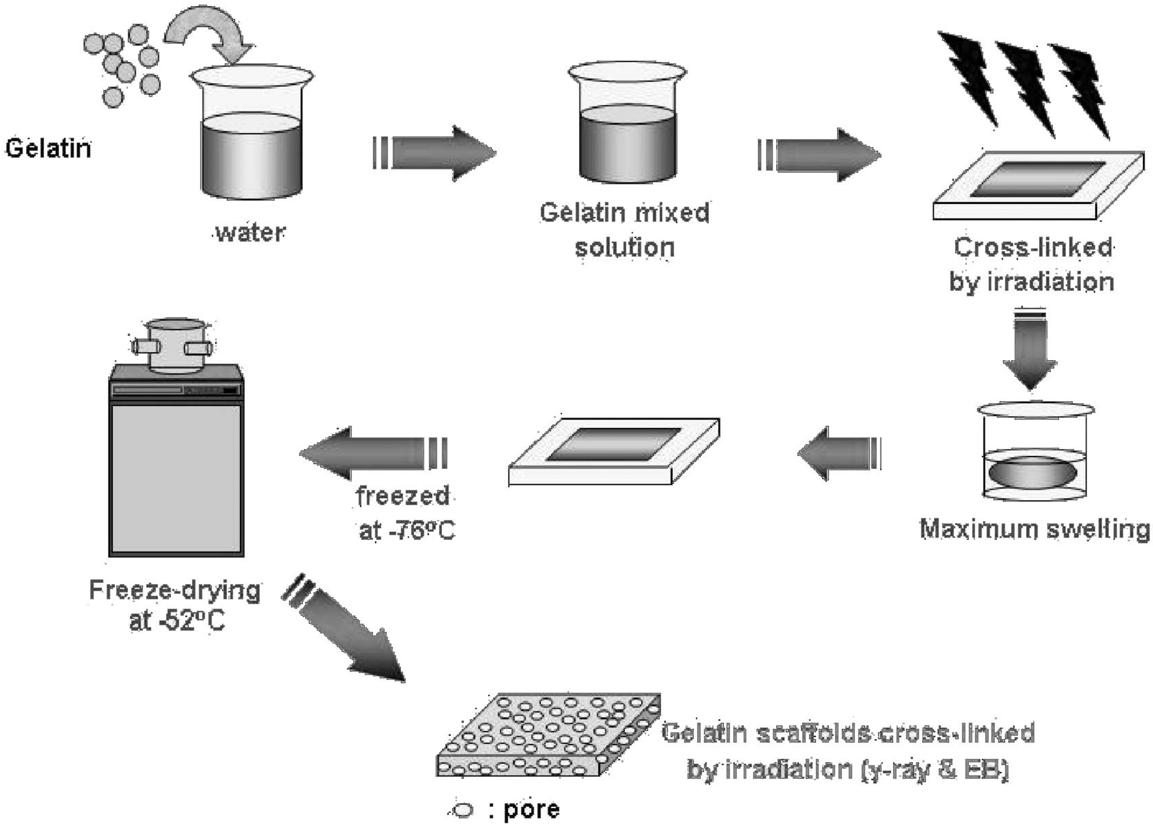

Fig. 2 Procedure for gelatin hydrogel scaffold

Tensile strength and gel fraction were measured to compare the gelatin hydrogels prepared by a gamma irradiation and an electron beam irradiation. The results indicated that no significant difference was observed between these hydrogels as shown in Figure 3.

The gelatin hydrogel scaffold obtained by freeze-drying methods, consists of large pores which provide a comfortable environment for a cell growth. SEM image (Figure 4) showed that fibroblast cells grew well in the scaffold and formed a tissue.

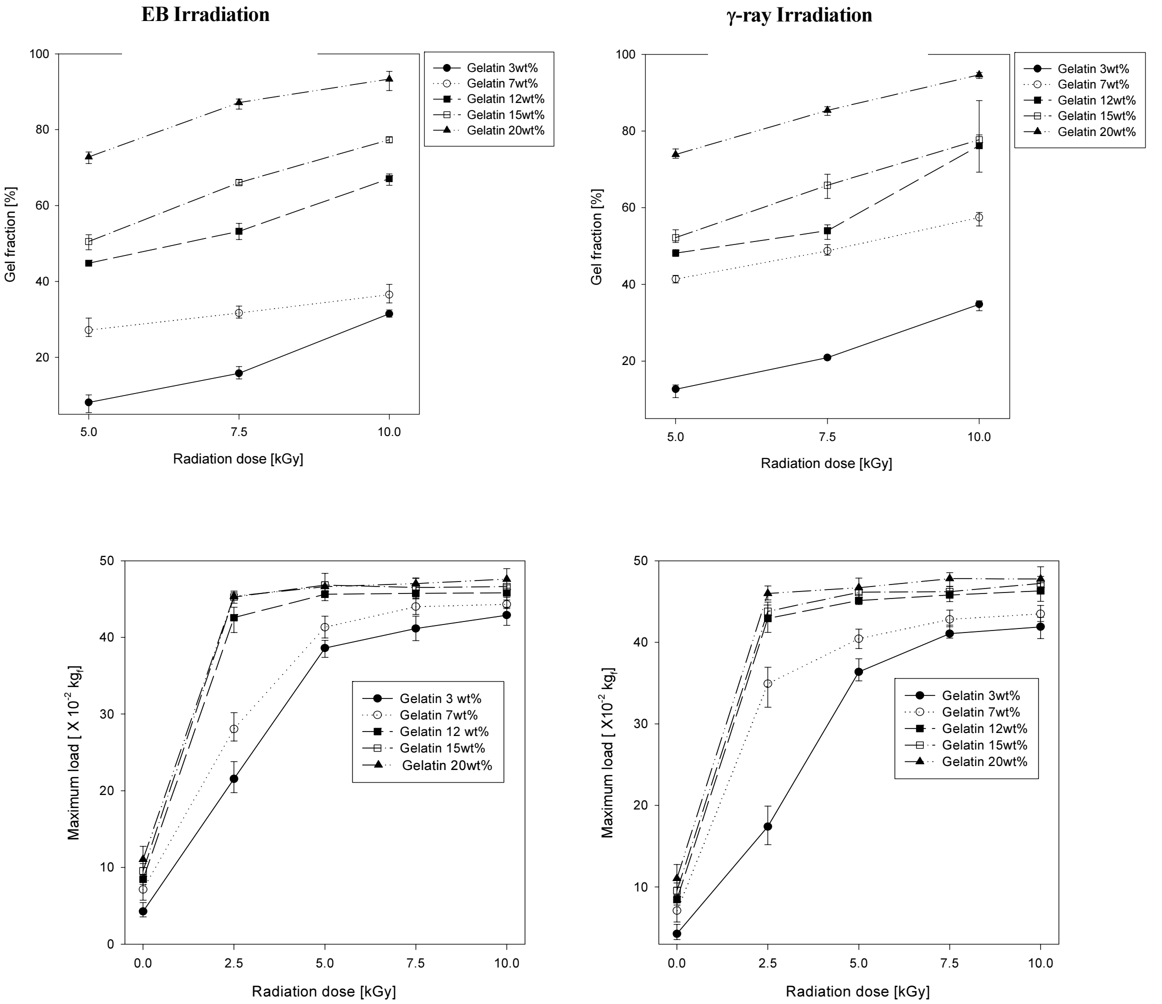

Fig. 3 Gel fraction (above) and tensile strength (bottom) of gelatin hydrogels prepared by an electron accelerator (left) and a gamma ray (right)

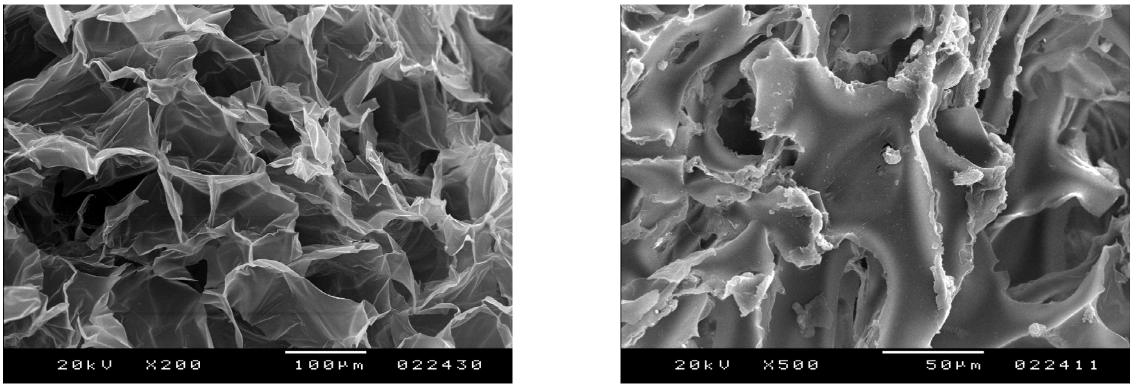

Fig. 4 SEM images before a cell culture (left) and after a cell culture (right)

We also found that the addition of DMSO to the reaction medium during γ-irradiation process provided gelatin hydrogels with a considerably high swelling property. The gel content of the hydrogels decreased as the DMSO contents or temperature increased (Table 1). During the swelling process, significant increases of the degree of swelling were observed from the hydrogels prepared in the DMSO rich solutions. The hydrogel prepared from the 30 % DMSO solution showed more than a 20-fold increased swelling at 37°C for 48 h, when compared to the hydrogel prepared in the absence of DMSO. Furthermore the degree of swelling of the hydrogels prepared in the absence of DMSO decreased as the temperature increased but the hydrogels prepared from the DMSO rich solutions showed a reverse pattern. Swelling rate of the hydrogels was measured at 37°C and is shown in Figure 5.

Table 1 Gel contents and degree of swelling of γ-irradiated gelatin hydrogels prepared in DMSO/water mixtures

DMSO Contents^{A} (%)	Gel Content ^{B} (%)			Degree of Swelling ^{B} (%)		
	Room Temp.	30°C	37°C	Room Temp.	30°C	37°C
0	92	80	76	1285	727	716
10	92	55	42	1787	3152	5358
20	92	48	39	1996	5504	9417
30	89	46	34	2440	8123	15895
50	84	37	^{C}	3406	11042	^{C}

^{A}: *DMSO contents are shown as a volume percentage of DMSO in the gelatin solution.*

^{B}: *Gel contents and degree of swelling of the hydrogels were measured after a 48 h immersion in a water bath at a given temperature.*

^{C}: *The hydrogel was dissolved at 37°C within 48 h.*

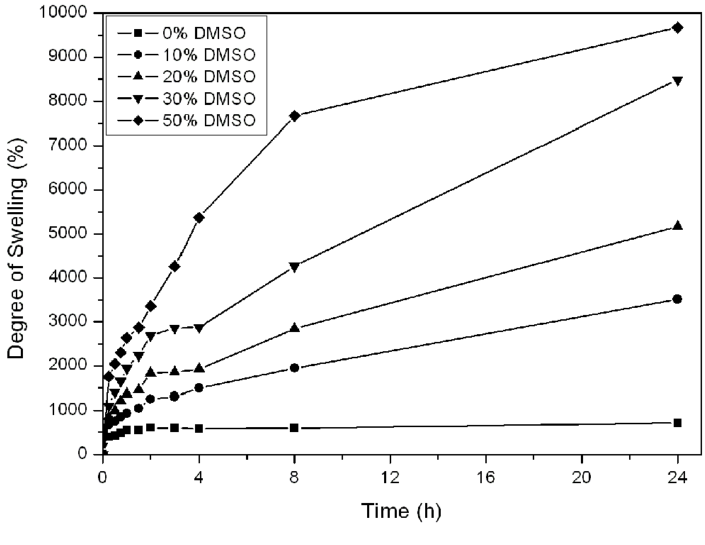

Fig. 5 Swelling (37°C) of γ-irradiated gelatin hydrogels prepared in the presence of DMSO

2. Establishment of the Advanced Radiation Technology Institute (ARTI)

Advanced Radiation Technology Institute (ARTI) of KAERI located at Jeongeup-si, Chollabuk-do, Korea (southeast area of Korea peninsula) held an opening ceremony on September 29, 2006 and many renowned celebrities attended to commemorate the ceremony. The purpose of our institute is aimed at developing radiation fusion technologies (RFT) to promote the quality of life for people throughout the world and contribute to the national economic development.

Radiation fusion technology is the advanced complex technology based on radiation technology (RT) into which the information technology (IT), nanotechnology (NT), biotechnology (BT), environmental technology (ET), space technology (ST), and military technology are merged. We are currently carrying out research on the development of radiation fusion technology in the fields of industry, environment, agri-bio resources, biotechnology, and utilization of radioisotopes, public health, and basic research.

The major radiation facilities of the institute are two Co-60 irradiators of 3 kCi and 490 kCi, a linear electron accelerator of 10 MeV and 1 mA (Figure 1), a ion implanter of 300 keV and 5 mA, and a gamma cell irradiator of Cs-137, and a gamma phytotron of 400 Ci. A cyclotron of 30 MeV is under construction and will be available in 2008. More detailed specification of the linear electron accelerator is indicated below.

Specification of the linear electron accelerator at ARTI:

- Model : UELV-10-10S
- RF energy source : klystron
- Beam energy : 10 MeV
- Beam current : 1 mA
- Beam power : 10 kV
- Scanning length : 800 mm × 200 mm (at 200 mm from extraction window)

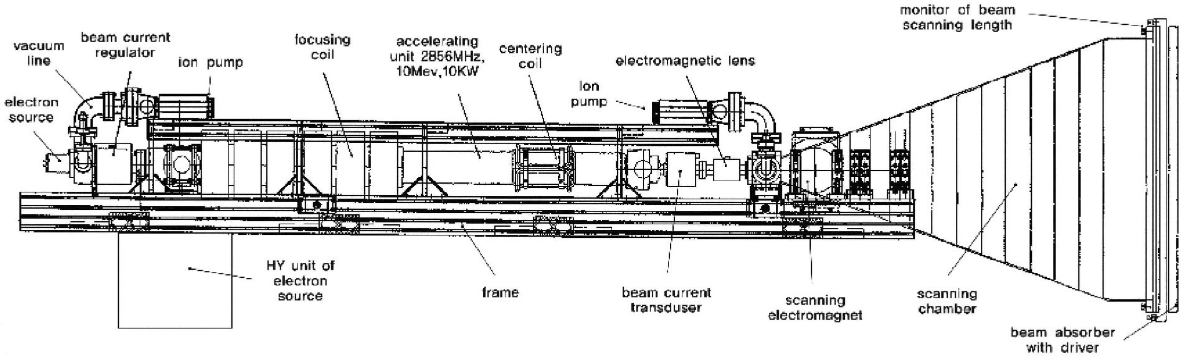

Fig. 6 Linear electron accelerator installed at ARTI in 2006

3.5 Radiation Processing of Natural Polymer in Malaysia

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Abstract

Research on radiation processing of natural polymer has been carried out by Nuclear Malaysia since 10 years ago. The progress of the research is at various stages. Radiation processing of sago hydrogel has been commercialized. Meanwhile sago film for packaging is at the pilot scale trial. Palm oil products are ready to be further developed for commercialization with any interested industrial partner. On the other hand, some new materials are being developed based on natural rubber such as liquid natural as compatibilizer, natural rubber thermoplastic nanoclay composites and natural rubber magnetic nano particles composites.

1. Introduction

Natural polymer or green polymer is becoming an important material for the future. With the increasing price of mineral oils, vis-à-vis the synthetic polymers, natural polymers is for seen as the alternative materials and received great attention such as in the development of biofuel, biodegradable plastic and environment friendly monomer/oligomer/polymer materials. Their unique characteristics such as inherent biocompatibility, biodegradability and relatively cheap and easy availability, has generated strong interest on its potential applications and economic competitiveness. Countries in this region is proud to be blessed with an extremely rich natural resources and biodiversity either forest or marine based. With modern technology, these natural resources are currently being planted or managed systematically to meet the industrial requirement in term of quantity, variety and quality.

Several types of natural polymers such as alginate, carrageen, chitosan, and starch have been the subjects of research and development by the countries in this region including Malaysia in the past several years. Radiation crosslinking of hydrogel comprising of water soluble synthetic polymers such as poly(vinyl alcohol) (PVA), poly(N-vinylpyrrolidone) (PVP) and natural polymers such as starch, chitosan, chitosan derivatives and agar have been developed in particular for healthcare and cosmetic applications. Radiation has been shown to cause the degradation of natural polymers. In hydrogel, the degraded natural polymer besides act as filler, it also provides balanced of mechanical properties and the one with the functional group provides the antibacterial and anti fungal properties. The derivatives of starch and cellulose that are water-soluble have been shown to crosslink by radiation that led to the development of new applications in the healthcare, medicine and environment.

2. Current Research and Development in Malaysia

Radiation processing of natural polymers such as sago starch, chitosan, carrageen, palm oil, natural rubber and derivatives of chitosan and starch are being carried out at various stages of R & D. Radiation processing of sago starch hydrogel has been transferred to industry for cosmetic and healthcare applications. Meanwhile, the radiation processing of biofoam and biofilm from sago starch is at the pilot scale trial. The development of carboxymethyl sago starch is now within the local industry capability. Research on hydrogel is now being extended into chitosan, chitosan derivatives and carrageenan for healthcare and biomedical applications.

Palm oil has been chemically modified into radiation curable acrylate. Currently, acrylated palm oil and its derivatives can be produced at semi-pilot scale production of 15 Liter per batch. Among the applications that have been developed by MINT are for the pressure sensitive adhesive (PSA) and industrial glue for wood products. MINT is looking for potential users and partners in the commercialization of the products and in developing other applications of palm oil acrylate.

Agrofibers polymer composite is an emerging application in many part of the world. However, in this application, the utilization of radiation has to be carefully manipulated, to be cost effective in comparison with conventional process. Current problems in the processing of agrofibers polymer composites are materials compatibility, inherent physical properties of lingo-cellulose fibers such as hydrophilicity and its structure.

Natural rubber and natural rubber latex is still one of the main natural polymers that warrant further investigation into new products and applications. Various studies have been conducted at Nuclear Malaysia onto natural rubber blends with synthetic polymers (PVC, PE and PP) for automotive parts and industrial goods. Recently, research work on radiation crosslinking of natural rubber/clay nanocomposite has been conducted to investigate the effects of nanosize clay and EB processing on the physical and mechanical properties of the composites. Natural rubber and nanosize inorganic material blend is also being investigated.

2.1 Sago hydrogel for wound dressing and bio-gel mask

Sago is non-toxic, biocompatible and biodegradable that make it suitable to be used in the health-care, cosmetic and medical products. The research activity in this area involved utilization of sago starch by solution blend with water-soluble polymer such as poly(N-vinylpyrrolidone), poly(vinyl alcohol) and carboxymethyl cellulose and by electron beam irradiation for crosslinking and sterilization of the hydrogel. Sago has been shown to improve the strength and elasticity of the hydrogel. The semi-gel property of the sago starch is an advantage in the manufacturing and handling of the product prior to electron beam irradiation.

Sago hydrogel is non-toxic, has good adhesion to skin and wound, readily remove without tendency to stick to the wound, exhibit high elasticity and also mechanical strength, ability to absorb fluid or exudates that come out from the wound, permeable for oxygen to get to the wound, prevent bacteria from environment to enter into the wound and good transparency for easy monitoring the healing process of the wound. These properties of sago hydrogel are also considered suitable to be used as bio-gel mask material. The water retaining capability of the hydrogel will keep the skin in moist condition especially for dry skin and its ability to absorb oil is advantage for oily skin. As a result of this study, sago hydrogel has been filled for patent in July 2002 under “Starch Hydrogel” with application No. Pl 20022825. The patent has also been filled in other country such as Thailand, Japan, Indonesia, China, Taiwan and Philippines.

Sago hydrogel has been licensed to Syraikat Rumbia Bio-Tech Sdn. Bhd. in September 2003 for commercialization as thin film sago hydrogel for facial mask and as sheet form sago hydrogel for wound dressing. Sago hydrogel as a bio-gel mask product for skin moisturizing and bio-cleansing is now undergoing market acceptance and promotion under the brand name **“Esllon”** by the Rumbia Biotech Sdn. Bhd. The product has been approved by the Ministry of Health, Malaysia, MAL: 05021222K. Meanwhile, sago hydrogel as wound dressing product will undergo clinical test in 2007.

At this stage, the company manages to produce 1,000 pieces per day facial mask at their GMP plant located at Nuclear Malaysia Technology Park. The sheet form wound dressings have been distributed to various local hospitals for performance evaluation of the product.

2.2 Bio-foams and Bio-films for packaging applications

Sago is an attractive indigenous polymer that can be used in the development of biodegradable raw materials and or as composites. Sago on its own cannot be expanded to produce foam. However, blending sago with other polymers notably the water-soluble type enables the blends to be expanded. Electron beam irradiation is used to induce crosslinking in the sago blends that will prevent the foam from collapse once it is cooled down. Foam expansion is achieved either by using microwave oven or extrusion process. The density of sago foam and the price of its starting materials in comparison with other foam materials are given in Table 1.

Table 1 Density of sago foam in comparison with other commercial foam products

Foam materials	Sago	Wheat	GM Corn	PE	PS
Density (kg/m^3)	0.2	0.7	0.9	0.06	0.05
Cost of raw materials (RM/Kg)	0.80	1.70	2.30	>5.00	>5.00

The mechanical properties of sago-PVP blend are given in Table 2. Figure 1 shows the effect of irradiation dose on the gel content of sago, sago-PVP hydrogel and PVP. Some sago blends such as sago-PVP formulations foamed very well but produced hard foams. On the other hand, sago-PVA blends have produced softer and more resilience foams. High irradiation dose will lead to the formation of rigid foam. As much as 80 % of sago can be added into the blends for eventual foam productions.

Table 2 Mechanical properties of sago-starch /PVA blend

Composition Sago/PVA	Dose (kGy)	Tensile Strength (MPa)	Elongation at Break (%)
0/100	0	67.01	227.00
	10	80.11	307.23
	15	89.10	246.07
	20	79.06	226.39
25/75	0	62.03	12.95
	10	60.39	5.01
	15	87.57	10.06
	20	89.30	11.47
50/50	0	53.52	11.11
	10	55.83	11.78
	15	56.49	7.18
	20	23.51	6.63
75/25	0	69.01	11.22
	10	76.87	10.55
	15	72.02	10.01
	20	47.01	6.61

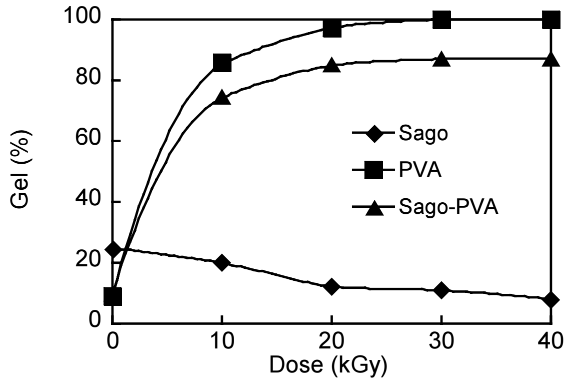

Fig. 1 Influence of dose to gel content of sago starch, PVA, blend sago-PVA films

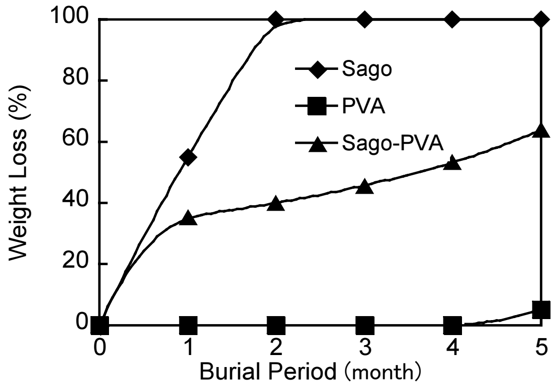

Fig. 2 Weight loss of 10 kGy irradiated sago starch PVA and blend sago-PVA films against time

On the biodegradability test, it was shown that there is a significant change in weight loss for the foam sample buried for 1 month. As much as 30 % weight loss was recorded. The weight loss was more prominent after 3 months burial that is more than 90 %. Figure 2 shows some results on the burial tests of the sago-PVP blend. Sago film is a 100 % biodegradable, compostable, and designed to replace non-degradable film made from synthetic polymer such as PE or PP. The film can be produced into various thicknesses depending on applications. Blends of sago film have been prepared into soft and hard formulation depending on its final applications. It has good mechanical strength and good water permeability. Further developmental work cum pilot scale production is required before the product can be tested commercially. Nuclear Malaysia together with the local company, Teguh Timur Sdn. Bhd. has applied the government Techno Fund to further develop the product at the pilot scale level. Meanwhile, sago film has been file for patented on 9 March 2005 with a patent no. PI20050126.

2.3 Radiation curable palm oil acrylates

Most of the radiation curable resins available commercially are derived from synthetic materials. Only a few known acrylated resins are obtained from indigenous raw materials such as soya bean, tung and linseed oils. Palm oil is a good candidate to be modified and used as radiation curable materials for coatings, adhesive, and printing ink. So far, there are three types of radiation curable resins that have been developed by Nuclear Malaysia, i.e. EPOLA (epoxidized palm oil acrylate), EPOMA (epoxidized palm oil methacrylate, and POBUA (palm oil based urethane acrylate). Of the three, POBUA has the characteristics comparable to commercial resins and is suitable to be used in coatings, pressure sensitive adhesives and printing ink. The characteristics of palm oil based PSA and palm oil acrylate resins developed at MINT are given in Table 3 and 4 respectively.

Table 3 Characterization of natural acrylate resins PSA products

Testing	PSA Properties
Rate of UV curing at conveyor speed of 10~25 m/min	Variable, 1 ~ 5 # passes
Peel Adhesion, g/inch (Paper/PET)	Variable, 280 ~ 873 g/inch
Tackiness, gf (PET)	Variable, 280 ~ 586 gf
Mode of failure	Mostly Clean Release Failure (CRF)
Environmental impact	Biodegradable, Environment friendly, Less volatile organic compound
Materials resources	Renewable

Table 4 Properties of palm oil based natural acrylate resins

Testing	Palm Oil Acrylates
Rate of UV curing at conveyor speed of 10~25 m/min	Varies, 1 ~ 5 # passes
Hardness (coatings)	20 ~ 40 %, Pendulum hardness
Adhesion (on Paper/PET/ wood substrates)	Superior, 80 ~ 100 %
Molecular weight (MW)	Variable, 2,000 ~ 20,000
Glossiness (coatings)	Standard, 60 ~ 90° at 60 degree
Environmental impact	Biodegradable, Environment friendly, Less volatile organic compound
Materials resources	Renewable

The applications of POBUA formulated resins on wood substrates (particleboards) showed very encouraging results such as; high gloss coatings, i.e., average 90 % of 60° gloss which is considered ultra gloss and high tape adhesion around 96 ~ 100 %.

The resulting pressure sensitive adhesives (PSAs) (on PET substrate) and its properties satisfactorily suggest that POBUA together with EPOLA and EPOMA have the potential to be used as oligomers in the formulation of radiation curable PSAs. POBUA on the other hand, has an added advantage of higher curing speed compare to EPOLA and EPOMA. The tackiness and peel strength values of 140 ~ 200 gf and 100 ~ 300 g/in respectively are considered sufficient for the specific PSA application such as office paper label or sticker. Efforts are being made to increase the adhesive strength (tackiness and peeling) and rate of curing of the PSAs so that they can also be used in other non-permanent type applications such as removable tapes and protective laminates. POBUA gives offset lithographic carton ink having a slightly less curing-property performances as compared to commercial acrylate oligomers. However, the POBUA made inks showed a slightly better adhesion & had almost equal apparent surface tension and IR recovery after emulsification as compared to commercial acrylate oligomer such as UCB EB-210. Efforts are being made to improve the compatibility of POBUA with other oligomers by increasing its functionalities.

Currently, three products have been filed for patent namely synthesis and production of palm oil based urethane acrylate (POBUA), pressure sensitive adhesive from epoxidized palm oil acrylate and production of hydroxyl containing palm oil based products with patent no. of PI 20031627, PI 20040082 and PI 20043088 respectively.

2.4 Liquid natural rubber and natural rubber based nanocomposites

Controlled reduction of molecular weight (MW) of solid-form epoxidized natural rubber by photochemical technique has been studied. The product would be used for preparing NR-based resin for radiation curing as well as radiation-sensitive compatibilizer for TPNR blends. The technique studied includes the effects of hydrogen peroxide on the rate of MW reduction of the solid rubber as well as its combination with reducing agent such as sodium nitrite. Analysis by FTIR spectroscopy suggests the formation of hydrogel and carbonyl groups as a result of the ring-opening of the epoxy groups of the rubber. NMR as well as IR spectra show the possible formation of furan-like species.

Among the large number of inorganic layered materials that exhibit intercalation capabilities, layered silicates is one of the most typical materials used because of the versatility of the reactions that can be designed. In particular, the smectite group of clay minerals such as montmorillonite, sponite and hectorite has excellent intercalation abilities. The combination of clay silicate layers and polymer matrices at nanoscale level constitutes the basis for preparing an important class of inorganic-organic nano-structured materials.

The use of radiation technique to process nanostructured materials or to produce nanostructured materials have been shown technically superior as alternative and viable techniques for further commercial exploitation. The main focus of this research is to utilize indigenous natural polymer for production of nanocomposites material. Natural rubber/clay composites and thermoplastic natural rubber/clay composites are important materials that currently being studied.

The natural rubber used in this work is of grade SMRL (Standard Malaysian Rubber) and the clay used is sodium montmorillonite modified with various types of cationic surfactants such as dodecylamine and octadecylamine, in order to make the galleries hydrophobic and thus more compatible with the elastomer. Organophillic clay (MMT) was prepared by cationic exchange process of sodium montmorillonite in dodecyl or octadecyl ammonium chloride aqueous solution. Natural rubber/clay nanocomposites with different contents of the organically modified clays were prepared by melt mixing using Haake internal mixer.

The compound was then irradiated using electron beam at optimum dose of 250 kGy. X-ray diffraction results indicated intercalation of the natural rubber into silicate interlayer. Upon irradiation at 250 kGy, the tensile strength of the NR/Na-MMT nanocomposites constantly reduced slightly with increasing clay loading, whereas the tensile strengths of NR/DDA-MMT and NR/ODA-MMT increases to optimum levels, 12.1 MPa and 9.5 MPa respectively at 3 phr clay contents. On the other hand, the elongation of NR/DDA-MMT nanocomposites is less affected with increasing clay content up to 3 phr. The results of tensile strength and elongation are shown in Figure 3. The effects of the natural rubber/EVA and nanosize clay blends have also been investigated.

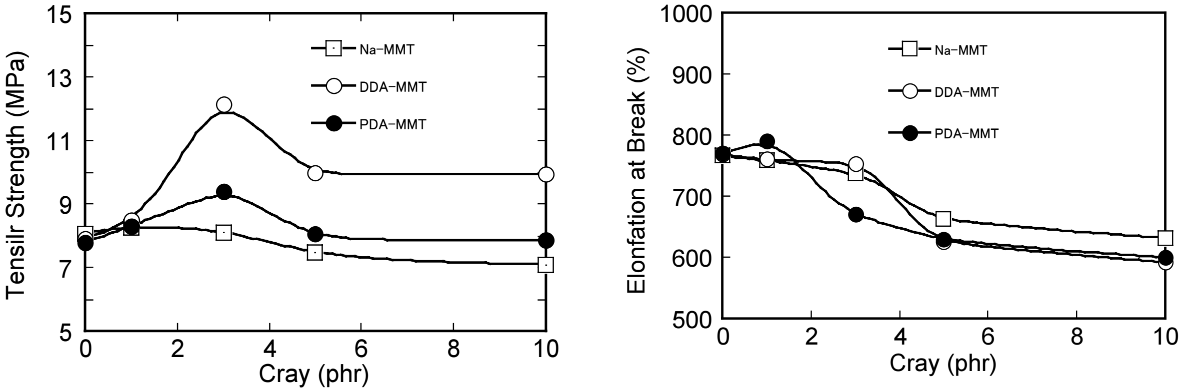

Fig. 3 Mechanical properties of NR/clay nanocomposites irradiated to 250 kGy

3. Technology Transfer and Commercialization

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.

Beginning the 9th Malaysian Plan, 2006, Techno Fund has been introduced to provide fund in the form of grants to upgrade the laboratory work into pilot scale for product development and market testing. With such fund, the technical and market components of the technology transfer can be performed to establish the commercial viability of the project. The government also provides the commercialization fund as a matching grant to assist company to commercialize new finding after the pilot scale study.

4. Conclusion

In Malaysia, radiation processing of natural polymers is at several stages of implementation. Some project has been transferred to industry and some still at the laboratory stage and others need to be further tested at the pilot scale level. At the same time, further effort is necessary to find industrial partner for commercialization in particular for a new technology or new materials. In this respect, government support in providing fund for research, for pilot scale project and commercialization are crucial for the successful technology transfer to industry.

References

1) K. Hashim, N. Mohid, K. Bahari, K. Zaman, "Radiation Processing of Starch/Water Soluble Polymer Blends for Hydrogel", *JAERI-Conf 2000-003*, p. 23 (2000).
2) K. Hashim, K. Zaman, K. Bahari, F. Yoshii, T. Kume, "Development of sago starch hydrogel for wound dressing", *JAERI-Conf 2001-005,* p. 66 (2001).
3) Z. Ghazali, K. Zaman, B. Wongsuban, S. Idris K. Muhamad, "Radiation processing of indigenous natural polymer", *JAERI-Conf 2001-005*, p. 75 (2001).
4) K. Hashim, A. S. Halim, M. T. M. Nor, K. Zaman, F. Yoshii, "PVA-Sago Starch Hydrogel and Preliminary Clinical Animal Study of the Hydrogel", *JAERI-Conf 2002-003*, p. 19 (2002).
5) Z. Ghazali, B. Wongsuban, S. Idris, N. M. Adzahan, L. Ithnin, K. Zaman, "Radiation Modified Sago-blends and Its Potential for Biodegradable Packaging Materials", *JAERI-Conf 2002-003*, p. 32 (2002).
6) K. Hashim, N. Yacob, "Radiation Processing of Sago Hydrogel Thin Film", *JAERI-Conf 2004-007*, p. 92 (2004).
7) K. Zaman, J. Sharif, "Application of Electron Beam in Nanotechnology", *JAERI-Conf 2005-005*, p. 42 (2005).
8) J. Sharif, W. M. Z. W. Yunus, K. Zaman, M. H. Ahmad, "Preparation and Properties of radiation crosslinked natural rubber/clay nanocomposites", *Polymer Testing*, **24,** 211 (2005).
9) H. M. Dahlan, K. Zaman, A. Ibrahim, "Degradation of natural rubber via UV irradiation", *Nucl. Sci. J. Mal.*, **18**, 9 (2000).
10) H. M. Dahlan, A. G. Harun, R. Mamat, "Production of liquid epoxidized natural (ENR) by photochemical technique", *Nucl. Sci. J. Mal.*, **17**, 1 (1999).
11) H. M. Dahlan, T. Rada, A. Zahid, K. N. K. Umar, M. N. H. Mussin, "Synthesis of EB-curable natural rubber-based oligomer", *Nucl. Sci. J. Mal.*, **20**, 56 (2002).

3.6 Progress in R&D on Radiation Processing of Natural Polymers in the Philippines

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1. Introduction

Radiation technology has emerged as an environment-friendly, commercially viable technology with broad applications that can essentially contribute to achieve the goal of sustainable development. Natural polymers are good raw materials since they are biodegradable, readily available in large quantity and at low cost. Radiation processing of natural polymers is a potential area to widen the prospect of industrial scale application of radiation technology in the Philippines.

2. Semi-commercialization of PVP-Carrageenan Hydrogel

The hydrogel prepared by irradiation of the mixture of poly(N-vinylpyrrolidone) (PVP) and carrageenan has undergone clinical testing at several major hospitals in Metro Manila. PVP-Carrageenan hydrogel has been found to be comparable to commercially available hydrocolloid in terms of efficacy and superior to saline/gauze 1, 2). It has already a pending patent application (No.1-2000-02471) at the Philippine Patent Office. The techno-economic feasibility study showed economic viability of the project. 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 very profitable business 3). To test the viability, semi-commercialization of the product through building a pilot plant at the Philippine Nuclear Research Institute (PNRI) compound. Hydrogels will be produced in two sizes 4” X 4” and 8” X 8” at 200 pieces per day. Semi-commercialization is being funded by the Technology Incubation for Commercialization (TECHNICOM) Program of the Department of Science and Technology (DOST). The program aims to provide technology to the country's micro, small and medium enterprises (MSMEs) by encouraging scientists and inventors to solve business problems through technological intervention.

The PNRI and St. Raphael Lifeline Company have agreed on the terms of the licensing agreement for the commercialization of the PVP-Carrageenan hydrogel. The St. Raphael Lifeline Company has submitted a Letter of Intent to undertake this work with the PNRI. The said company will establish trial centers at major hospitals to do market acceptability testing of the product. BFAD approval will also be sought by St. Raphael Lifeline Company with technical assistance from PNRI. After the marketability testing, the technology will be transferred completely to the company.

3. Preparation of Carrageenan Oligosaccharides

Degraded carrageenan by irradiation in powder and aqueous has been characterized 4). Carrageenan oligosaccharides with molecular Mw 5000 ~ 10000 were obtained using three different irradiation processes shown in Table 1. High dose irradiation for powder is not favorable for oligosaccharide production since it leads structural damage of the carrageenan structure at 200 kGy and above. This was proven by dynamic light scattering studies of irradiated carrageenan 5, 6). Low dose irradiation is suitable for production of oligosaccharides from carrageenan. This was done using dilute solution of carrageenan or using low molecular weight (LMW) carrageenan in concentrated solution as starting material. The first two processes required post-irradiation treatment of fractionating the carrageenan oligosaccharides and concentrating the dilute solution. Techno-economic feasibility of the three processes will be undertaken.

Table 1 Process for preparation of carrageenan oligosaccharides

Type of carrageenan	Irradiation condition	Bioactivity testing
kappa and iota	Solid state, 100 kGy, ambient	Rice seedling/Vegetable by hydroponics
kappa	1 %, 30 kGy	Tissue culture of potato
Hydrolyzed kappa	4 %, 15 kGy	Seed germination of soybean

4. Innovative Discovery in Radiation Processing

4.1 Animal study of chitosan-PVP hydrogel

Vesicoureteral reflux (VUR) refers to the retrograde flow of urine from the bladder into the upper urinary tract. It predisposes an individual to renal infection or pyelonephritis by facilitating the transport of bacteria from the bladder to the upper urinary tract 7). Endoscopic treatment of VUR has gained favor in recent years as a therapeutic alternative to long-term antibiotic prophylaxis and open surgery in 90 % of cases due to the following factors: minimally invasive or no incision, immediate protection against further reflux associated renal damage, high success rate, low morbidity, and the advantage as an outpatient procedure. Using different tissue augmenting implants injected in the periureteral area, a cure rate of 75 % has been achieved with one injection and of 90 % after two or three injections for grade I – IV reflux. Chitosan-PVP solution was crosslinked and sterilized by gamma-ray irradiation. Concentration of PVP and chitosan and irradiation dose was optimized so the gel can have a high insoluble fraction and will pass the G26 needle. Different molecular weights of chitosan were also tried. Figure 1a shows the Chitosan-PVP injectable gel. Animal testing of the gel was undertaken at the University of Santo Tomas Hospital (Figure 2). In this study, Chitosan-PVP hydrogel showed promising results as a possible ideal tissue augmenting implant for endoscopic treatment of VUR. It maintained its viscosity enough to allow easy injection to as small as G26 needle which is smaller than the standard Deflux metal needle (3.7FR X 23G [tip] X 350 mm), which is used in actual periureteral injection of Deflux in patients with vesicoureteral reflux. At the same time it maintained its stability over time.

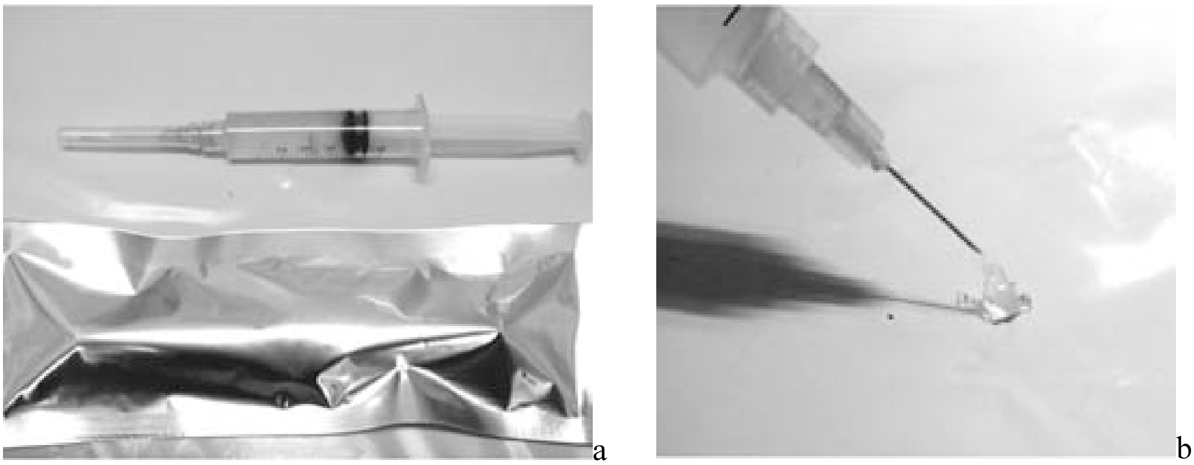

Fig. 1 a) Chitosan-PVP injectable gel and b) gel passing into G26 needle

The observed decrease of subcutaneous nodule volume and initial volume of the chitosan-PVP group from implantation to 6 months post-implantation is still clinically and statistically comparable with the Deflux group (Figure 3).

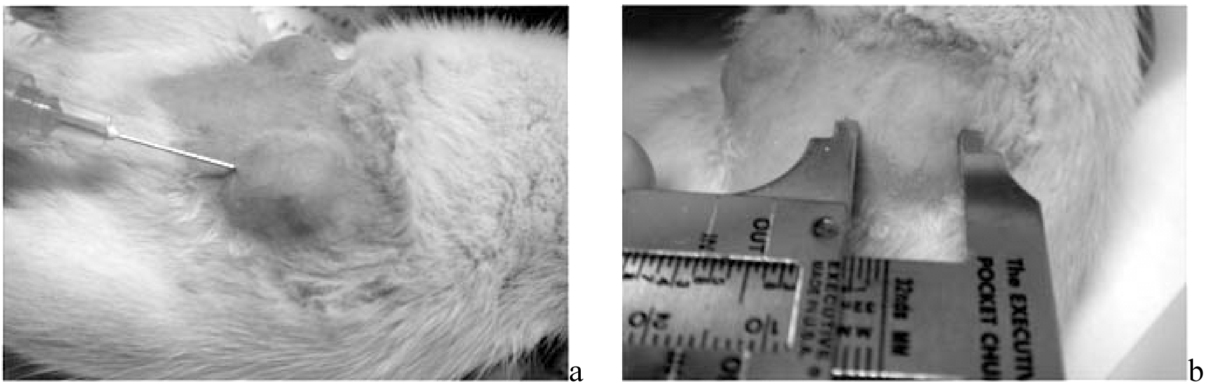

Fig. 2 Injection of gel in rat's abdomen (a) and measurement of Bulge Mean Volume of gel implant (b)

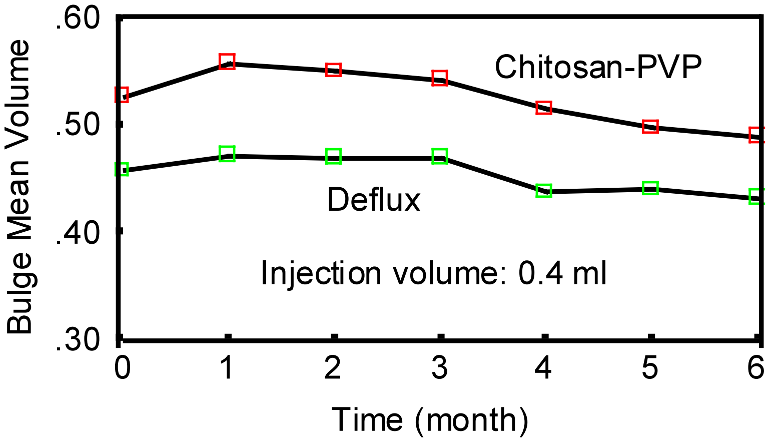

Fig. 3 Change in Bulge Mean Volume of gel after 6 months of implantation in rat

Both groups grossly retained their subcutaneous nodules and the implants within these nodules were retained after 6 months. The Chitosan-PVP gel implant can be considered biocompatible due to absence of gross local tissue inflammation, abscess, and tissue necrosis. Histologically, minimal local inflammatory reaction was noted with absence of granulation tissue, foreign body reaction, and scar formation. This new implant can also be considered non-migratory with the absence of inflammation, foreign body reaction, necrosis, or scarring in the liver, kidneys, and lungs.

4.2 Synthesis and radiation crosslinking of carboxymethyl κ-carrageenan (CM-κC)

Recently, studies have been carried out on polysaccharide derivatives to attempt radiation-induced crosslinking of these materials under various experimental conditions. It was discovered that water-soluble polysaccharide derivatives like carboxymethyl cellulose (CMC), carboxymethyl starch (CMS), carboxymethyl chitin (CMCT) and carboxymethyl chitosan (CMTS), predominantly undergo crosslinking reactions when irradiated as highly concentrated aqueous solution in paste-like state [8, 9, 10)]. With this successful scientific effort, the idea of derivatizing carrageenan by carboxymethylation process was put into research study in order to widen the application of carrageenan. Carboxymethylation of κ-carrageenan was accomplished by using the following reaction parameters: reaction medium, 80:20 isopropyl alcohol/water; NaOH, 4.5 moles/ disaccharide unit of κ-carrageenan; monochloroacetic acid (MCA), 2.5 moles/ disaccharide unit κ-carrageenan; reaction temperature, 40˚C; and reaction time, 3 hours. These parameters were also used for multi-step carboxymethylation. Multi-step carboxymethylation is needed for the preparation of carboxymethylated κ-carrageenan (CM-κC) with high degree of substitution (DS). High DS is favorable to crosslinking [8 ~ 10]. The presented data (Figure 4) is for the CM-κC prepared by 2-step carboxymethylation.

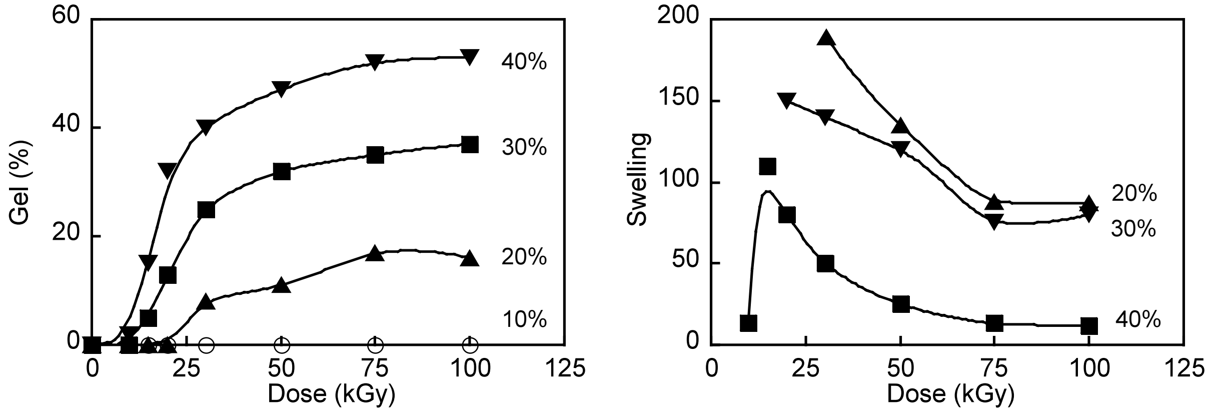

Fig. 4 Gel fraction and swelling of CM-κC hydrogel at various concentration as a function of radiation dose

The graph shows the dependence of gel fraction on concentration of polymer. Increase in concentration led to increase in gel content. The effect of CM-κC concentration on the crosslinking dose was also evident from the graphs. Increase in concentration of the polymer resulted to a decrease in crosslinking dose. The crosslinking dose is defined as the lowest dose where a measurable gel fraction is obtained. Figure 4 shows that hydrogel absorbs 100 ~ 200 g water/g dried gel depending on the dose and concentration of CM-κC.

5. Upgrading of PNRI Multi-purpose Co-60 Irradiation Facility

The present Co-60 loading (about 37 kCi) and manual product handling system translate to a low throughput of the facility. PNRI cannot meet the demand for radiation treatment of other products from new clients. Thus, currently a project is being implemented with the technical assistance from the IAEA, the DOST, and the Department of Agriculture (DA) to upgrade the pilot scale gamma irradiation facility at PNRI to a semi-commercial one. This entails the modification of its source rack, installation of a product handling system and loading additional Co-60 source. Modification of the source rack will increase the Co-60 positions in the rack, allowing loading of more Co-60 pencils without removing the old ones. Installation of a product handling system and increasing the Co-60 loading will improve the performance of the irradiator, resulting in a higher throughput for the facility. Table 2 shows the projected capacity of the semi-commercial irradiation facility in terms of mango irradiation. The upgraded capacity is estimated based on the following assumption.

1) Activity of source as of 2005: 50 kCi, Total activity of source by 2007: 140 kCi
2) Additional 30 min/load for loading and unloading
3) Full operation (8000 hrs/yr)
4) Box Size of Mangoes: 46 X 32 X 14 cm
5) Tote Box Size: 70 X 50 X 90 cm

Table 2 Projected capacity of semi-commercial Co-60 irradiation facility (Mangoes)

Parameters	Present	Upgraded
Min. dose (kGy)	0.3	0.3
No. of bags or boxes/load	48	180
Volume/load (m^3)	1.0	3.8
Irradiation time (hrs)	0.9	0.4
Total time/load (hrs)	1.4	0.9
No. of loads/year	5,882	9,302
Total volume/year (m^3)	5,929	35,163

References:

1) Santos R, Luna C, "Comparison of gamma-irradiated hydrocolloid versus saline gauze dressing in decubitus ulcers", Veterans Memorial Medical Center, (2004).
2) Guiteirrez M, Paliza A, "Single blind randomized controlled trial using carrageenan hydrogel compared with duoderm hydroactive gel for the debridement of ulcers", Department of Dermatology, University of Santo Tomas, Hospital, (2005).
3) Piñera A, Aranilla C, "Business Plan for the Semi-commercialization/Pilot Plant Production of PVP-Carrageenan Hydrogel Processed Through Radiation Technology", Philippine Nuclear Research Institute, (2005).
4) L. Relleve, N. Nagasawa, L. Luan, T. Yagi T, C. Aranilla, L. Abad, T. Kume, F. Yoshii, A. Dela Rosa, "Degradation of carrageenan by radiation", *Polym. Degradat. Stabil.,* **87**, 403 (2004).
5) L. Abad, I. Nasimova, L. Relleve, C. Aranilla, A. Dela Rosa, M. Shibayama, "Dynamic light scattering studies of irradiated kappa carrageenan", *Int. J. Biol. Macromol*., **34**, 81 (2004).
6) L. Abad, I. Nasimova, C. Aranilla, M. Shibayama, "Light scattering studies of irradiated κ- and ι-carrageenan", *Radiat. Phys. Chem*., **73**, 29 (2005).
7) J. Elder, P. Craig, B. Arant, D. Ewalt, et al., "Pediatric Vesicoureteral Reflux Guidelines Panel Summary Report on the Management of Primary Vesicoureteral Reflux in Children", *J. Urology*, **157**, 1846 (1997).
8) B. Fei, R. A. Wach, H. Mitomo, F. Yoshii, T. Kume, "Hydrogel of biodegradable cellulose derivatives I. Radiation-induced crosslinking of CMC", *J. Appl. Polym. Sci*., **78**, 278 (2000).
9) N. Nagasawa, Yagi T, T. Kume, F. Yoshii, "Radiation crosslinking of carboxymethyl starch", *Carbohydrate Polym*., **58**, 109 (2004).
10) L. Zhao, H. Mitomo, N. Nagasawa, F. Yoshii, T. Kume, "Radiation synthesis and characteristic of hydrogels based on carboxymethylated chitin derivatives". *Carbohydrate Polym*, **51**, 169 (2003).

3.7 Progress in R&D on Radiation Processing of Natural Polymer in Thailand

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1. Radiation Crosslinking

1.1 Hydrogel for wound dressing

The preparation of poly(vinyl alcohol)/silk fibroin (PVA/SF) hydrogel by gamma radiation for wound dressing purposed was carried out as follows:

1.1.1 Wound dressing of poly(vinyl alcohol)/silk fibroin hydrogel

Poly(vinyl alcohol)/silk fibroin (PVA/SF) hydrogels were prepared by γ-radiation. The preparation conditions such as absorbed doses and PVA/SF concentrations were investigated. When exposed to γ-radiation, PVA/SF was crosslinked to yield high water absorption materials with water content of 100 ~ 1,000 % of their dried weight depending on the preparation conditions. The crosslinked density seems to be the main factor governing the swelling of these gels. The swelling behaviors in NaCl aqueous solutions were also investigated. The swelling of PVA/SF hydrogels decreases when exposed to electrolyte solution. With an increase of absorbed does, the gel fraction of PVA/SF increases.

1.1.2 Properties of irradiated PVA/SF blend hydrogels for wound dressing

The preparation of hydrogels from PVA and blend solution of PVA/SF from silk waste and some properties as a wound dressing were studied. In the experiment, hydrogels were prepared from PVA and from blend solution of SF and PVA using γ-irradiation. The thickness of the hydrogel was controlled to be 3 mm. Some properties of hydrogel such as antibacterial activity, protection of wound from bacteria and water vapor permeability were tested. Escherichia coil, Staphylococcus aureus, and Psuedomonas aeruginosa were used as testing cultures. The results revealed that PVA hydrogel from 7 and 10 % PVA and the blend hydrogel containing 10 % SF in 7 and 10 % PVA (w/w) at the dose of 30 – 60 kGy showed good appearance. Although the gels did not showed the property for antibacterial but it caused the reduction of bacterial growth. The hydrogel was able to protect the wound from bacterial. The water vapor permeability coefficient of the films was in the range of 11,61 ~ 1,527 g m^{-2} day^{-1}.

1.1.3 Efficiency of the PVA/SF hydrogel wound dressing on wound healing in rat

The objective of this study was to compare between the PVA/SF hydrogel prepared by gamma radiation and commercial hydrogel on wound healing in rat. The wound was covered with hydrogels It was found the symptom nearly vanished with in 12 days incase of PVA/SF hydrogel prepared by gamma radiation as shown in Figure 1.

2. Radiation Degradation

2.1 Gamma degradation of Silk

The preparation of silk powder from gamma degradation of silk cocoon has already transferred to private company (Silk Valley Co., Ltd.). The products are now available in the market in form of soap and baht-gel and moisturizing cream. Production Scale is about 200,000 bars per year for local consumers and plan to produce for export in near future. Cost estimation for processing by gamma radiation is approximately 125 US$/kg (powder) and for processing by chemical is approximately 112.5 US$/kg (powder). Technical benefits in radiation degradation processing gives clean product no toxic chemical and environment friendly.

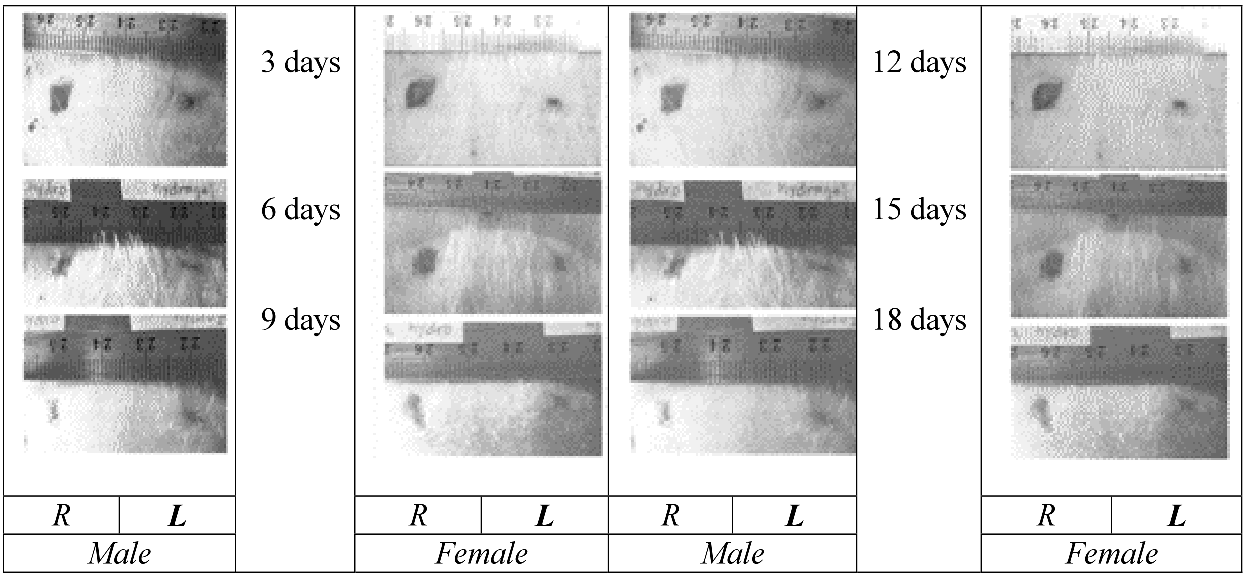

Fig. 1 Effect of hydrogel for wound healing in rat
(R= commercial hydrogel, L= PVA/SF hydrogel)

2.2 Gamma degradation of chitosan

Shrimp wastes are available in quantity and cheap in Thailand. Annual production of Black Tiger prawn from farming alone is more than 300,000 metric ton. Another same amount is from fishery. Wet shrimp waste which is about 40 ~ 50 % of the total amount will account for some 240,000 ton a year. One of the main shrimp waste products claimed to be high value-added is high protein shrimp extracts developed by Thailand Institute of Scientific and Technological Research (TISTR). This technology has been transferred to some private sectors. Exoskeleton of shrimp wastes has been purified to chitin and converted into chitosan for exporting by some 10 local companies.

Depolymerization of chitosan for unique applications like fungicide, plant growth promoter, animal feed additives has been developed later some last 5 years ago mostly by enzymatic and chemical methods by Asian Institute of Technology (AIT), TISTR and Chulalongkorn University (CU). Some studies of chitosan irradiation have been conducted at CU and Office of Atom for Peace (OAP). Depolymerization of chitosan flake can be achieved by gamma irradiation at the G value of main-chain scission, G(s) of about 1.1 at a dose of 100 kGy gamma ray can reduce Mv from 1.2×10^{6} to about 2×10^{5}. At 10 % chitosan concentration of this molecular weight in acetic acid, further reduction of molecular weight at G(s) of about 7.5 is observed. Addition dose of 75 kGy can render 10 % oligochitosan in 3 % acetic acid. The production cost of the above process cannot be competitive with chemical means using ozone bubble. Final adjustment is to combine chemical process with radiation process. First ozone bubble to get molecular weight of approximately 5×10^{4}. Radiation sterilization dose is then applied to produce oligochitosan. The latter is done in 10 % acetic acid solution form. The technology has been transferred to Sirikorn Enterprise Co. Monthly production is about 40 kg chitosan equivalent.

Recently, we have found that low molecular weight chitosan, Mv of 1.0×10^{5} obtained by any means can be radiation crosslinked at concentration > 45 % in acetic acid. Elucidation of the crosslinking mechanism is done by FT-IR and was speculated that crosslinking is via acetamide group of chitin left over in chitosan. First application was to use crosslinked chitosan as topcoat of PVA hydrogel for wound/burn dresser. Anti-microbial property of crosslinked chitosan has put to the test both by AATC 147-1998 (clear zone method) and FC-TM-19 (shake flask method) and found in good agreement that the chitosan retains its antimicrobial activity. As thin crosslinked chitosan is need on top of PVA gel, electron beam process can be adapted very well without vacuum-sealed as in case of gamma irradiation.

3. New Institute (TINT) and Nuclear Business Development Program

After several years of planning for Sustainable National Nuclear Institution the re-organization of the Office of Atoms for Peace (OAP) took effect on April 2006. OAP will remain responsible for policy and strategic plan formulation on all nuclear matters, radiation safety and all nuclear material regulatory authorities. A new institute name Thailand Institute of Nuclear Technology (TINT) was established and will be responsible for research and development, technology transfer and the application of services and products.

According to organization chart of TINT as shown in Figure 2, the nuclear business development section will be responsible for the commencement of radiation processing business. By cooperation between nuclear research and development section and nuclear business development section the information in laboratory, cost and quality of the product can be evaluated. Since color enhancement of gemstone by radiation is one of the successful business in Thailand. The Government of Thailand has already approved two years budget of installing the radiation source start from 2007. Electron accelerator of 20 MeV and Co-60 source of 60,000 Ci will install at TINT. By this strategy the acceleration of technology in Thailand may possible.

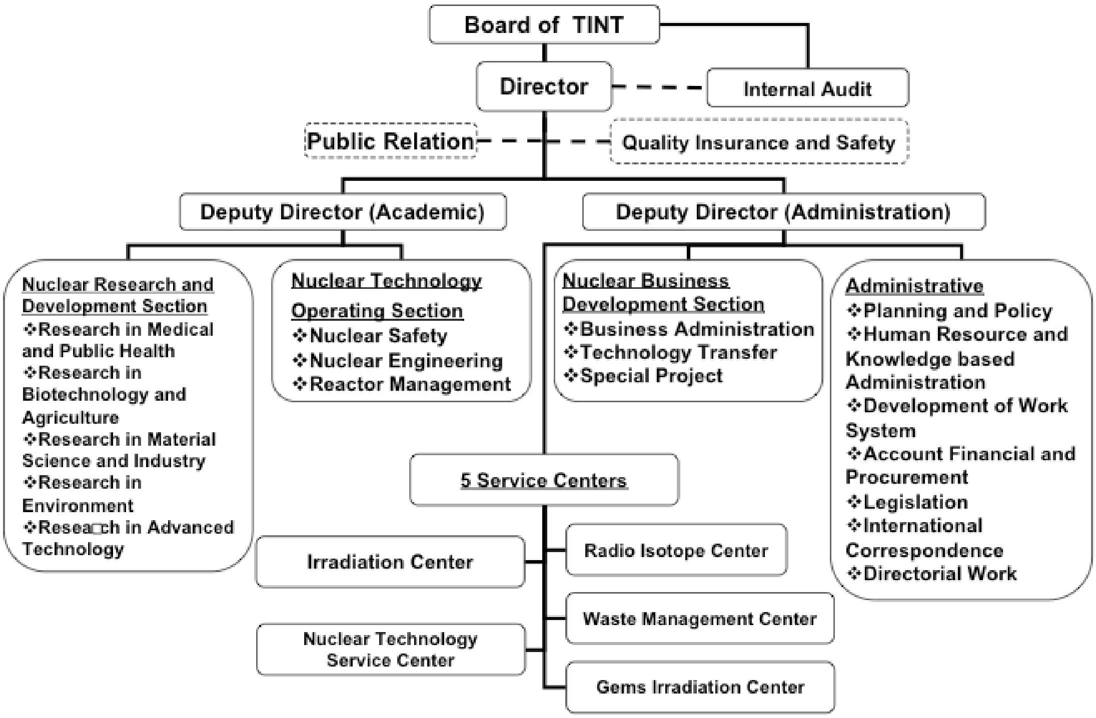

Fig. 2 TINT Organization chart

3.8 Application of Radiation Processing to Produce Biotic Elicitor for Sugarcane in Vietnam

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Abstract

Sugarcane is the main raw material for production of sugar and ethanol. In Vietnam, it was reported in 1998 that the area for sugarcane growth was about 257,000 ha. Up to now, the biotic elicitor, oligosaccharide has not been used for sugarcane yet. This study has been carried out to investigate the elicitation and the growth promotion effect of irradiated chitosan (oligochitosan) for sugarcane. The field test results indicated that alpha chitosan (shrimp shell) and beta chitosan (squid pen) samples with the content of water soluble oligomer of about 70 % were the most effective. The disease ratio of sugarcane tree-trunk treated with irradiated chitosan before harvesting time decreased to 30 ~ 40 % compared to non-treated one (100 %). In addition, the productivity of sugarcane increased to about 20 %. The combination of metal ion (Zn^{++}, Cu^{++}) with oligochitosan did not show the synergic elicitation effect. The results revealed that biotic elicitor made from chitosan by radiation degradation method is very promising for field application not only for protection of disease infection but also for growth promotion of plants. It is believed that this biotic elicitor could be largely used for safe and sustainable development of agriculture.

1. Introduction

Sugarcane is the main raw material for production of sugar and ethanol. In Vietnam, it was reported in 1998 that the area for sugar cane growth was about 257,000 ha 1). Up to present time, the biotic elicitor namely oligosaccharide has not been used for sugarcane yet. In 1985, a new plant regulator namely oligosaccharide was reported which also exhibits elicitation effect for plants 2). After that many research works were carried out 3 ~8), however up to now the product, oligosaccharide as elicitor, has been produced and commercialized only in some countries for instance “Enerplant”, produced by Biotec, Mexico; “Iodus 40”, by Goemar, France and “Osan” from radiation processed chitosan, by Chulalongkorn University, Bangkok, Thailand. In Vietnam, since 1996 research on radiation degradation of natural polysaccharides was carried out for preparation of growth-promoter and protector for plants 9, 10). In 2003, a product named Goldride (Permit No. 49/035RN) from irradiated chitosan to treat Pyricularia Oryzae for rice crop was commercialized by Research and Development Center for Radiation Technology and Phuoc Hung Co. Ltd. However, the product “Goldrice” was not completely as an elicitor for plants.

This research subject is to investigate the elicitation effect of oligochitosan from radiation degraded of chitosan particularly for sugarcane. The combination of ion Zn^{++}, Cu^{++} with oligochitosan for elicitation effect is also investigated.

2. Experimental

2.1 Materials

Alpha chitosan (aCTS) with degree of deacetylation (DD) 70 %, viscosity average molecular weight (Mv) 2.2×10^5 and beta chitosan (bCTS) with DD 90 %, Mv 9.6×10^4 were used for preparation of elicitor.

2.2 Methods

Mv was measured by viscosity method and calculated as follows [11]: $[\eta] = k \times M\alpha$

$k = 0.104 \times 10^{-3}$ mg/g and $\alpha = 1.12$ for aCTS, DD70 %

$k = 6.589 \times 10^{-3}$ mg/g and $\alpha = 0.80$ for bCTS, DD90 %

Chitosan was dissolved in dilute lactic acid solution with the concentration of 40 g/l. Chitosan and chitosan solution samples were irradiated on the gamma irradiator SV-ST Co-60/B at VINAGAMMA Center with doses up to 50 kGy.

The yield of water soluble oligochitosan was gravimetrically determined by neutralization of irradiated chitosan solution by NaOH 2M to pH 7. The percentage yield of water soluble oligochitosan was calculated as follows:

$$\% \text{ Yield} = (m - m_0)/ m_0 \times 100 \%$$

where m is total weight of water soluble oligochitosan after neutralization and m_0 is total weight of chitosan in lactic acid solution.

Samples and method of treatment were described in Table 1.

Table 1 Samples and method of treatment

No.	Sample	Treatment
1	A(0)	aCTS solution, 0 kGy
2	A(30)	aCTS solution, 30 kGy
3	A(50)	aCTS solution, 50 kGy
4	B(30)	bCTS solution, 30 kGy
5	$B(M^{++})$	B(30) + 40 g/l $Zn(NO_3)_2 \cdot 6H_2O$
6	$B(2M^{++})$	B(30) + 20 g/l $Zn(NO_3)_2 \cdot 6H_2O$ + 20g/l $Cu(NO_3)_2 \cdot 3H_2O$
7	Control	Water

2.2.5. Field test of elicitation effect for sugarcane

Field test of elicitation effect was carried out in the experimental field of the Institute of Sugarcane Research, Binh duong province. Field test was designed by random block for 7 treatments with triplicate. The area of block was 100 m^2 and spraying concentration was of 40ppm (dilution 1/1000). Sugarcane was sprayed three times as following. The first was carried out after 30days of sugarcane growing, the second was 15 days after the first and the third was 15days after the second. Disease index (DI) was counted after 1 and 2 months after the third spraying and before harvest. The productivity was also investigated. Data were processed by analysis of variance (ANOVA) method.

3. Results and Discussion

3.1 Radiation degradation of chitosan

The decrease of Mv by irradiation was described in Figure 1. Based on the results obtained, radiation degradation yield G_d was calculated based on equation [12]:

$$(1/Mv - 1/Mv_0) = 1.04 \times 10^{-7} \times G_d \times D(kGy)$$

G_d values were found out from results in Figure 2 to be of 0.203 and 1.76 for aCTS 70 and bCTS 90 irradiated in flake form respectively. The G_d value of bCTS was higher than that of aCTS. It indicated that bCTS is more sensitive degradation by radiation than aCTS.

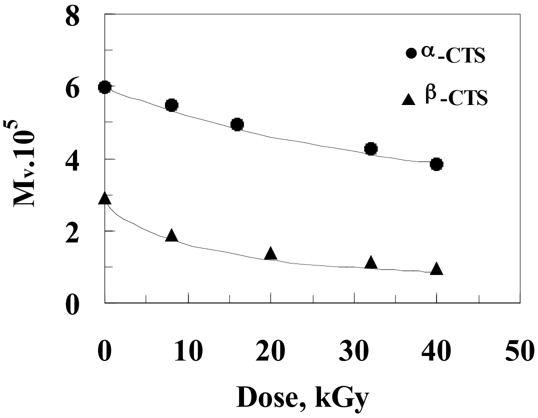

Fig. 1 Relationship between Mv and dose

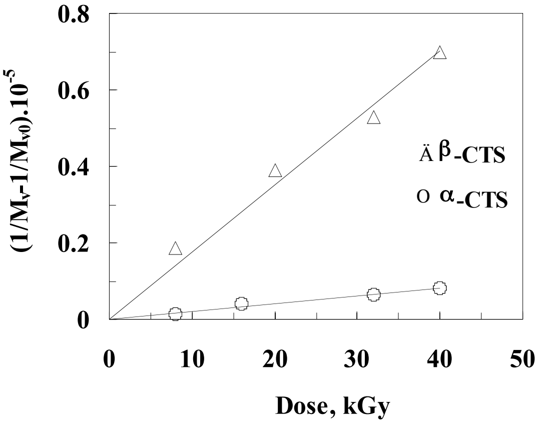

Fig. 2 Relationship between 1/Mv – 1/Mv$_0$ and dose

The yield of water soluble oligochitosan were of 43.39 %; 74.89 % and 69.12 % for A(30), A(50) and B(30) respectively. At the same dose of 30 kGy, the yield of water soluble oligochitosan of bCTS was higher compared to that of aCTS. It indicated again that even in solution state bCTS is also more sensitive radiation degradation than aCTS.

3.2 Elicitation effect

Results in Table 2 indicated that CTS, oligochitosan and oligochitosan combined with metal ion all exhibit the elicitation effect for decreasing disease index. The samples A(50) and B(30) with high content of water soluble oligochitosan (~70 %) were the most effective. Metal ion (Zn^{++}, Cu^{++}) combined with oligochitosan did not show synergic elicitation effect.

Table 2 Elicitation effect for sugarcane (variety VN85-1427)

No.	Sample	Leaf DI (%) (1 month)	Leaf DI (%) (2 months)	Trunk DI (%) (at harvest)	For control (%)
1	A (0)	8.10 b	9.36 b	6.16 bc	56.9
2	A (30)	6.17 c	7.82 b	7.43 b	68.7
3	A (50)	6.06 c	8.01 b	3.98 cd	36.8
4	B (30)	6.21 c	8.84 b	3.32 bcd	30.7
5	B(M^{++})	7.94 b	9.00 b	3.67 d	33.9
6	B($2M^{++}$)	7.22 bc	8.80 b	4.19 cd	37.7
7	Control	11.95 a	14.12 a	10.82 a	100.0
LSD $_{0.05}$		1.44	1.89	2.24	-

LSD $_{0.05}$: Least significant difference at probability level

3.3 Productivity and quality of sugarcane

Results in Table 3 indicated that the productivity increased from 4.74 to 10.67ton/ha (equiv. from 9.3 to 21.8 %) for all treatment compared to control. The highest productivity attained for two samples A(50) and B(30).

Table 3 Productivity and quality of sugarcane (variety VN85-1427)

No.	Sample	Ton/ha	Increase (ton/ha)	Increase (%)	CCS (%)
1	A (0)	53.65 c	4.54	9.3	11.65
2	A (30)	55.29 abc	6.33	12.9	11.71
3	A (50)	59.63 ab	10.67	21.8	11.54
4	B (30)	58.18 bc	9.22	18.8	11.96
5	B(M^{++})	55.06 bc	6.16	12.5	12.00
6	B($2M^{++}$)	56.12 abc	7.16	14.6	11.85
7	Control	48.96 d			11.36

CCS %: commercial content of sugar, %

4. Conclusion

Main conclusions are as follows.

- Two solution samples namely aCTS 50 kGy and bCTS 30 kGy with high yield of water soluble oligochitosan (~70 %) were the most effective.
- Besides elicitation effect oligochitosan has also growth-promotion by increasing productivity of sugarcane significantly (~20 %).
- Biotic elicitor from irradiated chitosan is very promising for field application not only for defense of disease but also for growth promotion of plants. It is believed that this biotic elicitor could be largely used for safe and sustainable development of agriculture.

References

1) H. U. Nguyen, *Sugarcane and growing*, Agriculture Press, Ho Chi Minh City, (2000) (in Vietnamese).
2) P. Albersheim, A. G. Darvill, *Oligosaccharin*, Scientific American, **253**, 44 (1985).
3) C. A. Ryan," Oligosaccharides as recognition signals for the expression of defensive genes in plants!, *Biochemistry*, **27**, 8879 (1988).
4) P. Vander, et al., "Comparison of the ability of partially N-acetylated chitosans and chitooligosaccharides to elicit resistance reactions in wheat leaves", *Plant Physiol.*, **118**,1353 1998).
5) C. Akimoto, H. Aoyagi, H. Tanaka, "Endogenous elicitor-like effects of alginate on physiological activities of plant cells", *Appl. Microbiol. Biotechnol.*, **52**, 429 (1999).
6) T. Kume, et al., "Utilization of carbohydrate by radiation processing", *Radiat. Phys. Chem.*, **63**, 625 (2000).
7) N. I. Vasyukova, et al., "Modulation of plant resistance disease by water soluble chitosan", *Applied Biochem. Microbiology*, **37**, 103 (2001).
8) L. A. Hadwiger, et al., "The mode of action of chitosan and its oligomers in inducing plant promoters and developing disease resistance in plants", *Adv. Chitin Sci.*, p. 452-457 (2002).
9) N. Q. Hien, et al., "Application of radiation processing for production of plant growth promoter from seaweed and plant protector from shrimp shell", *J. Chem. Appl.*, No. 11, 19 (2002) (in Vietnamese).
10) N. Q. Hien, "Radiation degradation of chitosan and some biological effects", *IAEA-TECDOC-1422*, p. 67 (2004).
11) W. Wang, et al., "Determination of the Mark-Houwink equation for chitosan with different degree of deacetylation", *Int. J. Biol. Macromol.*, **13**, 281 (1991).
12) A. Charlesby, "*Atomic Radiation and Polymer"*, Pergamon Press, p.161-164 (1960).

4. Process Development

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4.1 Preparation of Radiation-crosslinked Carboxymethyl Cellulose (CMC)

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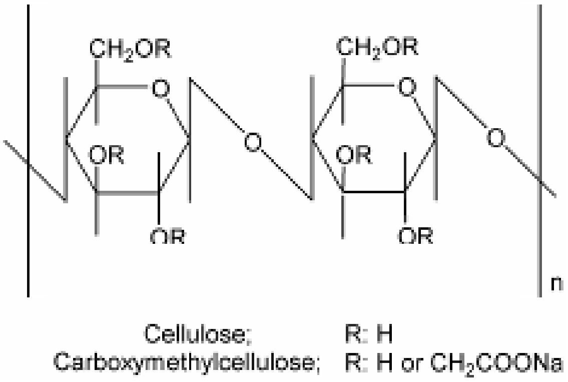
Quantum Beam Science Directorate, Japan Atomic Energy Agency

1. The Technology of Radiation Processing of Polysaccharides

Polysaccharides and their derivatives are typical degradation polymers in radiation processing. In several studies conducted, we found that water-soluble polysaccharide derivatives such as carboxymethyl cellulose (CMC), methyl cellulose, hydroxyethyl cellulose, hydroxylpropyl cellulose, hydroxypropylmethyl cellulose, carboxymethyl starch (CMS), carboxymethyl chitosan and carboxymethyl chitin etc., undergo crosslinking when irradiated at high concentrated solution called paste-like condition. When powders of these polysaccharide derivatives are kneaded homogeneously with water and then irradiated by electron beams or γ-rays, biodegradable hydrogels are formed.

2. Material Description and Specification

Carboxymethyl cellulose is a derivative of cellulose formed by its reaction with alkali and chloroacetic acid. The CMC structure is based on the β-(1$\rightarrow$4)-D-glucopyranose polymer of cellulose as shown in Scheme 1. Different preparations may have different degrees of substitution, but it is generally in the range 0.6 ~ 1.5 derivatives per monomer unit in commercial products. CMC is used in food science as a viscosity modifier or thickener, and to stabilize emulsions, for instance in ice cream, owing to its not toxic and non-allergenic. It is also a constituent of many non-food products, such as toothpaste, laxatives, diet pills, water-based paints, detergents, and various paper products. For hydrogel preparation, commercial grade CMC is used with a DS of 0.86 ~ 1.36 and a molecular weight of about 5×10^5 ~ 1×10^6.



Scheme 1 Structure of CMC

3. Preparation of CMC Hydrogel

3.1 Laboratory-scale procedures

① Weigh appropriate amounts of CMC powder to make 20 % paste solution and knead well with water with the use of blending machine.
② Pack in polyethylene/nylon blend bag and vacuum seal.
③ Irradiate the samples using an electron beam accelerator (2 MeV, 1 mA) at a dose per pass 10 kGy or γ-rays from Co-60 source at a dose rate of 10 kGy/h, at room temperature.
④ Drying in oven at 40 ℃ to continuous weight.
⑤ Characterize the formed hydrogel product.

3.2 Large-scale procedure

① Weigh appropriate amounts of CMC powder to make 20 % paste and knead well with water with the use of mixing machine (50 ~ 90kg/bacth).
② Pack a cardboard box with CMC paste put in polyethylene bag. For bedsore prevention

mat, CMC paste put in cylindrical polyethylene bag, use it for the post-irradiation as it is.

③ Transportation to irradiation service company, irradiate the samples using γ-rays from Co-60 source at a dose of 5 kGy, at inert temperature.

④ Drying using heater at 70 ~ 80 °C to continuous weight and then crushing. Usually, this heater is used for drying Amorphophalus konjac species to obtain konjac mannan.

⑤ Apply the formed hydrogel product.

4. Applications of Crosslinked CMC by Radiation

4.1 Bedsore prevention mats

Fig. 1 Bedsore prevention mats for in operation room

CMC soft hydrogel can be applied as a healthcare product by using it as a material for making bedsore prevention mats for hospitals especially during operation procedures (Figure 1). This product is used as follows: before operation is conducted, the mat is pre-heated to body temperature (37 °C) using an oven heater and the temperature is maintained for the duration of operation. The hydrogel mat is shown to disperse body pressure and improve circulation of blood during operation, thus, it could prevent bedsores in patients.

4.2 Cold insulator hydrogel

CMC hydrogel can be applied as material for production of cold insulator. CMC gel as cold insulator is a high quality and safe product to keep the flesh of fishes and vegetables at low temperature environment during transportation from the producing center to market. This cold insulator consists only of 2 % CMC dry gel swollen with other components.

4.3 Treatment of industrial and agricultural wastes by CMC dry gel

The pollution of global environment becomes a big social issue as the wastes of industry and agriculture increases. Generally, these wastes are destroyed by incineration or end up in landfill. The effluent control of these wastes has become severe. The global environment maintenance is one of our important concerns. Thus, it is desired to find new technology for reuse of these wastes. A technology for effective utilization of these wastes is described in the following situations which can be used as models by end-users.

4.3.1 Installation of practical plant for treatment of Japanese liquor, Shochu residue

Japanese liquor, Shochu (alcohol content, 25 %) is produce by fermentation of rice, wheat and sweet potato. Many residues after production of this liquor, which contain 90% water, are thrown away in the deep sea and rapidly gather molds. But throwing of these residues on the sea will be prohibited from end of March 2007. The residue is expected to be applied as an animal feed, because the residue has nutrient components. Therefore, a company of shochu-brewing industry at Kumamoto prefecture installed practical plant for processing of animal feeds from this residue. Corncob, which required 650 kg per ton of residue, is added into rotary oven to adsorb water from the residue. Required corncob was reduced to 200 kg when CMC dry gel (0.2 % or 2 kg) was added per one ton of residue as water absorption material. It was confirmed that water-absorption by CMC dry gel is effective to convert residue into animal feed.

4.3.2 Practical test of livestock excrement treatment

The field heaping and open storage of livestock excreta (release of excrement and urine from domestic animals, such as cattle and pigs, in river and penetration into underground) were legally-prohibited in Japan 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 undergo fermentation smoothly. Thus, present method consists of mixing sawdusts from 1.0 ~ 1.5 times (volume) with the excrement and urine to reduce 65% to 70% water content and enhancing fermentation. Addition of 0.2 % CMC dry gel to the process can reduce consumption of sawdust by 1/3 in comparison with the present method. This novel technology give following advantages: reduction of saw dusts, small storage area for saw dust, decrease in heavy work, and reduction of odor diffusion in environment.

5. Cost Considerations in Commercialization of CMC Gel Using Radiation Technology

In case of material development, irradiation cost is normally higher than conventional method, so it is necessary to find out big advantages of it. Since radiation technology can modify materials without additives, the product is preferable for medical/welfare and cosmetic field. One batch of 20 % CMC, with total weight of 750 kg, was irradiated to get dry gel. Furthermore, we have tried the application of CMC dry gel for fixing of water and carried out effectively fermentation of livestock excrement and shochu residue treatment in animal feed. It was evaluated that CMC dry gel is effective to adsorb water in waste material treatment. Cost reduction of dry gel for application in agriculture and industry is desired. Hence, further improvement of properties such as high swelling is essential to adopt radiation technology.

Cost of dry gel is estimated from price of raw material, irradiation, drying, crushing, transportation and crushing. The price of raw material and irradiation changes by consumption of dry gel and increase of its consumption induces reduction of cost.

Reference

1) B. Fei, R. A. Wach, H. Mitomo, F. Yoshii, T. Kume, “Hydrogel of Biodegradable Cellulose Derivatives. 1. Radiation-Induced Crosslinking of CMC”, *J. Appl. Polym. Sci.*, **78**, 278 (2000).
2) R. A. Wach, H. Mitomo, N. Nagasawa, F. Yoshii, “Radiation crosslinking of methylcellulose and hydroxyethylcellulose in concentrated aqueous solutions”, *Nucl. Instrum. Methods Phys. Res. B,* **211,** 533 (2003).
3) N. Pekel, F. Yoshii, T. Kume, O. Güven, “Radiation crosslinking of biodegradable hydroxypropylmethylcellulose”, *Carbohydrate Polym.*, **55**, 139 (2004).
4) N. Nagasawa, T. Kume, F. Yoshii, “Radiation crosslinking of carboxymethyl starch”, *Carbohydrate Polym.*, **58,** 109 (2004).
5) F. Yoshii, R. A. Wach, N. Nagasawa, L. Zhao, H. Mitomo, T. Kume, “Hydrogels of polysaccharide derivatives crosslinked with irradiation at paste-like condition”, *Nucl. Instrum. Methods Phys. Res. B,* **208,** 320 (2003).
6) L. Zhao, H. Mitomo, N. Nagasawa, F. Yoshii, T. Kume, “Radiation synthesis and characteristic of the hydrogels based on carboxymethylated chitin derivatives”, *Carbohydrate Polym.*, **51,** 169 (2003).

4.2 Manual of Radiation Processing of Cassava Starch Hydrogel

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1. Introduction of Cassava Starch

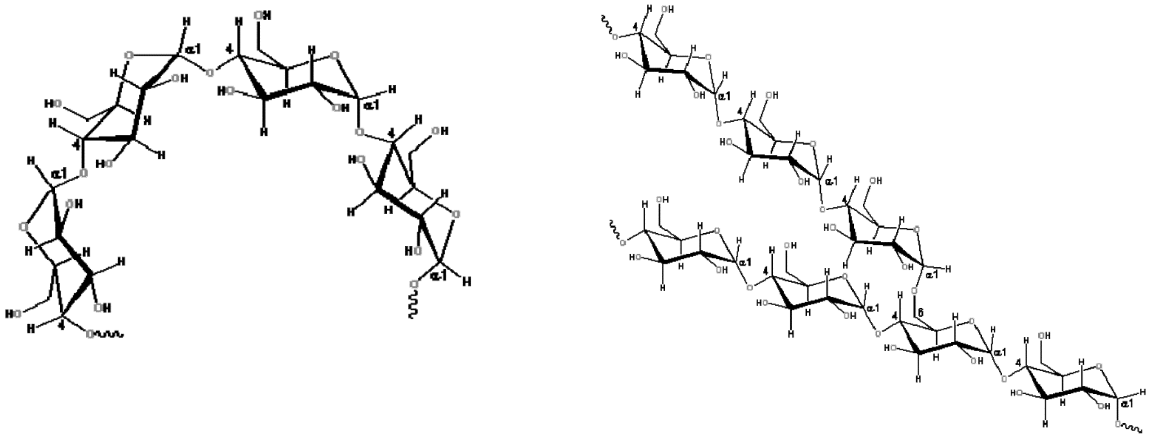
Starch or polysaccharides presents a link with the energy of the sun, which is partially captured during photosynthesis. Starch is a biological material and naturally occurs in a wide variety of plants and agricultural crop. The size of starch, ranging from about 3 to 100 μm, depends on the type of crops. For cassava starch (CS), its granular size ranges from 5 to 35 μm.

1.1 Chemistry of starch

Starch is a high polymer composed of repeating 1,4-α-D-glucopyranosyl units. These monomers, called anyhydroglucose unit (AGU), are joined together with α–glucosidic linkage. This bond is acetal, stable under alkaline conditions and hydrolyzed under acid conditions. The hydroxyl groups can react to form ethers and can be oxidized to aldehyde, ketone, and carbonyl groups. Although starch is a hydrophilic polymer, it is not all soluble in water. This property is influenced by the nature of monomer units, by the type of glucosidic linkage and by the presence or absence of hydrogen bonding between adjacent polysaccharide chains.

1.2 Chemical structure

Most starches are composed of two structurally different polysaccharides, the linear amylose and the branch amylopectin, Figure 1. Their relative amounts, structures and molecular masses are determined by means of genetic and environmental control, and therefore wide variation occurs among plants.



Amylose

Amylopectine

Fig. 1 Schematic structures of amylose (left) and amylopectin (right)

1.2.1 Amylose

Amylose is the linear component, produced by 1,4-α-D-glucosidic linkage. It is a minor component, typically ranging from 20% to 30%. Its molecular weight is about 0.2 ~ 2 millions. For cassava starch, the amylose content is about 16.5 ~ 22%.

1.2.2 Amylopectin

Amylopectin is the branched component which is composed of short 1,4-α-linked chains connected to each other by and α(1,6) glucosidic linkage. The molecular mass of amylopectin is about 100-400 millions, but the average chain length is only 20 ~ 30 glucose units.

1.3 Starch modification

The characteristics of starch can be modified by chemical treatment to enhance or repress its intrinsic properties or to impart new ones. Graft copolymerization method and the derivatization of the glucosidic hydroxyl groups have gained importance in chemical modification of starches.

1.3.1 Graft copolymerization

Most graft copolymers are formed by free radical graft copolymerizations, a free radical produced on starch reacts with vinyl monomer. A number of initiating methods have been used to prepare graft copolymers, and these may be divided into two broad categories:

i) Chemical methods

There are several methods of chemical initiation, but the most widely used method is the reaction of starch with ceric salts, such as ceric ammonium nitrate dissolved in dilute nitric acid. Pretreatment of starch with ozone-oxygen mixtures has also been used.

ii) Radiation methods

Starch free radicals have been produced to initiate graft copolymerization by interaction with electromagnetic radical. The most popular technique is initiation by means of gamma-ray irradiation, which offers certain advantages over chemical methods. Radiation methods for preparation of graft copolymers are often easier to handle than most conventional chemical methods. When high-energy radiation interacts with matter its intensity decreases, primarily because of scattering and energy absorption by some irradiated molecules. Three major processes are operative, photoelectric effect, Compton scattering, and production of electron pairs.

For gamma rays from Co-60, the predominant effect in organic material is Compton scattering. In the Compton effect the incident gamma ray interacts with an orbital electron ejecting the electron from its orbital and producing another photon of low energy. Both the electron and photon subsequently interact with the material or surrounding giving rise to essentially two processes, one of ionization and the other of excitation, In the case of ionization, the Compton electron transfers sufficient energy to the orbital electron of another atom to overcome the force binding it to the nucleus. The electron is therefore ejected, leaving behind a positive ion. If the energy is insufficient to cause ejection of an electron, the energy level of the atom is raised and the atom is said to be in an excited state. The ions and excited molecules are very reactive; they either react with other materials present in the system or decompose into radicals and atoms or molecules. The free radical produced upon irradiation of polymeric systems may be used to initiate graft copolymerization.

There are many different methods of radiation grafting such as direct or mutual irradiation of a polymer in the presence of a monomer and in the absence of air, pre-irradiation of a polymer in air to yield peroxy groups and the subsequent contact with a monomer in the absence of air. Pre-irradiation of a polymer in a vacuum yields trapped radicals followed by heating in the presence of another monomer. In the absence of air, irradiation of two polymeric substrates is in intimate contact. In the absence and presence of air, polymer lattice swollen with monomer are irradiated. The direct or mutual irradiation is the simplest grafting method, involving the irradiation of a polymeric substrate in the presence of a monomer and in the absence of oxygen.

Graft copolymerization of the monomer to the polymer is then initiated through the free radicals generated in the latter.

A number of important factors must be considered, however, before applying the direct radiation method to a given polymer-monomer system. Ionizing radiation as such is unselective. One must consider not only the effect of irradiation on the polymeric substrate, but also the effect on the monomer, the solvent, or any other substance present in the system. Together with the radiation sensitivity of the polymer-monomer combination one must also consider the effect of the radiation on the actual polymeric substrate. In general, polymer either degrade or crosslink under irradiation. If the polymer degrades then irradiation in the presence of a monomer will lead predominantly to block-type copolymer, if the polymer crosslinks, graft structures will result. This may be represented schematically as follow:

$$P \longrightarrow P_1\bullet + P_2\bullet \xrightarrow{+\,nM} P_1\text{-}M + M\text{-}P_2 \tag{1.1}$$

$$P \longrightarrow P\bullet + R\bullet \xrightarrow{+\,nM} P + M_q \tag{1.2}$$

Here $P_1\bullet$, $P_2\bullet$ and $P\bullet$ represent polymeric free radicals derived from P, and $R\bullet$ represents a low molecular weight radical or hydrogen atom. The homopolymer (Mq) arises from initiation by small radicals $R\bullet$ and also by radiolysis of the monomer M.

$$M \longrightarrow R\bullet \longrightarrow R(M_q) \tag{1.3}$$

Kinetic features of radical grafting

For the simplest case of polymer swollen by or immersed in a monomer, the polymer is completely insoluble in the monomer. If one assumes that the graft copolymerization occurs by a radical chain process, then, the overall reaction scheme can be divided into three main stems: initiation, propagation, and termination. This may be represented as follows;

Initiation:

$$P \longrightarrow P\bullet \tag{1.4}$$

$$r = kI \tag{1.5}$$

Addition of the first monomer to initial radical:

$$P\bullet + M \longrightarrow PM\bullet \tag{1.6}$$

$$r_i = k_i\,[P\bullet][M] \tag{1.7}$$

Propagation:

$$PM_n\bullet + M \longrightarrow PM_{n+1}\bullet \tag{1.8}$$

$$r_p = k_p\,[PM_n\bullet]\,[\,M\,] \tag{1.9}$$

Termination by two growing radicals:

$$PM_m\bullet + PM_n\bullet \longrightarrow PM_{m+n} \quad \text{or} \quad PM_m \;+\; PM_n \tag{1.10}$$

$$r_t \;= 2\,k_t\,[PM_m\bullet]\,[\,PM_n\bullet] \sim 2\,k_t[PM_n]^2 \tag{1.11}$$

If one makes the normal assumption that the length of the polymer chains is long, then the reaction (1.6) can be neglected with respect to the reaction (1.8), and one obtains the following relation for the rate of graft copolymerization.

$$r_p = k_p[PMn\bullet][M] \qquad (1.12)$$

Introducing the conventional steady-state assumption that the rate of change of the radical concentration is small compared to its rates of formation and disappearance, then

$$k_i[P\bullet][M] = 2k_i[PM_n]^2 \qquad (1.13)$$

i.e.

$$r_i = 2\,k_t\,[\,PM_n\bullet]^2 \qquad (1.14)$$

$$[PMn\bullet] = (r_i/2k_i)^{1/2} \qquad (1.15)$$

On combining equation 1.12 and 1.15, one obtains for the rate of graft copolymerization:

$$r_p = k_p[M](r_i/2k_i)^{1/2} \qquad (1.16)$$

Where

I = intensity of radiation

P = backbone polymer

$P\bullet$ = polymer radical

PM_m, PM_n, P_{m+n} = graft copolymer

M = grafting monomer

r = rate of initiation of polymer radicals

r_i = rate of initiation of graft reaction

r_p, r_t = rate of propagation and termination, respectively

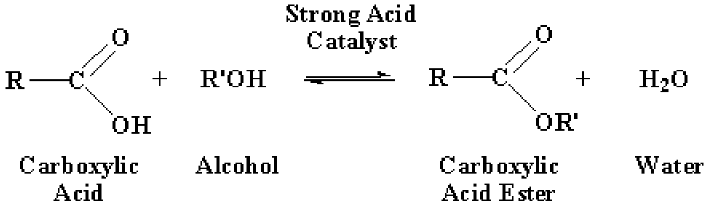
k = rate constant for initiation of polymer radicals

k_i = rate constant for initiation of graft reaction

In practice, however, the situation is not quite as straightforward as this, because of the number of specific features resulting from the special reaction condition also prevailing in most grafting systems. The gel effect, chain transfer, phase separation, and diffusion effects are, but a few of the many factors, which can seriously affect the reaction kinetics.

1.3.2 Esterification of carboxylic acid group

The formation of a carboxylic acid ester (usually called simply an ester) can be prepared by treatment of a carboxylic acid with an alcohol in the presence of an acid catalyst. The acids most commonly used are sulfuric acid, hydrochloric acid as a gas bubble in the reaction medium and p-toluenesulfonic acid. The conversion of carboxylic acid and alcohol to an ester is given the special name Fischer Esterification after the German chemist Emil Fischer. The general reaction equation is presented as follow:



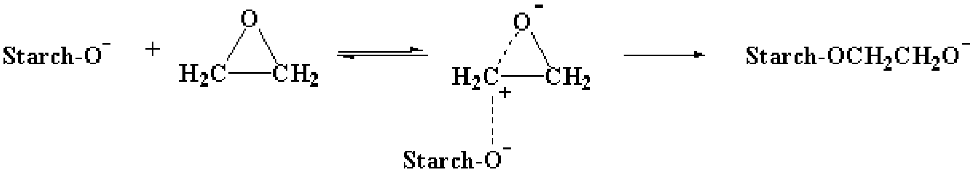
(1.17)

Fischer esterification is a reversible reaction, and generally appreciable concentration of both the carboxylic acid and ester are present at equilibrium. Therefore, to obtain a good yield of ester, it is necessary to force the reaction to completion either by removing the water as it is formed or using excess of the reactants. The equilibrium is frequently shifted to product using an alcohol as both a solvent and a reactant.

1.3.3 Starch Etherification

Starch molecule can be etherified at the reactive hydroxyl group in the presence of alkaline catalyst. There are three principal methods for the etherification, the ring opening of epoxides, the nucleophilic displacement of aliphatic halogens or sulfate groups (the Williamson synthesis), and the Michael-type addition. The most widely known method is ring opening of epoxides. The procedure proceeds by the attack of polysaccharide anion to epoxides. The most common of epoxide used is ethylene oxide. The reaction mechanism is shown below.

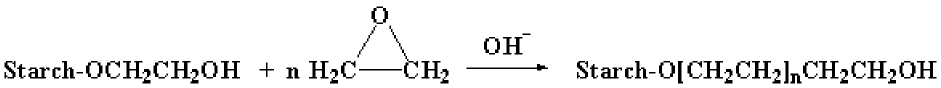
$$\text{Starch-OH} + \text{OH}^- \rightleftharpoons \text{Starch-O}^- + H_2O \quad (1.18)$$



(1.19)

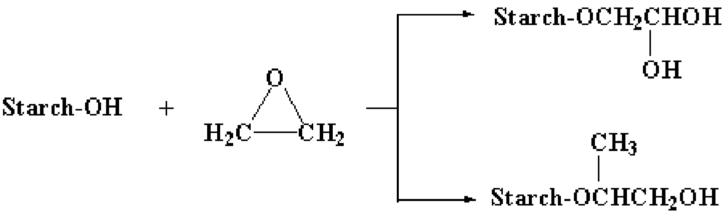
$$\text{Starch-OCH}_2\text{CH}_2\text{O}^- + H_2O \rightleftharpoons \text{Starch-OCH}_2\text{CH}_2\text{OH} + \text{OH}^- \quad (1.20)$$

At high degree of substitution, some polyoxyethyl groups are formed.



(1.21)

If starch reacts with propylene oxide, two different starch ethers may result depending on whether the nucleophilic attack takes place at the primary or at the secondary carbon atom.



(1.22)

(1.23)

The major and usually the only product is that resulting from a nucleophilic attach at the least-hindered (primary) carbon.

2. Cassava Starch Hydrogel by Gamma Radiation

2.1 Syntheses and characterization of PVP-grafted-starch hydrogels

2.1.1 Methodology

Cassava starch was mixed with distilled water and heated at 80°C for 1 hour under nitrogen atmosphere to give gelatinized starch. Then, the gelatinized starch was mixed with vinylpyrrolidone and subjected to gamma radiation at different total doses. The obtained hydrogels were washed with distilled water to remove unreacted water-soluble reactants. Fourier Transform Infrared Spectrometer (FTIR) was used to confirm the grafting reaction between poly(vinylpyrrolidone) and starch. The Equilibrium Degree of Swelling (EDS) of the obtained hydrogels were identified by immersing the gels into distilled water for 72 hours and measuring the weight of the swollen and the dried gels. The gel fraction was determined by autoclaving the gels at 121°C for 2 hours and measuring the weight of the gels before and after extraction. The thermal properties of the hydrogels also was characterized using differential scanning calorimeter (DSC) and thermal gravimetric analyzer (TGA.)

2.1.2 Results

The FTIR spectra of the PVP-grafted-starch hydrogels show a number of characteristic peaks that confirm the grafting reaction. The swelling behavior of PVP-grafted-starch hydrogels is shown in Figure 2, along with those of PVP and PVP-blended-starch hydrogels. It is obvious that the equilibrium degree of swelling of these three different hydrogels decreases with increasing radiation dose. This can be explained from the fact that the crosslinking density of the hydrogels 3D network increases with the radiation dose, resulting in a smaller amount of water that can be absorbed. Figure 3 shows that the gel strength of the PVP-grafted-starch hydrogels increases dramatically with dose increment. And at the same dose, the gel strength of these PVP-grafted-starch hydrogels is much higher than that of the PVP and PVP-blended-starch hydrogels.

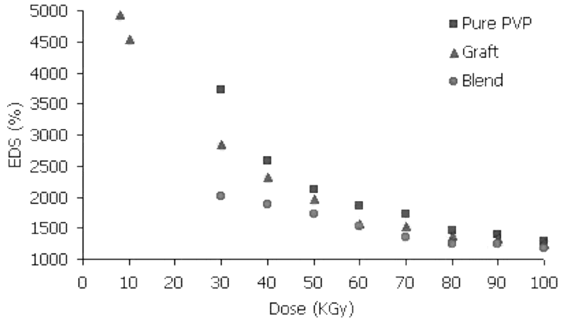


Fig. 2 Degree of swelling

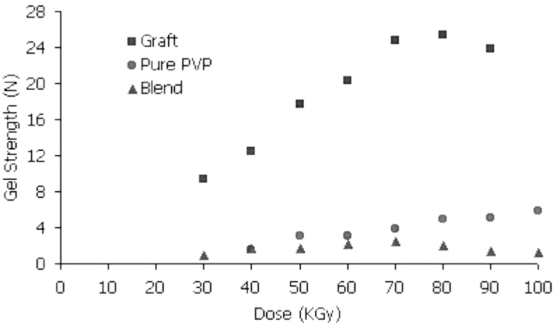


Fig. 3 Gel strength

2.1.3 Conclusion

A series of hydrogels were prepared from gelatinized CSand vinylpyrrolidone by radiation-induced graft copolymerization. Gel fraction, swelling ratio and gel strength of the obtained hydrogels were characterized. The experimental results show that the swelling ratio is inversely dependent on the radiation dose. The results from PVP-grafted-starch were subsequently compared with those of PVP hydrogels and PVP-blended-starch hydrogels. It was found that, 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.

2.2 Hydrogel prepared from radiation-induced crosslinking of carboxymethyl starch

2.2.1 Methodology

Cassava starch (CS) 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. Sodium monochloroacetic acid (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 hours. The synthesized carboxymethyl starch (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 4. The dried CMS samples were mixed with deionized water to the desired concentration. The CMS aqueous solution was irradiated in a gamma radiation chamber (Gammacell 220 Excel from MDS Nordion). The crosslinked CMS were filtered, washed with water, and dried in an oven at 50°C. The swelling ratio of the obtained hydrogel 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).

2.2.2 Results

For the carboxymethylation process, the DS of CMS is plotted as a function of SMCA content, as seen in Figure 4 Initially, the DS gradually increases with % SMCA, but does so significantly after 20% SMCA. Figure 5 shows that there is no obvious correlation between the swelling ratio and dose. However, the swelling ratio tends to increase with SMCA concentration. This can be explained from the fact that the degree of substitution increases with % SMCA. With higher concentration of SMCA, more hydroxyl groups are replaced with carboxymethyl groups. Naturally, hydroxyl is a highly hydrophilic functional group. However, most of the hydroxyl groups in CS are not free, but rather hydrogen-bonded ones. This makes CS insoluble in water, at room temperature. On the other hand, carboxymethyl group is also hydrophilic but much less likely to form hydrogen bonding. As a result, CMS with higher DS is more hydrophilic and able to swell better than CMS with lower DS.

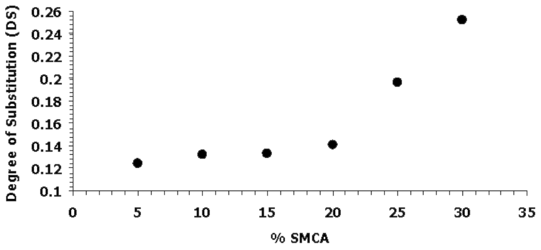


Fig. 4 Degree of substitution (DS)

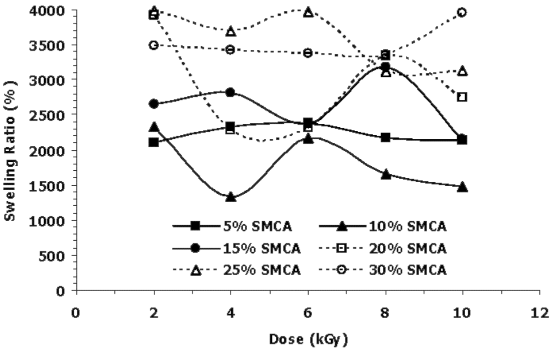


Fig. 5 Swelling ratio

The gel fraction increases with dose up to 2 kGy, then tends to decrease with increasing dose as seen in Figure 6. At higher, doses, the gel fraction tends to diminish due to the domination of degradation over crosslinking.

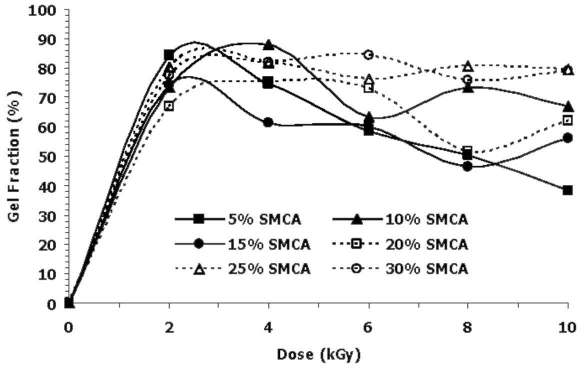


Fig. 6 Gel fraction

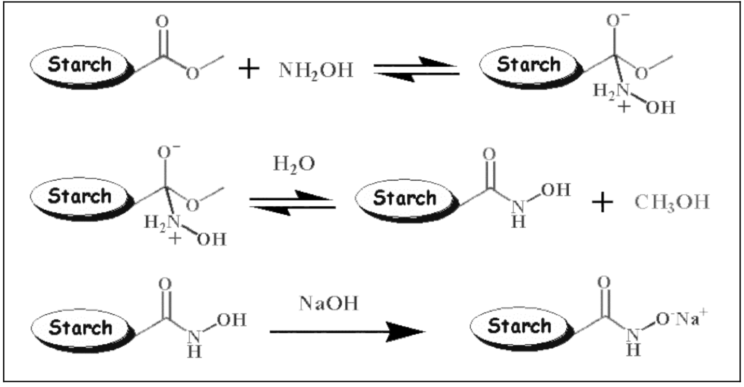
2.2.3 Conclusion

CS was chemically modified by SMCA to yield CMS. The DS increased with increasing percentage of SMCA. The aqueous solution of CMS was irradiated and underwent radiation-induced crosslinking, resulting in a crosslinked CMS hydrogel. The swelling ratio and the gel fraction of the obtained hydrogels were determined. The results indicated that the optimum condition for obtaining hydrogels with desirable properties is irradiation at low dose. At higher doses, the gel fraction tends to diminish, due to the domination of degradation over crosslinking.

2.3 Chelating resin from poly(methylacrylate)-grafted cassava starch

2.3.1 Methodology

Cassava starch was mixed with distilled water and heated at 80°C for 1 hour under nitrogen atmosphere to give gelatinized starch. Then, the gelatinized starch was mixed with poly(methyl acrylate) and subjected to gamma radiation at different total doses for grafting. The optimum conditions for grafting have been studied in terms of % grafting efficiency, % grafting, % total conversion, and % homopolymer. Conversion of the ester groups of the poly(methyl acrylate) (PMA)-grafted copolymer into hydroxamic acid was carried out by treatment of an ester with hydroxylamine in an alkaline solution. The reaction mechanism of converting poly(acrylate ester) into poly(hydroxamic acid) is as shown below. The poly(hydroxamic acid) chelating resin was characterized by FTIR spectroscopy, TGA, and DSC analyses.



2.3.2 Results

The optimum conditions obtained for the grafting of methyl acrylate onto CS were: 15 ml of methyl acrylate, 10 g of cassava starch, and a total irradiation dose of 7.5 kGy. These conditions gave % grafting efficiency, % grafting, % total conversion, and % homopolymer corresponding to 30, 43, 41, and 11, respectively. The FTIR spectrum of CSshowed the characteristic absorption bands at 3482 and 2932 cm^{-1} due to O-H and C-H stretching modes, respectively, and other absorption bands at 1650 and 1015 cm^{-1} for O-H and C-H bending, respectively. The FTIR spectrum of purified poly(methyl acrylate)-grafted CSshows a new absorption band characteristic of an ester at 1740 cm^{-1} (C=O stretching mode) in addition to the same absorption bands of cassava starch. This band had disappeared and a new band associated with hydroxamic acid (C=O at 1659 cm^{-1}) and an amide II band (N-H at 1571 cm^{-1}) appeared. TGA, and DSC analyses also show the different in thermal properties among starch graft copolymer and hydroxamic acid groups in the grafted copolymer. These provide strong evidence for the presence of hydroxamic acid groups in the grafted copolymer.

2.3.3 Conclusion

Polymeric chelating resins containing the hydroxamic acid groups were synthesized from PMA-grafted CS via gamma radiation. The optimum conditions obtained for the grafting of methyl acrylate onto CS were: 15 ml of methyl acrylate, 10 g of cassava starch, and a total irradiation dose of 7.5 kGy. These conditions gave % grafting efficiency, % grafting, % total conversion, and % homopolymer corresponding to 30, 43, 41, and 11, respectively. The poly(hydroxamic acid) chelating resin was characterized by FTIR spectroscopy, TGA, and DSC analyses. These provide strong evidence for the presence of hydroxamic acid groups in the grafted copolymer.

4.3 Process Development on Commercialization of Sago Hydrogel

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1. Radiation Processing of Sago Hydrogel

Sago hydrogel has been successfully developed at laboratory scale and undertake by local company for commercialization process into potential market driven product such as facial mask and wound dressing in cosmetic skin care and pharmaceutical medical device, respectively. We managed to utilize and increase the value added of sago which is one of the commodity product abundantly produce in East Malaysia.

Sago hydrogel produced by mixing sago starch with water-soluble polymers such as polyvinyl alcohol and poly(vinylpyrrolidone) in distill water until homogenous solution was formed. The solution continuously stirred and heated at gelation temperature about 80˚C until clear gel solution was formed. The gel solution was coated on the PE film at specify thickness and covered with cotton gauze. It then cut according to the size of facial mask and vacuum seal prior for irradiation. The product was irradiated at 25 kGy irradiation dose for crosslinking and sterilization process.

2. Searching for Potential Partner

Sago hydrogel in marketable form has been exhibited at various event such as expo S&T November 2002, innovation event, international or national level conference and seminar, show case for small and medium industry (SMI) and entrepreneur program, in searching for the potential partner that willing to take it for commercialization purpose.

Another approach is by direct contact with individual interested partner, entrepreneur and venture capital that willing to invest on new area or product, which is not available in the market. Try to match the product performance or application with company area of interest that looking for new product to be include in their line of products.

3. Process of Transfer Intellect Property (IP)

Firstly, the intellect property has to be secure before process of transfer to other party could be carried out. The technology of processing sago hydrogel has to be filed for patent by Nuclear Malaysia through local patent agent in Malaysia in July 2002 and other country in following year. We think that sago hydrogel has potential marketable value in the future.

After finding the right partner or company that willing to commercialize the sago hydrogel, preparation of draft licensing and technical agreements has to be prepared by the Nuclear Malaysia legal adviser with the feedback from the industry. The signing event between Nuclear Malaysia and Rumbia Bio-Tech Sdn. Bhd. took place on 3rd. September 2003 after both parties agree on the term and condition of the agreements.

4. Financial Assistant

In manufacturing process, the company needs large amount of money for rental and modified building into GMP plant, purchasing of machinery and materials, hire new staff and logistic management from production until marketing. In order to lighten the company financial problem, Nuclear Malaysia technical staff will assist the company in preparing proposal and technical presentation in the process of acquire loan from the bank and government fund. The company managed to secure loan from bank in term of credit limit in the sum of RM0.9 million. Since the technology to be commercialized come from the research activity carried out by government institution, Malaysia Nuclear Agency, the company was given techno-fund by Malaysian Government in the sum of RM1.7 million.

We also assist company in term of technical back up in pursuing venture capital to join and funding the company in commercialization of sago hydrogel. Together with the company, we make a proposal and negotiate with Malaysian Industrial development agency (MIDA) in getting premier status for the company. With this status, the company could eligible get tax exempted for 5 years on purchasing of imported item such as raw materials and machineries.

To minimize the financial burden of the company, Nuclear Malaysia does not impose consultant fees on the service given by our technical staff, even though it has been clearly state in the technical assistant agreement between both parties. On top of this, Nuclear Malaysia gives low rental of building and facility at our electron beam building to be use by the company, and also free radiation service during development process of product for marketing purpose.

5. Transfer of Technology Know-how

Process of transfer technology to the industry in production of sago hydrogel could be divided into two phases of transition. The first transition is from laboratory scale to pilot scale and the second transition from pilot scale to semi commercial scale. According to technical assistant agreement, we will assist the company in the process of manufacturing sago hydrogel and product development to end-user.

he technical assistant will provided consists of purchasing raw material and chemicals, develop experimental and operating procedures, analysis of product, help setting-up quality control, find the right company personals for the job as operator, supervisor and engineer, and provide training for the company staff in manufacturing sago hydrogel in every stages. It took us nearly a year in 2004 to develop technique of coating using prototype coating machine which is being modified from un use two roll mill machine, identified suitable raw and coating materials, cutting process either before or after irradiation, material and type of packaging, bio-burden study and performance of finishing product.

In order to make the commercialization process successful for both parties, the semi commercial scale good manufacturing practice (GMP) plant has to be set-up at Nuclear Malaysia. It took 6 months from November 2004 until May 2005 to modified existing store and area at the electron beam building into GMP plant. This set-up has an advantage to company where:

- Technical assistant from Nuclear Malaysia staffs can easily be available when needed and help to supervise the manufacturing process.
- Easy excess to electron beam or gamma irradiation facility in producing sago hydrogel exist at the site.
- Company can make full use of the laboratory and analytical instruments facility available at Nuclear Malaysia for processing and characterization of product.
- Company staff with guidance by Nuclear Malaysia technical staff could performance quality control during product development.

Beside production, we were also help the company in getting manufacturing license from city council district, safety approval from fire brigade department and any approval needed for commencing of GMP plant. On top of that, we also help the company in getting approval from the Ministry of Health Authority on facial mask sago hydrogel for marketing purpose.

6. Survey Demand and Prospect Product

After signing the agreement, the company decided to market the sago hydrogel in the form of facial mask for skin care cosmetic application. 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 of 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 individual, friend, beauty salon, entrepreneur and marketing people on skin care product. The feed back from them will be use to make perfect the product performance and presentable form according to market need.

7. Marketing Process to Potential Client

Marketing process will determine the success of commercialization of product or technology to be delivered to end user or client. 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. In this aspect, the Nuclear Malaysia technical staffs together with the company have to make road show in explaining to the multi level marketing company about the product. At the same time the company will give free sample to be test by relevance end user in order to evaluate the performance of the product in comparison with existing product in the marker.

8. Conclusion

Commercialization of sago hydrogel as facial mask could be considered as one of the successful story of radiation processing of natural polymer. However, the commercialization of sago hydrogel is still in early stage because so many potential products such as wound dressing, cool fever, bedsores mattress could be explore and develop from it.

4.4 Radiation Degradation of Chitosan and Its Application in Aquiculture and Plant

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Chitosan is an amino-polysaccharide derived from chitin by deacetylation. It is one of the most abundant resources in nature. Due to the poor microbial property and low bioactivity of high molecular weight chitosan, it's essential to decrease its molecular weight. Chitosan with low molecular weight is preferred for its extraordinary characteristics such as improving antivirus property of plant and animal, accelerating plant growth, etc. Therefore it may be a substitute for pesticide or antibiotic in the fields of aquiculture and crops in China. Antibiotic is an exceptive type of reagent because of its drug tolerance, which will increase drug dose and reduce drug effect. As a result, antibiotic may make the disease difficult to restrain and augment economic expenses. Chitosan can be degraded by three methods, i.e. chemical hydrolysis or oxidation, enzymatic catalysis, and radiation. The application of radiation to prepare low-molecular-weight chitosan has some advantages over other methods. For example, the depolymerization of chitosan can be carried out in the solid state without destroying the structure of amino group on the molecular chain. Moreover, it is easy to control the molecular weight by simply controlling the radiation dose.

A highly bioactive solution reagent was obtained by using the gamma-degraded chitosan possessing molecular weight <50,000. In cooperation with fishing pharmaceutical company, we have carried out some experiments on this solution reagent and gained positive effects in aquiculture. After splashing this chitosan solution (shown in Figure 1) into the rearing pond periodically, we used flow cytometry to test the fish blood. The results showed that it could enhance the breeding of DNA, RNA and protein without affecting the fish cellular growth cycle. At the same time, we also did some trials on the cucumber and tobacco in a similar way. The results indicated that it could restrain the incidence of powdery mildew of cucumber and mosaic virus disease of tobacco.

Fig.1 Chitosan solution for aquaculture

We also prepared water-soluble chitosan quaternary ammonium salt by reacting radiation-degraded chitosan with epoxypropyl thrimethylammonium chloride. This chitosan derivative has better antibacterial effect than does the chitosan without modification. The minimal inhibitory concentration of chitosan quaternary ammonium salt is 100 ppm.

5. Lectures at Seminar

5.1 Prospect of Radiation Application in Industry and Agriculture

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1. Impact of Radiation Application

The economic scale of nuclear (nuclear energy + radiation application) in Japan and in U.S.A. was studied in 1997 base$^{1)}$. The results in Figure 1 show that the economic scale of nuclear in Japan was 99 b$ (billion dollars) consisting of radiation by 52 b$ (53 %) and nuclear energy by 47 b$ (47 %), while that in U.S.A. was 158 b$ consisting of radiation by 119 b$ (75 %) and nuclear energy by 39 b$ (25 %). For the radiation application, only limited items such as semiconductors, radial tires for industry, diagnostic imaging and medical equipment for medicine, food irradiation, mutation breeding for agriculture, were calculated because a comparison between Japan and U.S.A. could not cover all related items. A ratio of GDP between Japan and U.S.A. in 1997 was about 2 and the nuclear market in two countries became about 2 % of GDP. The economic scale of radiation and nuclear energy in Japan is almost even, while that in U.S.A. is larger in magnitude than that of nuclear energy to the factor of 3.

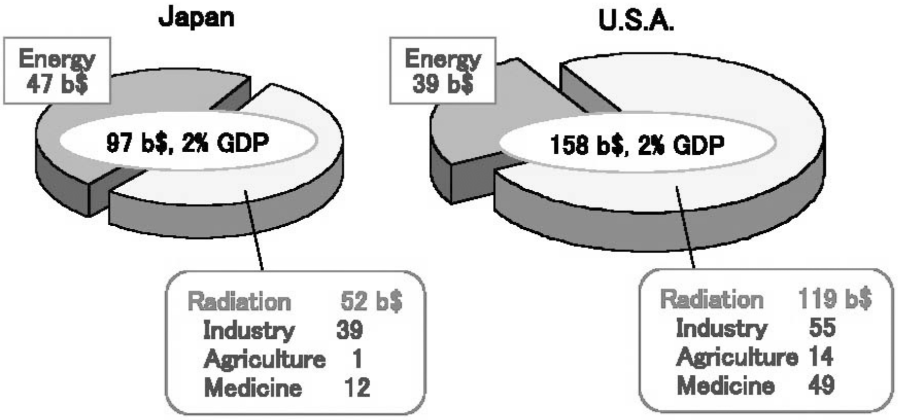

Fig. 1 Economic scale of nuclear in Japan and U.S.A.

The economic scale of radiation application in Japan was 52 b$ consisting of 39 b$ in industry, 1 b$ in agriculture and 12 b$ in medicine. While that in U.S.A. was 119 b$ consisting of 55 b$ in industry, 15 b$ in agriculture and 49 b$ in medicine. In U.S.A., the radiation applications not only in industry but also in medicine and agriculture are significantly advanced. However, in Japan, the radiation applications in medicine and especially in agriculture are relatively small.

Radiation application is aiming at increasing the welfare and the quality of life of our peoples holding a big share of GDP such as 1.4 % in Japan and 1.2 % in U.S.A. Therefore radiation application has a large potential to expand at various fields of industry, agriculture and medicine.

2. Radiation Application in Industry

2.1 Economic scale of radiation processing in Japan

Utilization of radiation has been actively promoted by using γ-rays, electron beams (EB) and ion beams. Gamma-rays and EB are commonly used for the radiation application. Gamma and EB irradiation induces the ionization or excitation of atoms or molecules in materials and can induce chemical reactions without using catalyst at room temperature. Main processes are 1) crosslinking, 2) degradation, and 3) graft polymerization.

Recently the ion beam has also been developed as a tool for radiation application. Characteristic properties of energetic ions injected into matter are 1) highly-localized ionization and excitation, 2) implantation of foreign atoms, 3) production of secondary particles and nuclear transmutation of atoms. Highly-localized ionization and excitation cause the energy transfer in a localized area along the nearly straight ion track causing the high density of the ionization and excitation. Implantation of foreign atoms into solid substance with controllable implantation depth is commercially used for fabrication of semiconductors. Nuclear transmutation of atoms could be used for the production of radioactive isotopes.

The total economic scale of industry in Japan was 59.8 b$. It consists that semiconductors by ion beam: 44.3 b$ (73 %), radiation processing: 9.1 b$ (15 %), production of medical irradiation instruments/equipments: 3.1 b$ (6 %), radiation sterilization of medical devices: 2.3 b$ (4 %), production of radiation instrument/equipment: 1.0 b$ (2 %) and radiographic testing: 0.26 b$ (0.4 %)2).

Approximately 73 % of the total production value was brought about by ion beam processing for the fabrication of semiconductors. Radiation processing (15 %) is the second big field consisting of the crosslinking, degradation and graft polymerization using polymer materials.

2.2 Radiation processing of polymers

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. 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. Radiation processing of rubber by EB treatment is used for production of radial tires. It has advantages such as partial curing of calendared fabric, reduction of rubber coating gauge, prevention of ply movement during final curing, reduction of operating costs and increase in production rates. The applied technology in a new field has been developed for these ten years in Japan.

Graft polymerization is useful for modification of polymers. Acrylic acid grafted polyethylene fibers are used as a battery separator. The radiation graft polymerization can be applied for the preparation of absorbents for various pollutants from water and air.

New functional materials can be created using ion beams. Heavy ions with high linear energy transfer (LET) can produce cylindrical nanopores with an extremely high aspect ratio in polymeric membranes; the diameter of the pores ranges from 0.01mm to 1mm which is one-ten thousandth of the thickness of a membrane. Such nanopores cannot be produced with other existing techniques like photolithography or laser processing. A polymeric membrane irradiated with high-energy heavy ions may have ion tracks through the membrane, where the material is damaged. These latent ion-tracks can be selectively dissolved with a chemical regent, and nanopores are produced. The inner diameter can be changed by controlling the conditions of the chemical treatment. Membranes with functional pores are expected to perform selective separation of proteins and useful substances (Figure 2) 3).

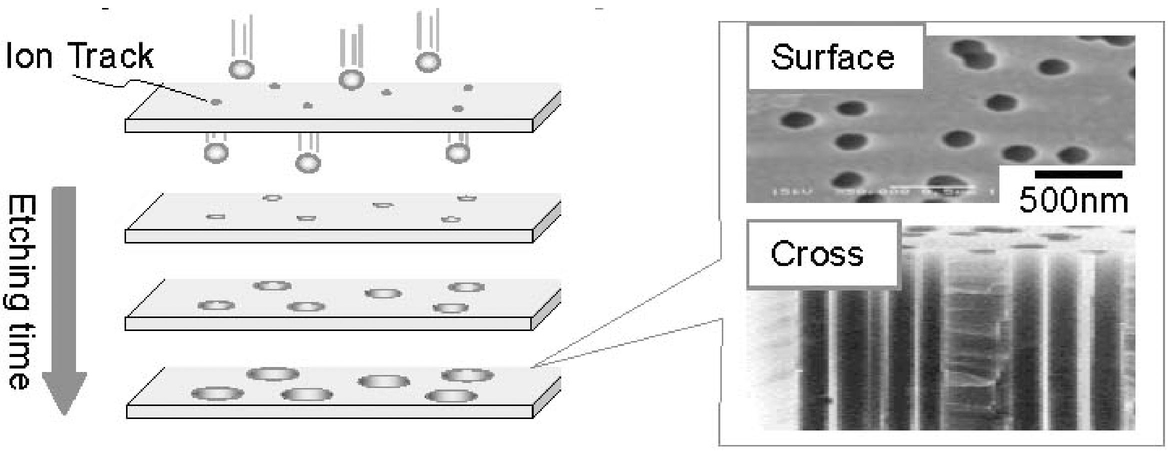

Fig. 2 Ion track membrane

3. Application in Agriculture

3.1 Food irradiation

Food irradiation has been widely used to reduce spoilage, improve food hygiene and kill insect pest of fruits and vegetable, replacing methyl bromide fumigation which depletes the ozone layer. The data base of FAO/IAEA shows the latest approvals for food irradiation in January, 2006 [4]. In the list, 57 countries are registered and the irradiated foods are classified into the following eight classes: 1) bulbs, roots and tubers, 2) fresh fruits and vegetables, 3) cereals and their milled products, nuts, oil seeds, pulses, dried fruits, 4) fish, seafood and their products (fresh and frozen), 5) raw poultry, meat and their products (fresh and frozen), 6) dry vegetables, spices, condiments, animal feed, dry herbal and herbal teas, 7) dried food for animal origin, 8) miscellaneous foods including but not limited to honey, space foods, hospital foods, military rations, liquid egg thickness. The total amount of irradiated foods increases rapidly and is presumed to reach 350,000 tons in the world. Especially, the irradiation of spices shares 1/3 of whole irradiated foods.

In Japan 8,000 ~15,000 tons of potatoes per year are irradiated at Shihoro, Hokkaido (Figure 3). The irradiation of potato for sprout inhibition is continued more than 30 years but other food item is not approved in Japan[5]. Recently it is expected to commercialize the radiation processing of spices.

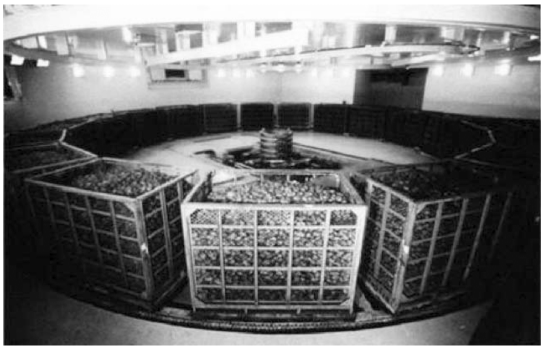

Fig. 3 Shihoro potato irradiator

3.2 Sterile insect technique (SIT)

It is estimated that the insect pests reduce world food production by 25 % to 35 % in spite of enormous amounts of pesticide applications. To replace insecticide SIT is very useful and important technique to eradicate the insect pests such as fruit flies, screwworm, tsetse flies, etc. without the environmental hazard. The principle of SIT is that; male insects sexually sterilized by radiation after mass-rearing are released into the filed, then the wild female insects mate with sterile males, and the eggs cannot hatch. The insect cannot produce offspring leading a fall in populations and finally eradication.

The SIT has been used successfully to eradicate or control medfly in U.S.A., Mexico, Guatemala, Chile, Argentina and Peru. In Japan, the project of SIT in Okinawa Island was conducted in 1977 and succeeded to eradicate the melon fly from whole Okinawa area in 1993.

3.3 Mutation breeding

Plant mutation breeding by radiation has been investigated for long time in many countries. 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. By using radiation technique (γ-rays, X-rays and EB) 128 varieties were developed in Japan. Many new species were developed for disease resistant crops, i.e. 55 species of rice, 10 of barley and 2 of wheat. Other species of beans, fruits including pears resistant for black spot decease, grasses, vegetables, etc, were also developed. 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 (Figure 4) and carnation with complex and striped flower-color, and new flower-shape have been produced and commercialized$^{6)}$.

Fig. 4 New variety of chrysanthemum reducing axillary buds induced by ion beams

3.4 New field: Positron imaging system for plant

Various kinds of radioisotopes can be produced by ion beams from cyclotron and utilized in medical and biological fields. Positron Emitting Tracer Imaging System (PETIS) has been developed as the world's first system that is designed for real-time imaging of the distribution of a positron-emitting radioisotope in a plant$^{7)}$. Uptake and translocation of nutrients fed from roots or leaves, and products in assimilation have been visualized for higher plants such as rice, barley and bean. The effects of elevated CO_2 concentrations on crop harvesting, possibilities of removal of toxic substances by plants, and others related to the security of food resources or the conservation of the environment are the subjects of research.

4. Sterilization

Radiation is commercially used in Japan for sterilization of medical products, food packaging materials and laboratory animal feeds. Radiation is widely used for sterilization of medical products to avoid disease infection. The total volume of disposable medical devices sterilized in Japan was 0.6Mm^3. The share of γ: EB: EOG (ethylene oxide): autoclave is 0.56: 0.04: 0.3: 0.1. Thus, the share of radiation (γ and EB) was 60 % (Figure 5)$^{2)}$. The share of γ-ray irradiation is big but high energy (10 MeV) EB is increasing because of better public acceptance and economics for large throughput. EB sterilization will expand further in the future, while the use of γ-rays is suitable in the product of complex shape and with high density.

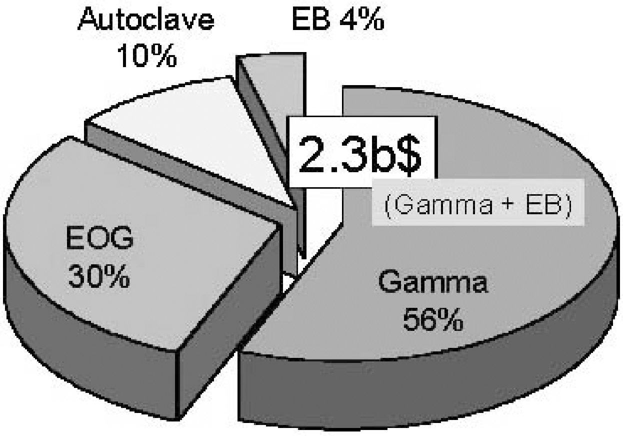

Fig. 5 Sterilization of medical devices

Sterilization or pasteurization of substrate for fermentation and inoculants of bio-fertilizer have been investigated under the bilateral cooperation between JAERI (Japan Atomic Energy Research Institute) and MINT (Malaysia Institute for Nuclear Technology Research) and UNDP/RCA/IAEA. Upgrading of oil palm empty fruit bunch to animal feeds has been applied and the process was shown in Figure 6. The cellulosic wastes can be converted to animal feeds and mushrooms by radiation pasteurization/sterilization and fermentation treatments[8].

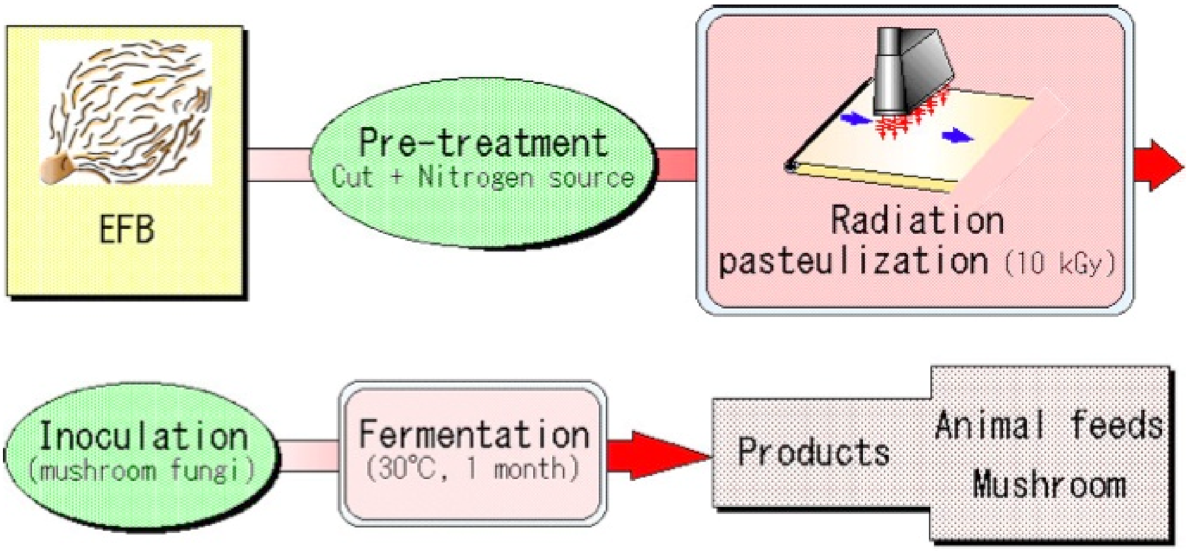

Fig. 6 Process for upgrading of oil palm wastes by radiation and fermentation treatment

5. Environmental Conservation: Purification of Flue Gas and Wastewater

The technology to remove SO_2 and NO_x from coal and oil burning power plants was developed using EB. By the irradiation of flue gas added gaseous ammonia, SO_2 and NO_x are converted into a powdery ammonium sulfate and nitrate. These by-products are used as fertilizers. The technology was developed in Japan but the industrial plants were constructed in China. Two plants to remove SO_2 in flue gas from a coal burning power station by EB were constructed and operating in Chengdu (1997) and Hangzhou (2003). In addition, another plant is being constructed at Jingfeng coal thermal power plant in Beijing. In Poland, a power station was constructed and operation started in 2000 and a pilot plant was constructed in Bulgaria in 2003.

The EB technology is also effective to remove dioxins in flue gas from municipal waste incineration facilities and toxic volatile organic compounds (VOC) in off-gas from painting or clearing factories.

Radiation technology is applicable to destroy or remove of pollutants in wastewater. In Korea a pilot plant for a large-scale test (1,000m^3/day) of textile dyeing wastewater was constructed with EB of 1 MeV, 40 kW. Based on the evaluation of economics and efficiency, an industrial plant was started to construct from 2003 and completed in 2006. The commercial plant has EB of 1 MeV, 400 kW for the treatment of 10,000 m^3/day wastewater[9)].

6. Upgrading of Natural Polymers

Polysaccharides such as chitosan and sodium alginate were easily degraded by irradiation and induced various kinds of biological activities, e.g. anti-microbial activity, promotion of plant growth, suppression of heavy metal stress, phytoalexins induction (Figure 7) [10)].

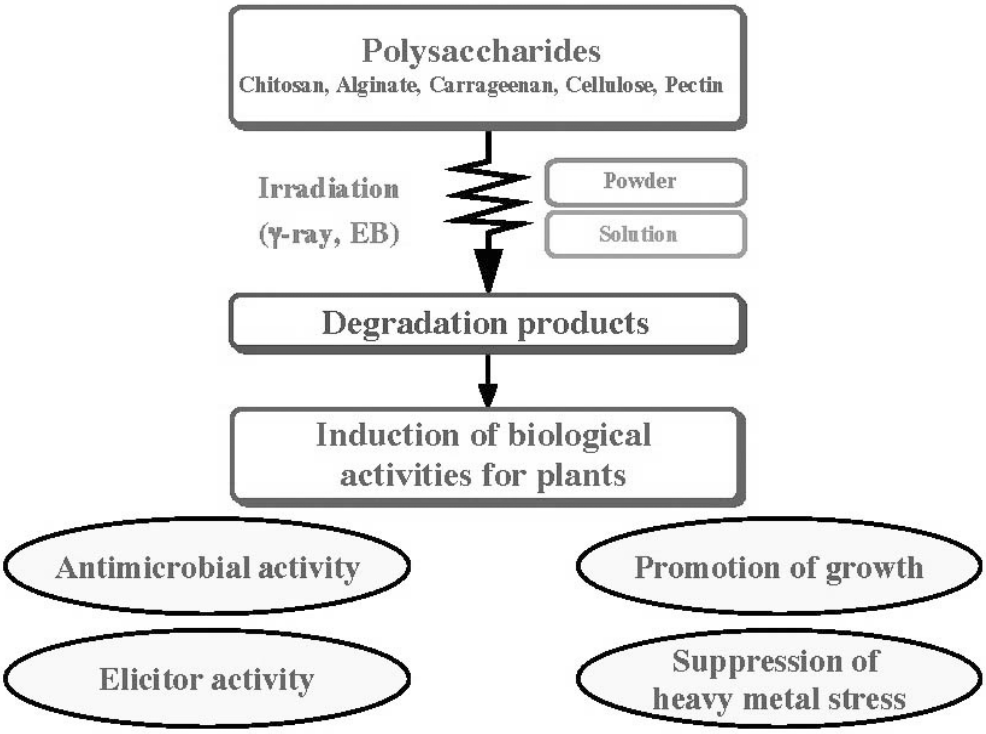

Fig. 7 Induction of biological activities on radiation degraded polysaccharides

The main advantages of radiation processing of polysaccharides are 1) the degradation reaction can be performed at room temperature, 2) the degraded polysaccharides can be used without purification, 3) the simplicity of controlling the whole process, and above all, 4) large-scale application. Radiation degraded polysaccharides was also effective to enhance the growth of plants in tissue culture.

Polysaccharides have been recognized as a degradable type of polymer. However, we found that carboxymethyl-cellulose (CMC) could be crosslinked under certain radiation condition at a high concentration (50-60 %) in an aqueous solution [11)]. 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.

Radiation processing is a clean process without use of chemical initiator, catalyses and solvent. The synthetic polymers were commonly used for the radiation processing of polymers. However, it is concerned the depletion of resources such as coal and petroleum for the synthetic polymers. On the other hand, natural polymers including polysaccharides are abundant resources with unique characteristics such as biodegradability and renewable. It is, therefore, important to convert the resources for radiation processing from synthetic polymers to natural polymers for recycling the bio-resources and reducing the environmental pollution, especially for tropical and sub-tropical countries where the natural polymers produced abundantly through the year.

The main irradiation sources are γ-ray from Co-60 and EB generated from electron accelerator. Due to the high penetration power, γ-ray is widely used for sterilization of medical supplies and food irradiation that are bulky and packed with high-density. The penetration power of EB is limited but the EB irradiation system has a variety of applications controlling the penetration with energy and good safety features. Especially a self-shielded low energy accelerator system needs an initial investment much lower than a Co-60 facility and its operation is simple and safe. Further development of irradiation system using low energy EB is expected to reduce the cost of radiation processing.

References

1) K Yanagisawa, *et al.*, “An Economic Index regarding Market Creation of Products Obtained form Utilization of Radiation and Nuclear Energy (4): Comparison between Japan and U.S.A.”, *J. Nucl. Sci. Tech.*, **39**, 1120 (2002).
2) JAERI: Special Committee for Evaluation of Economy on Utilization of Radiation, “FY 1999, Study on Influence of Utilization of Radiation on Japanese People’s Life”, Report prepared for STA (2000). [in Japanese]
3) M. Asano, *et al.*, “Production of Fuel Cell Membrane by Radiation”, *Radiation & Industries*, **101**, 75 (2004). [in Japanese]
4) Supplement Database on Approvals For Irradiated Foods, *Food and Environmental Protection Newsletter*, Vol. 9, No. 1, p. 20, 2006, (http://www-naweb.iaea.org/nafa/fep/public/fep-nl-9-1.pdf)
5) T. Kume, *et al.*, “Economic Scale of Utilization of Radiation (2): Agriculture”, *J. Nucl. Sci. Tech.*, **39**, 1106 (2002).
6) A. Tanaka, “Mutation induction by ion beams in Arabidopsis”, *Proc. Gamma Fields Symposia* No. 38, p. 19 (1999).
7) T. Kume, *et al.*, “Uptake and Transport of Positron-emitting Tracer (^{18}F) in Plants”, *Appl. Radiat. Isot.*, **48**, 1035 (1997).
8) T. Kume, *et al.*, “Study on Upgrading of Oil Palm Wastes to Animal Feeds by Radiation and Fermentation Processing,” *JAERI-Research 98-013* (1998).
9) M. J. Lee, et al., “Present Status on the Use of Electron Accelerator for Wastewater Treatment in Korea,” *JAEA-Conf 2006-006*, p. 94 (2006).
10) T. Kume, *et al.*, “Utilization of carbohydrates by radiation processing”, *Radiat. Phys. Chem.*, **63**, 625 (2002).
11) B. Fei, *et al.*, “Hydrogel of biodegradable cellulose derivatives, I. Radiation-induced crosslinking of CMC”, *J. Appl. Polym. Sci.*, **78**, 278 (2000).

5.2 Radiation Processing Program at the Malaysian Nuclear Agency

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Abstract

Radiation processing technology has been proven to enhance industrial efficiency and productivity, improve product quality and competitiveness. For many years, variety 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. In this respect, the most challenging issues are to develop new materials/products that have commercial value and to bring the products from laboratory to market.

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. The government supports R & D and technologies that promote growth (increase export & reduce import); enhanced industrial efficiency, productivity and competitiveness; generate homegrown technology with own brands of goods and services; reduce labor with increasing automation and improve quality of life. In the Second Malaysian Industrial Master Plan (IMP 2) for 1996 ~ 2005 that focused on the manufacturing strategy and cluster-based development, emphasis was given on the full integration of operations along the value chain R & D and product designs to marketing and distribution. Within the manufacturing industry, advanced materials such as composites, either polymer-based, metal-based or ceramic-based were given priority. It is much so, when resource based materials are integrated into the development of advanced materials. In this case, natural rubber, oil palm, starch and other marine polysaccharides products are the potential resources. The secondary or by-products of the resource based materials such as rubber wood, rubber wood fibers, oil palm fronds and empty fruit bunches too can be upgraded and transform into high value added products and at the same time meeting the zero waste concept. Subsequently, in 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.

2. Radiation Processing in Malaysia

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 shrinkable tube and heat shrinkable 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 shrinkable 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 3.0 MeV, 90 kW and a 200 keV, 4 kW. Gamma irradiation plant and gamma cells are also available with the Cobalt-60 strength of 1.0 MCi and < 20,000 Ci respectively. Two laboratory units of UV irradiation system of 100 W/cm^2 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:

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

2.1 Scope of research and development

2.1.1 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.

2.1.2 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 poly(vinyl chloride), 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.

2.1.3 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.

2.1.4 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.

2.2 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 laboratory scale research, developmental or pilot scale research and technology transfer and commercialization.

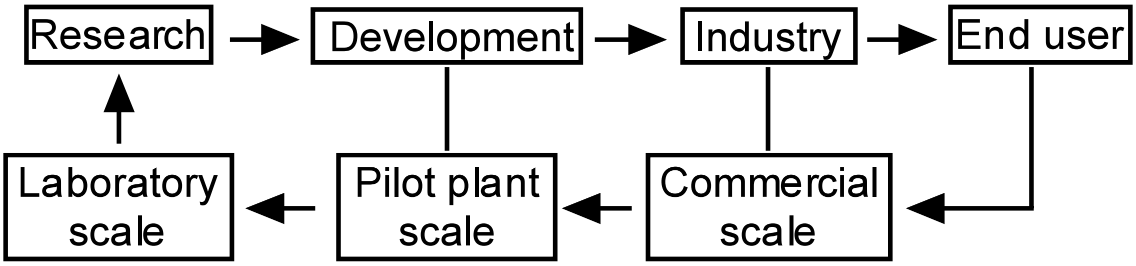

Fig. 1 R&D cycle

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.

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/h gas from diesel generator.
- Synthesis plant 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/h 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 - has been commercialized
- Starch modified compounds for biodegradable packaging film: in the process of commercialization.
- Modified sago-starch
- Starch modified compounds for biodegradable foam products
- Flame retardant compounds for wire insulation: in the process of commercialization
- Heat shrinkable compounds for tube: in the process of commercialization
- PVN-epoxidized natural rubber compounds for under-hood automotive parts
- Radiation resistant PVC compounds for medical product disposable items: in the process of commercialization
- 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.

3. 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 Techno Fund or the Commercialization of Research and Development Fund (CRDF) for pilot scale trial, production, market acceptance tests and market promotion.

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.

4. 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.

Reference

1) Ninth Malaysian Plan, 2006-2010, Chapter 12, Harnessing Science, Technology and Innovation, p. 263 (2006).
2) K. Zaman, K. Hashim, Z. Ghazali, M. Hilmi, J. Sharif, “Radiation Processing of Natural Polymer”, *JAEA-Conf 2006-006*, p. 14 (2006).
3) K. Zaman, H. M. Dahlan, “Radiation Processing Facilities: Malaysian Experience”, *IAEA-TECDOC-1386*, p. 37 (2003).

5.3 Radiation Processing of Natural Rubber and Its Applications

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1. Introduction

No doubts natural rubber (NR) and its related industries still commands a good position in Malaysian economy. In 2005, for example, it contributed nearly US$ 6 billion to the national export earning – equivalent to 4 % of industrial total output – with the employment size of more than 62,000 workers. Malaysia's natural rubber production in 2005 totaled 1.13 million tones compared with almost 1.0 million tones in 2003. In 2005, the rubber products industry consumed 500,000 tones of rubber, with the latex products were the largest consumers followed by industrial and general rubber products and tires 1). But with the recent trend in the global economic scenario and in the government policy itself of promoting value-added products in resource-based industries to diversify the country's sources of economic growth, it is high time for the rubber sector to look for new inventions to broaden the scope of applications of rubber. Taking this into account, continuous research has been carried out for the last couples of decades to search for the new applications of rubber by conducting chemical reaction on the rubber chain itself. Products such as MG rubber, which is commercially available, in which poly(methyl methacrylate) (PMMA) is grafted to natural rubber is such an example 2). Others such as epoxidized natural rubber (ENR) and liquid natural rubber were introduced later 3, 4).

Another important attempt is to make natural rubber more resistant against heat, oxidative and radiation induced degradation by the process called hydrogenation 2). Hydrogenated NR has a structure of alternated copolymer of ethylene and propylene. Such hydrogenated NR has potential to be used in the field where good thermal properties are required like vibration isolators at high temperature. Development of thermoplastic natural rubber (TPNR) is another important initiative to produce value-added NR products capable of competing with other thermoplastic elastomers. It is a blend of natural rubber and thermoplastic materials such as polyethylene, PVC, polystyrene etc. 5). Realizing the importance of natural rubber to the national economy, the Malaysian Nuclear Agency since late 1980's with cooperation from the Japan Atomic Energy Agency (JAEA) and IAEA has also embarked on research in using radiation for the vulcanization of natural rubber latex (RVNRL) 6, 7). Besides RVNRL, other research activities involving natural rubber such as TPNR blends have also been actively carried out. Some are explained below.

2. Radiation Vulcanization of Natural Rubber Latex (RVNRL)

Currently the Agency maintains a pilot plant for RVNRL using cobalt source. The pilot plant with capacity to irradiate 2.5 tones of latex per day at 12 kGy irradiation dose was opened in 1998. Figure 1 shows the irradiation facilities which consist of various processing tanks. The process of preparing pre-vulcanized natural rubber latex is continuous one which comprises pumping a latex composition made of high ammonia natural rubber latex, a stabilizer (normally KOH), an acrylate monomer, an anti-oxidant and water, through corrosion resistant piping system, past a source of gamma radiation at a certain rate flow. The rate flow is pre-determined to ensure a constant radiation dose between 8 and 15 kGy, preferably between 10 and 12 kGy.

The advantages offered by RVNRL over the sulfur-based vulcanization are as follows;

- Free from nitrosamines and low in nitrosatable amines
- Free from chemical accelerators induced allergies

- Highly leachable protein
- Lower ash residue and acid combustion gases
- Non-copper staining
- Non-toxic effluent
- Biodegradability

RAYMINTEX plant *Formulation and storage tanks*

Fig. 1 RVNRL semi industrial plant at Malaysian Nuclear Agency

At present RVNRL is proven to be popular with finger coat and fingerstall manufacturers. The latex has also been tested for manufacturing the products like examination gloves, balloons and dental covers. Other potential products using RVNRL include condoms, catheters, baby teats and rubber thread.

3. Plasticizer-Free Thermoplastics/Epoxidized Natural Rubber Blend Compounds

The project relates to the development of plasticizer-free thermoplastic elastomers (TPE) compounds based on polyvinylchloride (PVC) and epoxidized natural rubber (ENR) which are suitable to be processed by using common processing techniques such as single screw extruder and injection molding. The compounds are also radiation crosslinkable. The radiation processed PVC/ENR blends are found to render enhanced mechanical properties. In the Second Industrial Master Plan (1996 ~ 2005) of Malaysia, rubber product manufacturing is identified as one of the activities under the resource–based cluster. The plan calls for a diversification of the current range of rubber products, which is dominated by latex dipped goods, and identifies, for example, value addition of such products as for engineering applications. Thus, the development of new compounds based on ENR and PVC that exhibit properties comparable to synthetic polymers will generate a new growth in the utilization of natural rubber and diversification of the current range of rubber products. Tables 1 and 2 show some of the blend properties generated from this project.

Table 1 Properties of soft ENR/PVC blend compounds for weather strips, gear knobs, hoses etc.

Properties	Test Methods	Units	Results
Tensile Strength	ASTM D 638	MPa	4 ~ 18
Elongation at break	ASTM D 638	%	250 - 400
Hardness	ASTM D 2240	Shore A	50 - 70
Specific Gravity	ASTM D 1505-72	-	1.2
Retention in Elongation (at 70°C/ 7 days)	BS 903: AA19	%	90 ~ 100

Table 2 Properties of hard grade PVC/ENR blend compounds for armrest, dashboard etc.

Properties	Test methods	Formulation A	Formulation A	Radiation crosslinkable formulation
		Unirradiated	Irradiated	
Tensile strength (MPa)	ASTM D638	32 ~ 33	35 ~ 37	50 ~ 55
Elongation at break (%)	ASTM D638	350 ~ 400	200 ~ 250	350 ~ 400
Flexural Modulus (MPa)	ASTM D790	1700 ~ 1750	2400 ~ 2600	2600 ~ 2800
Izod Impact Strength (notched) (J/m)	ASTM D256	32 ~ 33	35 ~ 37	38 ~ 42
Shore D Hardness	ASTM D2240	55 ~ 58	60 ~ 62	62 ~ 64
Retention in Tensile (%)	BS903 Pt A 19	80 ~ 90	70 ~ 80	100

The Innovation

Durable, superior strength, recyclable; plasticizer-, cadmium- and lead-free flexible PVC compounds have been successfully developed by using indigenous material i.e. epoxidized natural rubber – patented under Malaysian Patent (PI20043088). The Innovation is inline with commitments of Vinyl 2010 of EU for sustainable development of PVC.

Main Advantages:

- Eliminate phthalate plasticizers consumption in respective applications
- Rubber acts as permanent plasticizer thus no hardening of the product due to plasticizer migration
- Improved elastic and adhesive properties with the addition of rubber
- Enhanced mechanical properties by irradiation
- Cheaper in comparison with corresponding applications of Santoprene rubber
- Cadmium and lead free

Applications:

- Automotive interior/exterior parts such as body & side protection strips, weather strips and window sealing profiles
- Building profiles such as door and window sealing profiles
- Fuel & Industrial hoses

Target Market

- Automotive
- Construction/building

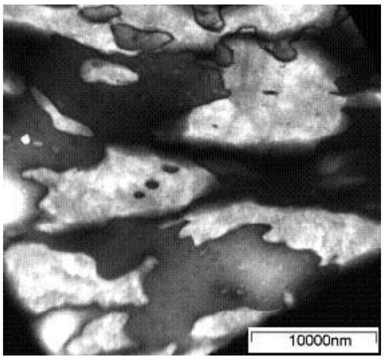
4. Radiation Sensitive NR-based Compatibilizer for TPNR Blends

4.1 Structural studies on liquid ENR acrylate as compatibilizer

Development of modified NR as compatibilizer in immiscible NR/polyolefin (PO) blends has always attracted our interest. Since couple of years ago we have reported some progress along this line [8, 9]. We have carried out the miscibility study by using various normal instrumental techniques such as physical properties by universal testing machine; morphological studies by scanning electron microscopy; dynamic mechanical studies by dynamic mechanical analysis; and thermal studies by differential scanning calorimetry. However we are aware that the mechanical property of those blends depends on the multi-phase structure and the interfacial property of the blends which those mentioned techniques could not reveal very much. In 2005

Yamauchi, et al. published a paper on the possibility of using small angle scattering technique (SANS and SAXS) to study such a problem [10]. In their paper, they show that the requirement of deuterated polymers as normally the case with SANS technique was no longer necessary – making the technique more accessible to the larger group of people. SANS is much more sensitive to composition difference than density difference as compared to Transmission Electron Microscopy (TEM) and Small Angle X-ray Scattering (SAXS) especially in the case of hydrogen and deuterium. By taking this advantage, information on the phase-separated structure can be extracted from a more complex structure in which crystalline/amorphous and phase-separated structures coexist, leading to the interface thickness between the phases separated domains. This data is so important to the researchers because it is quantitative indicator to the miscibility of the two polymers. In this work we report the utilizations of TEM and SANS techniques to study the morphology and phase behavior of rubber dominant NR/HDPE blends upon addition of LENRA and EB irradiation. It is a further work to the one reported previously [9].

Figure 2 of TEM image shows the dark and bright areas correspond to NR domains stained with OsO_4 and unstained HDPE domains, respectively.



TEM image
Fig. 2 NR/HDPE, 500X

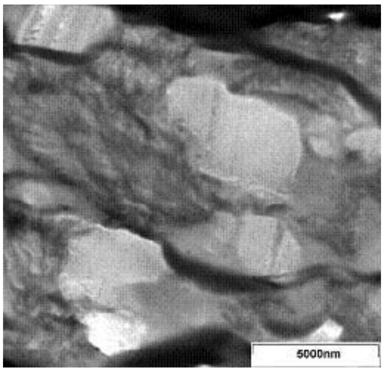


Fig. 3 NR/HDPE, 5% LENRA, 0 kGy, 1000X

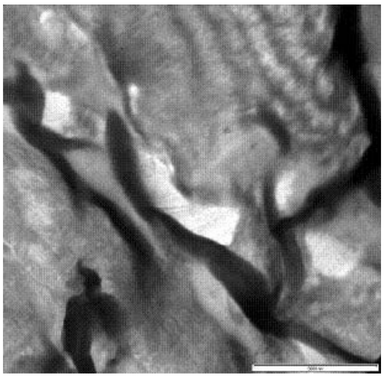


Fig. 4 NR/HDPE, 15% LENRA, 200 kGy, 1000X

A phase separated structure of HDPE domains of irregular shapes was observed, imbedded in NR matrix and vice versa. When LENRA was added to the blend formulation, the well separated domains were no longer observed in the TEM image as shown Figure 3, instead some mix-up does show up. It is due to the dynamic vulcanization process of NR domains caused by addition of LENRA. When the blends were further treated with EB radiation of 200 kGy dose, the TEM image shown in Figure 4, is almost covered up by the dark domain meaning that the crosslinked phase of the NR domains has been transformed into a co-continuous structure induced by EB radiation and LENRA.

4.2 Evaluation of miscibility

Improving understanding on how two immiscible blend components arrange themselves at interface is of paramount important to researchers. By doing this we can determine the interface thickness, t which is a good measure of the miscibility of two polymers and related to Flory-Huggins interaction parameter, χ for the strong segregation limit by the following equation [11].

$$t = 2l / (6\chi)^2 \cdots\cdots\cdots\cdots (1)$$

where *l* is the statistical segment length of polymers.

The interface thickness, *t* can be obtained by plotting in I (q)q^4 against q^2 from the data derived from SANS analysis of Porod region when the slope of the scattering curve approaches to or exceeds – 4 in the Porod equation [10, 12, 13]. By following the Porod equation, finally *t* can be determined by this relationship,

$$t^2 = 2\pi \sigma^2 \quad \cdots\cdots (2)$$

where σ^2 is the slope of the scattering curve.

Figures 5 and 6 are examples of the Porod plots of scattering curves for the NR/HDPE blend samples containing 5 % and 15 % of LENRA, respectively.

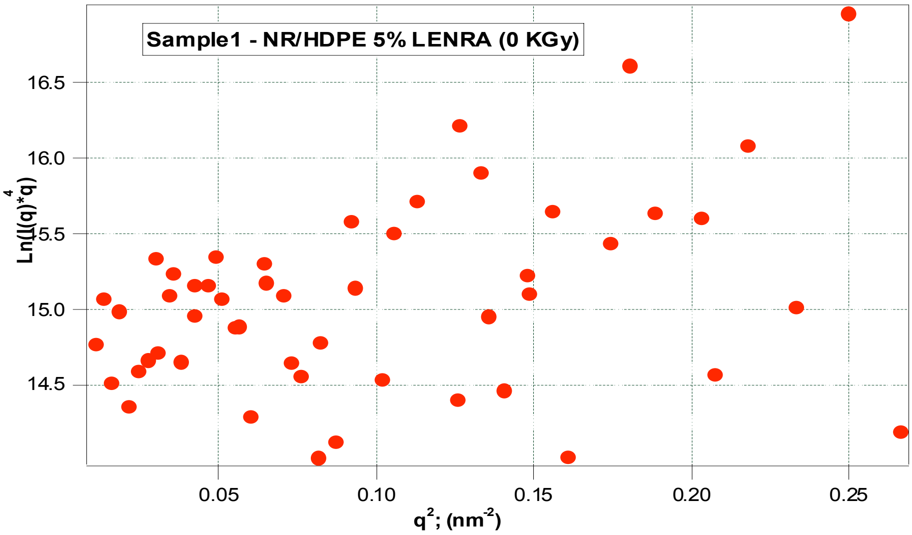


Fig. 5 Porod plot of NR/HDPE blend containing 5% LENRA (0 kGy)

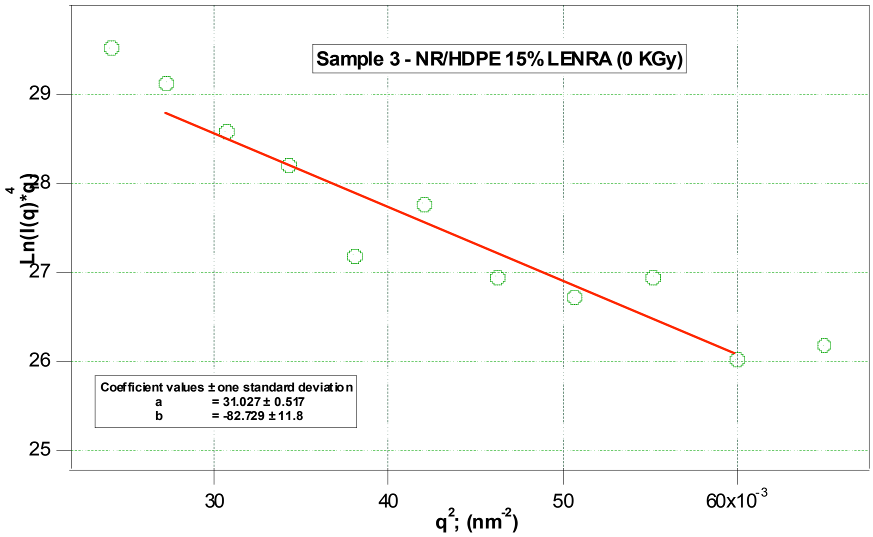


Fig. 6 Porod plot of NR/HDPE blend containing 15% LENRA (0 kGy)

By curve fitting the slopes of the curves can be evaluated leading to the determination of interface thickness, t as given in Table 3.

Table 3 Calculated values of interface thickness t

Sample	σ (nm)	t (nm)
NR/HDPE – 5% LENRA (0 kGy)	No Porod plot observed	
NR/HDPE - 10% LENRA (0 kGy)	No Porod plot observed	
NR/HDPE - 15% LENRA (0 kGy)	9.09	22.80
NR/HDPE - 0% LENRA (200 kGy)	5.59	14.02
NR/HDPE - 15% LENRA (200 kGy)	6.62	16.59

5. Conclusions

Research in natural rubber is still offering good and exciting opportunities especially in making NR into superior products and as a source for new chemicals by modification of its structure. As in the case of LENRA, it has been shown that it has the ability to induce the interfacial interaction between NR and polyolefin i.e. HDPE as demonstrated by TEM and SANS techniques. For NR/HDPE blend, without deuteration technique, SANS was able to induce some scattering data leading to fruitful information on the interfacial interaction between the blend compositions.

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References

1) Malaysian NR Statistics, http://www.lgm.gov.my/nrstat/nrstatframe.html (visited Dec 2006)
2) J. I. Kroschwitz, *Encyclopedia of Polymer Science and Engineering*, John Wiley & Sons, New York (1987).
3) R. Gelling, *Rubb. Chem. Tech.*, **58**,86 (1985).
4) L. M. K. Tillekeratne, UNIDO Workshop on Liquid Natural Rubber, Abidjan, Ivory Coast (1986).
5) A. Ibrahim, H. M. Dahlan, M, *Prog. Polym. Sci.*, **23**, 665(1998).
6) W. M. Wan Zin, N. Mohid, M. Y. Razali, *Radiat. Phys. Chem.*, **46**, 1019(1995).
7) K. Makuuchi, *An Introduction to RVNRL*, TRI Global Co., Ltd., Bangkok (2003).
8) H. M. Dahlan, K. Zaman, A. Ibrahim, *J. Appl. Polym. Sci.*, **78**, 1776(2000).
9) M. Mahathir, H. M. Dahlan, *Proceeding of MINT R&D Seminar*, 12-15 July, 2004, Bangi.
10) K. Yamauchi, S. Akasaka, H. Hasegawa, S. Koizumi, C. Deeprasertkul, C. J. Laokijcharoen, , A. Kornduangkaeo, *Composites*: Part A, **36**, 423 (2005).
11) E. J. Helfand, A. M. Sapse, *J. Chem. Phys.* **62**, 1327 (1975).
12) G. Porod, *Kolloid Z.* **24**, 83 (1951).
13) G. Porod, *Kolloid Z .* **25**, 51, 108 (1952).

5.4 Radiation Curing Applications of Palm Oil Acrylates

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Abstract

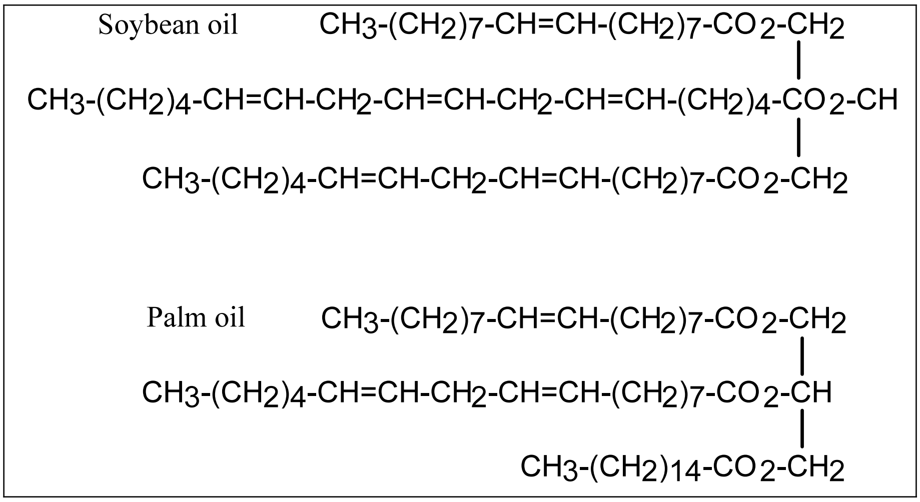
Various palm oil based urethan acrylate prepolymers (UP) were prepared from palm oil based polyols, diisocyanate compounds and hydroxyl terminated acrylate monomers by following procedure derived from established methods. The products were compared with each other in term of their molecular weights (MW), viscosities, curing speed by UV irradiation, gel contents and film hardness. The molecular structure of diisocyanate compounds and hydroxyl acrylate monomers were tend to determine the molecular weights and hence viscosities of the final products of urethan acrylate prepolymers (UP), whereas, the MW of the UP has no direct effects on the UV curing properties of the prepolymers.

1. Introduction

Natural acrylate is made from vegetable oils - palm oil (RBD palm olein). It is synthesized by introducing the acrylate groups onto the carbon-carbon double bonds of the molecular chain of the palm oils. It requires a synthesis chemical plant to produce natural acrylate at a commercial scale. Natural acrylate is in liquid form and it is used in the formulation of adhesives, printing inks and coatings materials. Starting materials for natural acrylate is RBD palm olein, current market price is RM1.70/kg. Natural acrylate (palm oil based) resins price are estimated in the range of RM 4.90 ~ RM 7.00/kg (e.g. polyester and polyurethane). Price of commercial acrylate resins in the market is ranging from RM 20.0 ~ RM 40.0/kg (e.g. polyester and polyurethane).

2. Palm oil based urethane resins and applications in surface coatings

The presence of unsaturation in the fatty acids of vegetable oils such as palm oil, technically paves the way for the production of radiation curable (acrylated) oligomers/resins. The more unsaturated the oil, the better it will perform in the radiation curing related applications. Palm oil (PO) and its products contain level of unsaturation that is half or less than half of that of soybean oil as shown in Figure 1.



Soybean oil
$$CH_3\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}CO_2\text{-}CH_2$$
$$CH_3\text{-}(CH_2)_4\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_4\text{-}CO_2\text{-}CH$$
$$CH_3\text{-}(CH_2)_4\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}CO_2\text{-}CH_2$$

Palm oil
$$CH_3\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}CO_2\text{-}CH_2$$
$$CH_3\text{-}(CH_2)_4\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}CO_2\text{-}CH$$
$$CH_3\text{-}(CH_2)_{14}\text{-}CO_2\text{-}CH_2$$

Fig. 1 Chemical structures of triglyceride oil

It has therefore never being thought of as suitable raw materials for the production of resins. However it was of interest to find out to what extent could PO or its products can be used as radiation curable resins compare with linseed oil, soybean oil, etc., as even a slight substitution is a step towards changing the situation from having to import to being self sufficient.

The first acrylated palm oil was synthesized from epoxidized palm oil (RBD palm olein) products (EPOP) in early 1989, through acrylation and methacrylation processes at MINT laboratory. The reaction scheme for the synthesis of palm oil acrylates is given in Figure 2. The acrylated products namely Epoxidized Palm Oil Acrylate/Methacrylate (EPOLA/EPOMA), with the molecular weight around 2000-3000, was found curable when subjected to UV or EB irradiations.

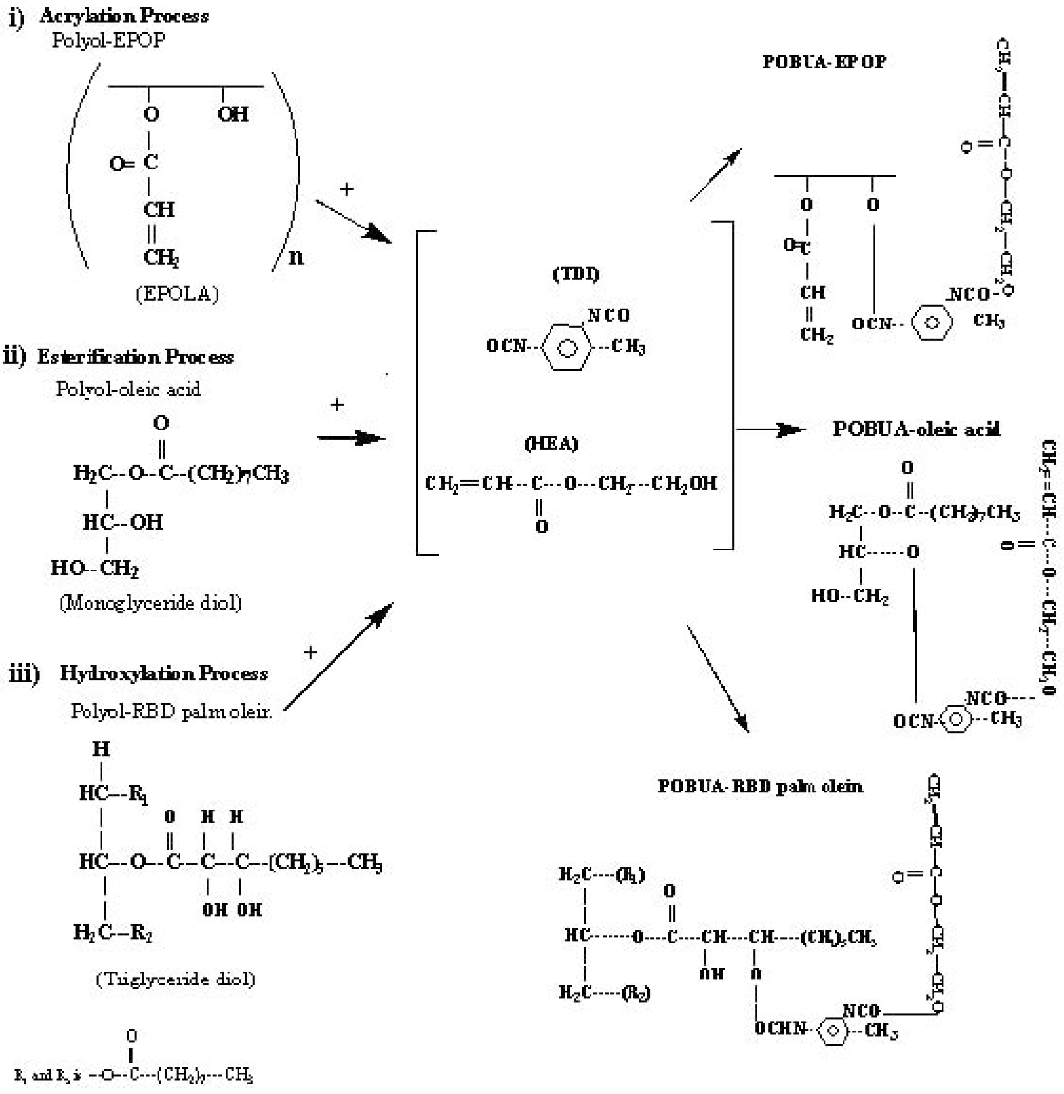


Fig. 2 Reaction scheme for synthesis of palm oil acrylate

Isocyanation of EPOLAs resulted in a resin called Palm Oil Based Urethane Acrylate (POBUA). This latest resin possess certain advantages over EPOLA such as much higher molecular weight (between 5,000 to 20,000), better curing speed, crosslinking density, higher abrasion resistance, higher tensile properties and also higher pendulum hardness. The following is the performance of palm oil based resin in comparison to the petroleum based (Table 1)

Table 1 Curing/coatings performances of palm oil based resin vs. petroleum based resin

Properties	Petroleum Acrylates	Palm Oil Acrylates
Rate of UV cure (10-25m/min conveyor speed, 7.5 A current)	Varies (structural dependence)	Varies (structural dependence) i.e., 1-5 # passes
Hardness (coatings)	Standard (40-60% Pendulum hardness)	Less/softer (20-40% Pendulum hardness)
Tensile Strength	Standard	Less/inferior
Adhesion (On Paper/PET/ wood substrates)	Standard	Superior (80-100%)
Molecular weight (MW)	Variable/adjustable (could be very high, up to 106)	Variable/adjustable (2,000-20,000)
Glossiness (coatings)	Standard	Standard (60-90° at 60 degree)
Environmental impact	Maximum	Biodegradable Environmental friendly Less VOC
Price	Expensive	Cheaper
Materials resources	Non-renewable	Renewable

3. Applications

The current applications of palm oil acrylates are in the field of pressure sensitive adhesives (PSA), printing inks and surface coatings of wood substrates such as parquet, tabletop etc. The potentials future applications of the acrylates are permanent glues for consumers (e.g. students & domestic users), PU foams/elastomers for industrial applications and medical tapes/labels (PSA products)

3.1 Development of non-permanent type PSA

Most of PSA formulations that were carried out at MINT laboratory had satisfactorily utilized epoxidized RBD palm olein acrylate/methacrylate (EPOLA/EPOMA) and palm oil based urethane acrylate (POBUA) synthesized at MINT. These formulations are non-permanent type PSAs which form a permanently tacky film after drying of liquid formulations by means of radiation (UV/EB) curing. Bonding is effective by slightly pressing the adhesive surface onto the adherent.

PSA can be classified as either non-permanent (272.2 to 907.2 g/in of 180° peel adhesion) or permanent (above 907.2 g/in 180° peel adhesion). Adhesives included in the former category find utility in the manufacture of removable tapes (paper), labels (paper), protective laminates (PET films), surgical/medical tapes (paper), electrical insulation tapes (PET films), masking tapes (paper), packaging tapes (paper/clothes), cellophane tapes (cellulose) and other less durable products, whereas the more permanent adhesives are used for plastic decals, backings for floor tiles, etc. The following is the performance of PSA developed by MINT (Table 2).

3.2 Development of printing inks

The current focus of the present work was to evaluate the application of radiation curable palm oil resins, particularly POBUA in the printing inks formulation. The results in Table 3 have indicated that acrylated palm oil resins could be introduced into the radiation curable ink system.

Table 2 Performance trials: mint palm oil based PSA products vs. petroleum based

Properties	Petroleum based	Palm Oil derivatives
Rate of UV cure (10 ~ 25m/min conveyor, 7.5 mA current)	Variable	Variable/ 1-5 # passes (structural dependence), satisfactory
Peel Adhesion, g/inch (Paper/PET)	Variable	Variable/ 280 ~ 873 g/inch, satisfactory
Tackiness, gf (PET)	Variable	Variable/ 280 ~ 586 gf
Mode of failure	Varies	Mostly Clean Release Failure (CRF)
Environmental impact	Maximum	Biodegradable Environmental friendly Less VOC
Price	Expensive	Cheaper
Materials resources	Non-renewable	Renewable

Table 3 Performance trials: petroleum based ink vs palm oil based (POBUA) ink

Properties	Petroleum based	Palm Oil derivatives
Rate of cure	Fast curing	Satisfactorily Fast Curing (under structural mode. to improve cure)
Adhesion (Paper/PET)	Standard	Superior
Tack; Stability	Standard (IR = 10±0.5, SR =18±0.5)	Standard IR = 10±0.5, SR =18±0.5)
Glossiness	Standard	Standard
Price	Expensive	Cheaper
Materials resources	Non-renewable	renewable

IR; Ink-o-meter reading, SR; Spread-o-meter

Further work is required to improve curing property such as modification of palm oil during synthesis by introducing more functionality. It is generally accepted that products derived from natural oils and fats are more readily biodegradable than the corresponding products made from petroleum. Palm oil based ink may therefore be expected to be environmentally friendlier than petroleum based ink. It is therefore envisaged that its future use in printing industries will results in a healthier working environment.

4. Commercialization

4.1 Benefits/advantages of palm oil based resins

- Environmental friendly (biodegradable vegetable oil)
- Locally produced (currently most acrylate resins are imported)
- Local technical support (home grown technical know how) in the production of resins and the applications. Products could be tailored made according to needs (e.g. polyester…or polyurethanes-aliphatic or aromatic of different MW)
- Future products development (products improvement, e.g. enhancement of curing speed or crosslinking density)
- Renewable resources – palm oils
- Standard and fast start-up (easy to handle) synthesis plant

The UV/EB curable process for making finished products (e.g. coatings, PSA & printing inks) from acrylated resins is an environmental friendly (not involve the evaporation of solvents into the environment such as occurring in a conventional heat/oven drying process).

4.2 Estimated market size

Industry (Acrylate resins for PSA, printing inks and coatings)

	Year	Tons	Potential growth
Malaysia	1998	1,570	Average 10% per annum
	2003	2,537	
China and Japan	2000	50,350	10% in China
	2003	71,949	7% in Japan

4.3 Potential partners

- Local companies – palm oil derivatives manufacturers and finished products manufacturers (For manufacturing of palm oil based acrylated resins & products development)
- Regional/International companies- manufacturers of acrylated resins & finished products

4.4 Intellectual property rights

- Patent PI 2003 1627 - The synthesis and production of palm oil based urethane acrylates (POBUA) for use in UV/EB curing of coatings, adhesives and printing inks
- Patent PI 2004 0082 - Radiation curable Pressure Sensitive Adhesives (PSA) from palm oil based resins/oligomers and manufacturing method thereof
- Patent PI 2004 3190 – Methods for Production of Palm Oil Based Polyols for Use In Making Polyurethane Materials

4.5 Current status and development

Scale up process to produce 25 kg of natural acrylates at Nuclear Malaysia

4.6 Status of Commercialization

Recently, one local company have shown interests in commercializing our palm oil acrylate products by signing Non Disclosure Agreement (NDA) with ANM (formerly known as MINT). A Local Company namely Usaha Kurnia Enterprise has signed the NDA on 30th March 2006. However, to date the progress on the commercialization process has been very slow

5. Conclusions

The presence of double bonds in the triglyceride molecule open the way for the synthesis of several products from palm oil (RBD Palm Olein) such as epoxidized palm oil products (EPOP), palm oil polyols, palm oil based PUs and the acrylated palm oil products. From these acrylate resins several applications have been developed such as for pressure sensitive adhesive and for printing inks. However, the physical properties of the cured products such as flexibility, modulus, hardness and the curing speed could be further enhanced by modifications of the triglyceride molecule. The addition of other linear & longer polymers as well as more branched & higher functional monomers during formulations could also improve those physical properties.

5.5 Environmental Application of Radiation Grafting

Masao Tamada
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Abstract

Adsorbent having high selectivity against a certain metal ion was synthesized by means of radiation-induced graft polymerization for the purpose of environmental application. The resulting adsorbents were utilized for the removal of toxic metal from scallop waste and the collection of uranium from seawater. As a novel application of grafting, the biodegradability of poly-hydroxybutylate was controlled by grafting. The biodegradability could be depressed by the graft chain and then recovered by external stimuli such as thermal and chemical treatments.

1. Introduction

Radiation-induced graft polymerization can impart the desired function into a trunk polymer. Polyethylene, one of general-purpose artificial polymer, is widely used for the trunk polymer of the graft polymerization. When the functional group having the selective affinity against metal ions is introduced into the trunk polymer, the tailored adsorbent can be synthesized by the graft polymerization. Such adsorbents for metal ions can be applied in the environmental preservation which removes the toxic metal ions and the collection of significant metal without producing any slag. In the present paper, the synthesis of metal ion adsorbent with radiation-induced graft polymerization and the applications of the resulting metal ion adsorbents for the environmental preservation are described. The control of biodegradability by grafting is mentioned as a new topic of radiation grafting on natural polymer.

2. Radiation-induced Graft Polymerization and Metal ion Adsorbent

In Japan, the industrial commodities such as separator membrane of button battery and gas adsorption filter are well known products which were highly functionalized by radiation-induced graft polymerization. In the industrial grafting, the pre-irradiation is mainly adopted since the processes of the irradiation and the grafting can be discrete and the homopolymer is depresses in the grafting process.

Figure 1 shows the schematic process of the pre-irradiation grafting. First, electron beam and gamma rays were irradiated to the trunk polymer. Then, monomer was reacted with irradiated trunk polymer. Graft chain propagated from the radicals in the irradiated trunk polymer.

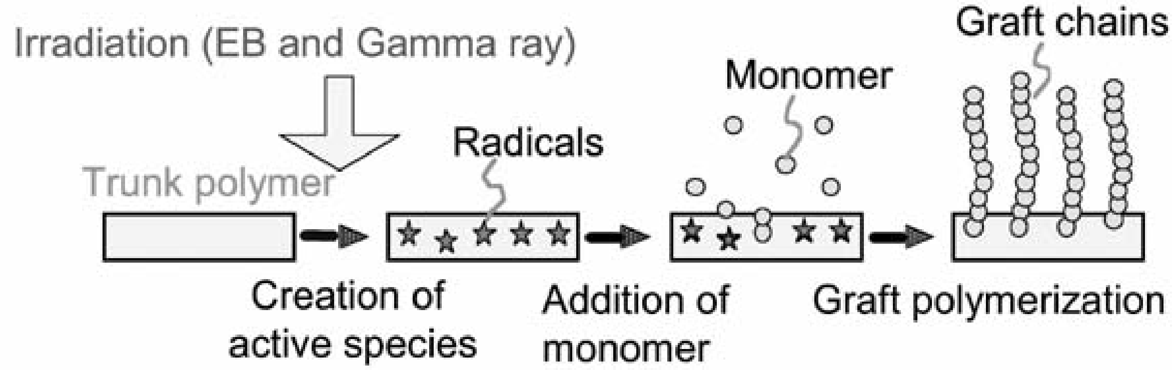
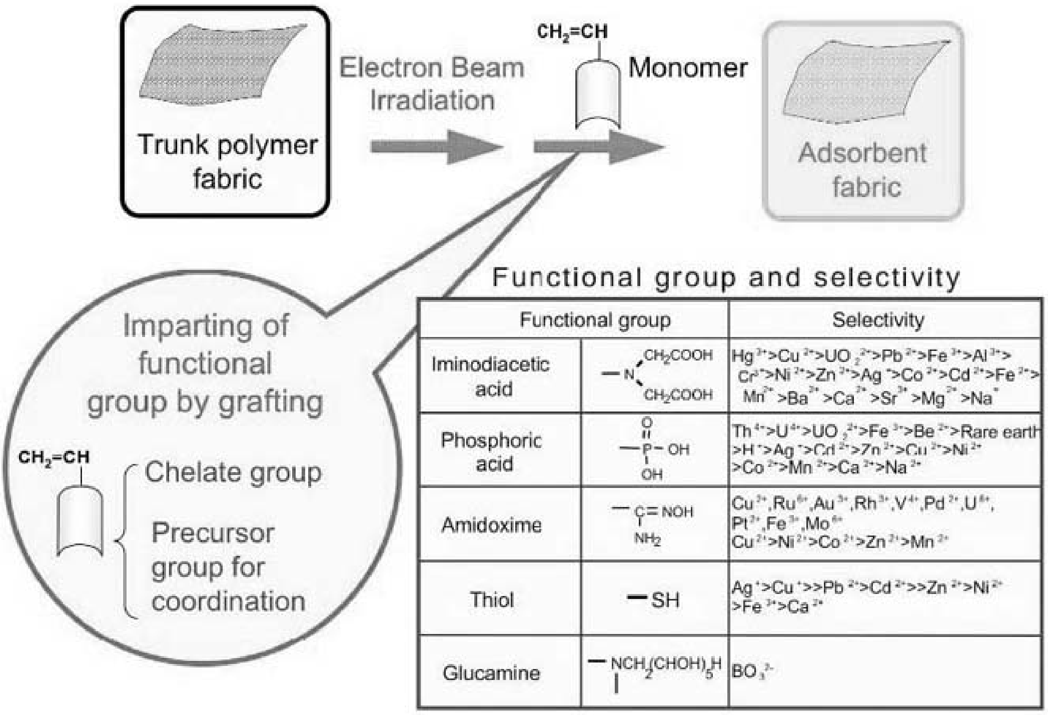


Fig. 1 Pre-irradiation grafting process

On the point of the view of environmental preservation, the metal ion adsorbent was extensively synthesized by the radiation-induced graft polymerization. In this case, the functional monomer must have a chelate group, which creates a coordinate bond with metal ion, in its pendant position and its precursor as shown in Figure 2. When the precursor monomer is grafted, the subsequent chemical modification imparts the chelate group into the grafted trunk polymer.



Functional group		Selectivity
Iminodiacetic acid	$-N<$ CH_2COOH CH_2COOH	$Hg^{2+}>Cu^{2+}>UO_2^{2+}>Pb^{2+}>Fe^{3+}>Al^{3+}>Cr^{3+}>Ni^{2+}>Zn^{2+}>Ag^{+}>Co^{2+}>Cd^{2+}>Fe^{2+}>Mn^{2+}>Ba^{2+}>Ca^{2+}>Sr^{3+}>Mg^{2+}>Na^{+}$
Phosphoric acid	$-P(=O)(OH)-OH$	$Th^{4+}>U^{4+}>UO_2^{2+}>Fe^{3+}>Be^{2+}>$Rare earth $>H^{+}>Ag^{+}>Cd^{2+}>Zn^{2+}>Cu^{2+}>Ni^{2+}>Co^{2+}>Mn^{2+}>Ca^{2+}>Na^{2+}$
Amidoxime	$-C(NH_2)=NOH$	$Cu^{2+}, Ru^{6+}, Au^{3+}, Rh^{3+}, V^{4+}, Pd^{2+}, U^{6+}, Pt^{2+}, Fe^{3+}, Mo^{6+}$ $Cu^{2+}>Ni^{2+}>Co^{2+}>Zn^{2+}>Mn^{2+}$
Thiol	$-SH$	$Ag^{+}>Cu^{+}>>Pb^{2+}>Cd^{2+}>>Zn^{2+}>Ni^{2+}>Fe^{3+}>Ca^{2+}$
Glucamine	$-NCH_2(CHOH)_5H$	BO_3^{3-}

Fig. 2 Synthesis of metal ion adsorbent by grafting

As a trunk polymer for grafting, the polyethylene nonwoven fabric in Figure 3 was selected by the rational cost and the convenient handing. The resulting fibrous adsorbent performed the swift adsorption of metal ion owing to the large surface area. The adsorption rate is generally 100 times faster than that of the commercial resin adsorbent. When the fibrous adsorbent was put into the solution of metal ion, the adsorbed metal ion on the adsorbent was easy removed by taking the adsorbent from the solution.

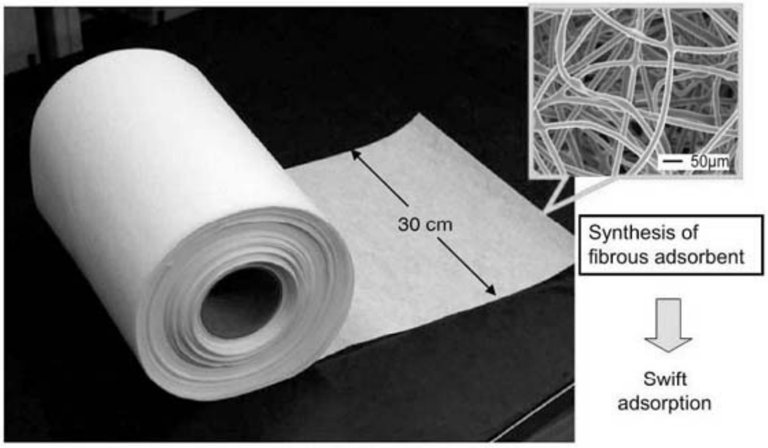
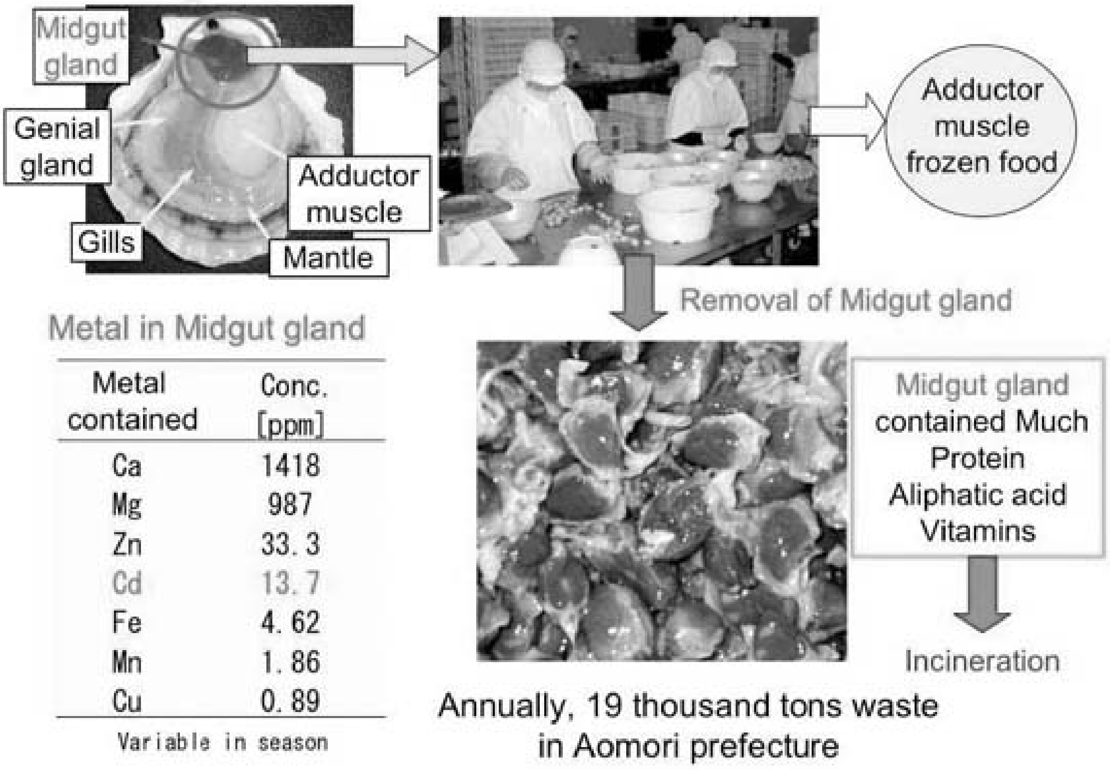


Fig. 3 Polyethylene nonwoven fabric

3. Current Applications of Grafting on Synthesized Polymer

3.1 Removal of toxic metal

A scallop, eatable bivalve, is cultured in the northern sea area in Japan. Annual production of the cultured scallops is one hundred thousands tons. After the scallop processing of boiling and packing adductor muscle in cans as shown in Figure 4, 19 thousands tons of midgut gland and genial gland were discarded.



Metal in Midgut gland

Metal contained	Conc. [ppm]
Ca	1418
Mg	987
Zn	33.3
Cd	13.7
Fe	4.62
Mn	1.86
Cu	0.89

Variable in season

Fig. 4 Cadmium contaminated waste from scallop processing

The waste midgut glands have been incinerated since they were contaminated by the toxic cadmium in the range from 10 to 20 ppm. However, they contain the significant compounds such as docosahexaenoic acid, eicosapentaenoic acid, vitamins and mineral. The removal of cadmium from midgut glands will lead the utilization as animal feed and fertilizer. 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 1). Cadmium in the midgut gland of scallop was extracted by malic acid solution to adsorb it with the fibrous adsorbent. Cadmium ions in malic acid solution were pumped into the column packed with the fibrous adsorbent as shown in Figure 5.

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. g

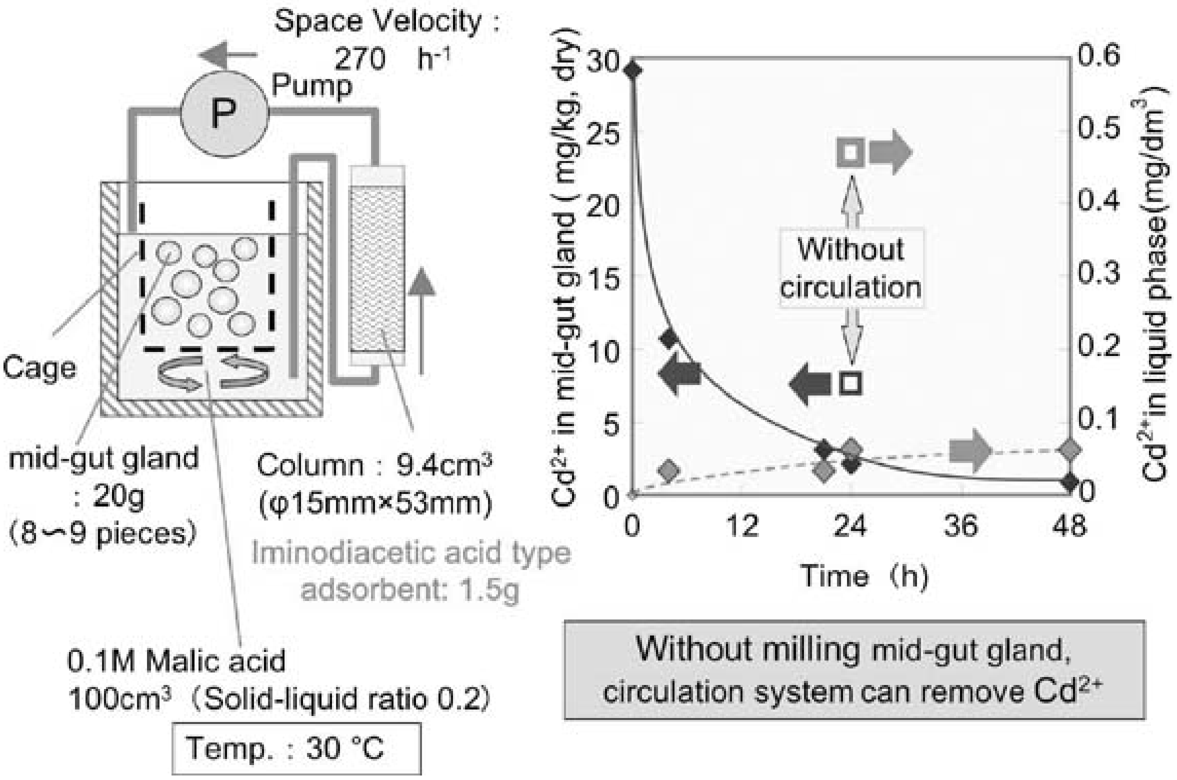
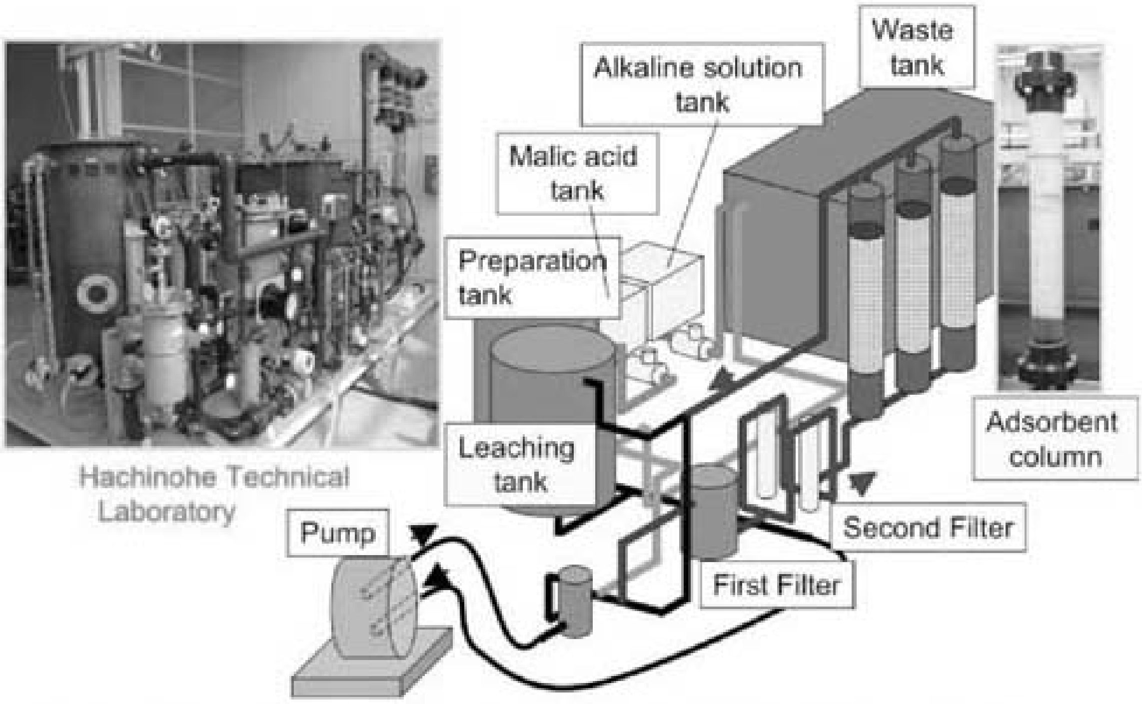


Fig. 5 Removal of cadmium from midgut gland with graft adsorbent

Figure 6 shows the bench scale equipment for the midgut gland treatment. This equipment can treat 30 kg of the midgut gland in one batch treatment.



Scale : Mid-gut gland 20～40kg、 Leaching tank : 200L、 Column : 5L×3 lines

Fig. 6 Bench scale equipment for removal of cadmium from scallop waste

3.2 Recovery of significant metals

Whole amount of the necessary uranium fuel for power generation in Japan depends on its import, though the electric power of the nuclear power generation occupies 34% of that of total Japanese electric power. When the collection of uranium in seawater will be commercialized, the energy security of our country becomes stronger, and can give extra time until an ideal nuclear fuel cycle system is completed. The total amount of uranium in seawater is 4.5 billion tons while uranium concentration in seawater is very low, 3.3 ppb (3.3mg-U in one ton of seawater). This total amount equals to 1000 times of that in the uranium mine. Moreover, the annual amount of the uranium carried by the Black Current, which flows near Japan, is estimated at 5.2 million tons. Collection of 0.2% uranium in the Black Current can cover the supply of nuclear fuel for the power generation in Japan.

To collect the uranium in seawater, the amidoxime type adsorbent was selected. This adsorbent was synthesized by the co-grafting of acrylonitrile and methacrylic acid onto the polyethylene nonwoven fabric and the subsequent chemical reaction with hydrohylamine. The stacks of fibrous adsorbents (350kg) were soaked in the northern part of sea.

Figure 7 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.

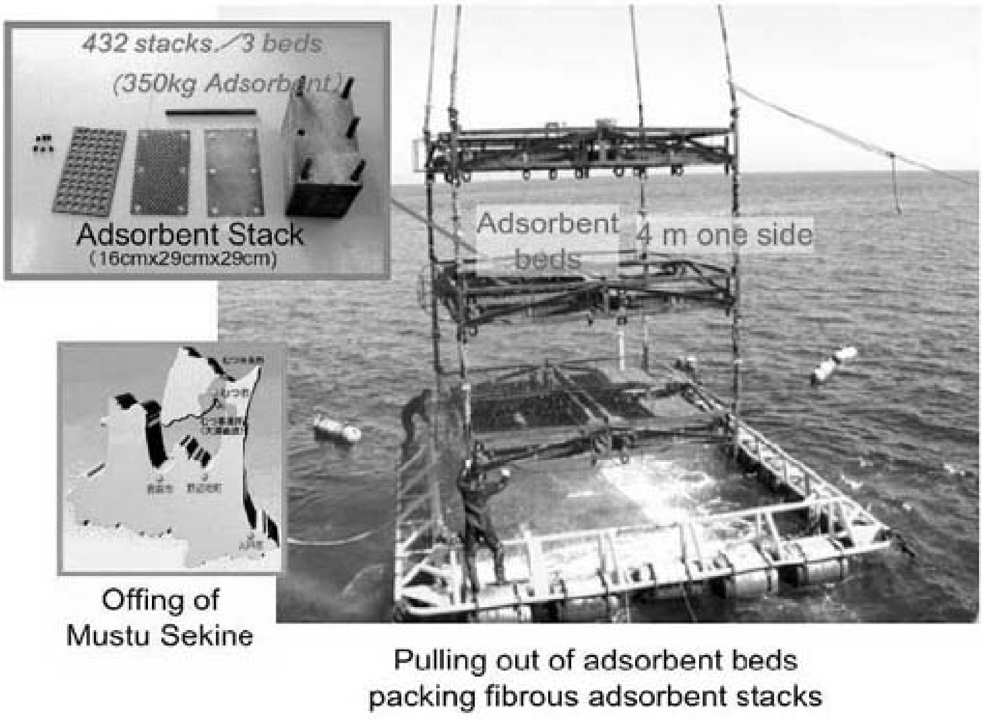
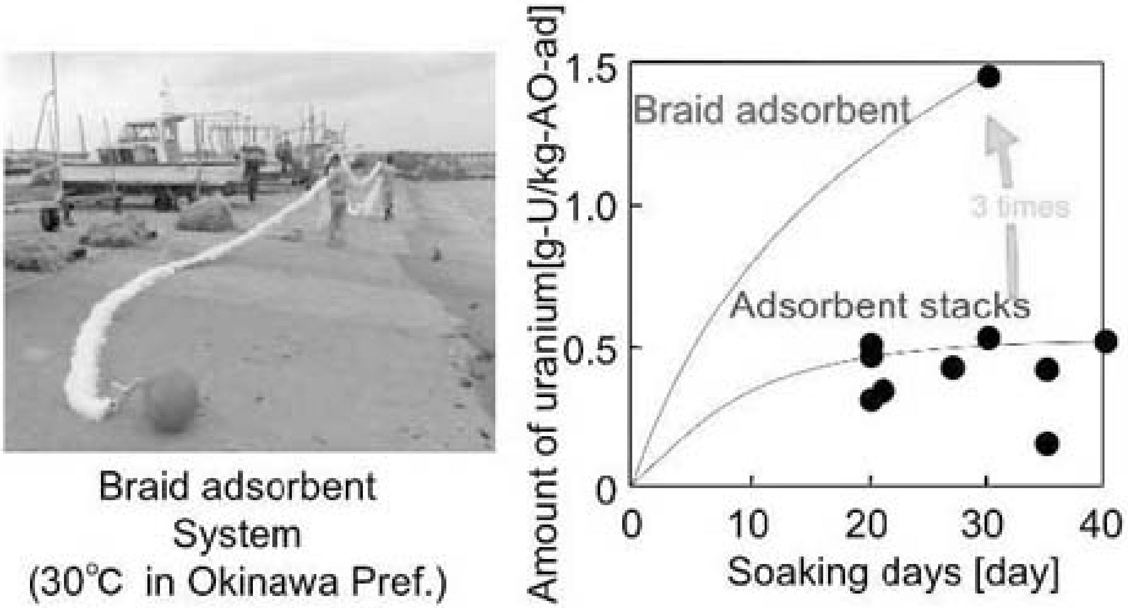


Fig. 7 Uranium collection system of adsorbent stacks

The collection system using adsorption bed packed with fibrous adsorbent stacks was improved to that of a braid type adsorbent. Figure 8 shows the preparation of the soaking of the braid adsorbent and the absorption performance of the adsorbent stacks and the braid type adsorbent.



Braid adsorbent
System
(30°C in Okinawa Pref.)

Fig. 8 Preparation for soaking of braid type adsorbent and performance of uranium adsorption

The braid type adsorbent was produced by imparting the amidoxime group into the polyethylene fiber with grafting and chemical modification. Then, the obtained fibers were braided by incorporating the linear float. 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. This braid type adsorbent was effective to realize the rational cost for the uranium collection from seawater.

3.3 Cost of uranium collection from seawater

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 d and the repetition usage of 6 times, the uranium cost was calculated at 88,000 yen/kg-U by summating the cost of adsorbent production, uranium recovery and uranium purification. 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 yen. This price level is equivalent to that of the highest cost of the minable uranium.

4. Application of Radiation Grafting on Natural Polymer

To reduce the production of carbon dioxide causing global warming, synthesized polymers should be replaced by biopolymer which can be regenerated by metabolism of microorganisms and plants. Polysaccharides such as starch, cellulose, chitosan, alginate, and carrageenan are a typical naturally occurring polymer. By using such polysaccharide derivatives, the radiation-induced crosslinking leads the biodegradable hydrogels which were applied for bedsore prevention mat and water adsorbent.

In the general application as sheet, fabric, food container, tray, stationery, and cabinet of electric appliance, the mechanical strength is an important factor. Some aliphatic polyesters such as poly(caprolactone) (PCL), poly(butylene-succinate), poly(lactic acid) (PLC), and poly(hydroxybutylate) (PHB) were promising for these usages. Biodegradability of PCL and PHB is higher than other two polymers. However, PCL is synthesized by ring-opening polymerization of ε-caprolactone which is petrochemical product. PHB is the most attractive biopolymer.

4.1 Control of Biodegradability of PHB by Graft Polymerization

The biodegradability of PHB powder could be controlled by radiation-induced graft polymerization. A certain amount of grafting of hydrophilic monomer such as acrylic acid and hydroxyethyl methacrylate could accelerate the biodegradation of PHB. It was found that the biodegradability of PHB film was lost by grafting of acrylic acid and then recovered by thermal treatment. Figure 9 shows the biodegradability of the grafted PHB and the thermally treated grafted-PHB. More than 5% of degree of acrylic acid grafting depressed the degradability. After thermal treatment at 190°C, the grafting accelerated the biodegradation at the degree of grafting of 10%. This acceleration was caused by the increment of amorphous region by grafted PHB.

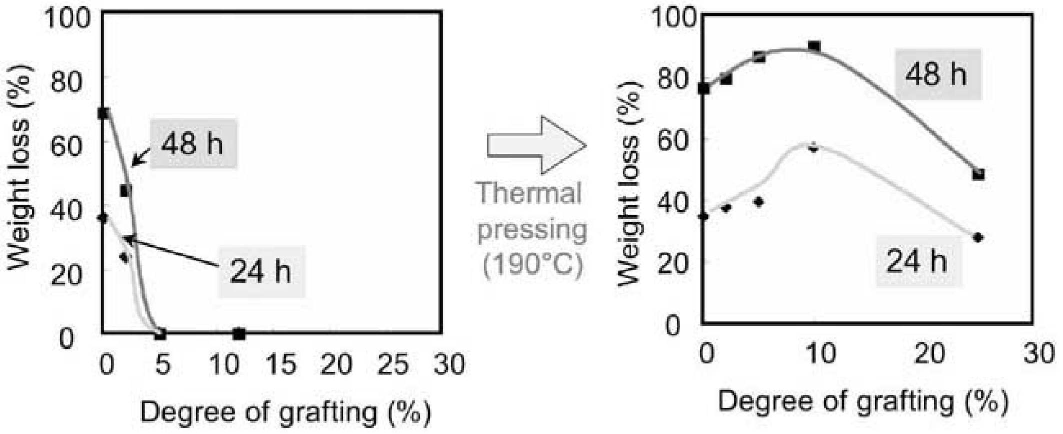


Fig. 9 Biodegradability of PHB grafted with acrylic acid before and thermal treatment

4.2 Introduction of biodegradable grafted chains

Grafted poly(acrylic acid) is non-biodegradable. After degradation of poly(acrylic acid) grafted PHB has a possibility of contamination with poly(acrylic acid). In this reason, the polyvinyl alcohol was used for the control of PHB degradability as shown in Figure 10.

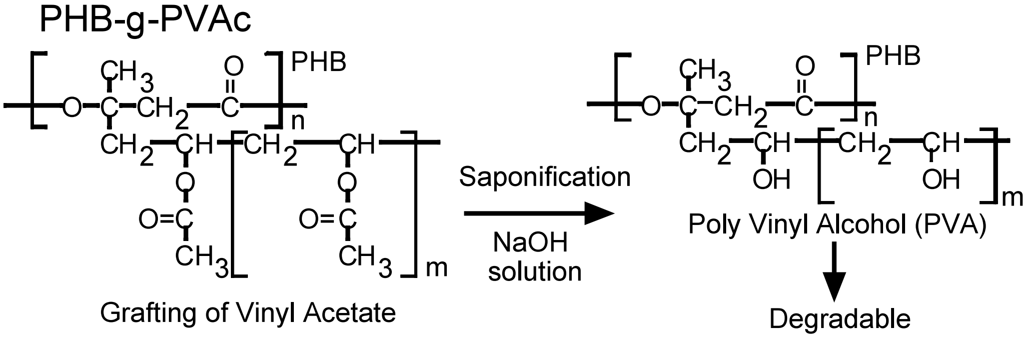


Fig. 10 Preparation of PHB film having chemically induced biodegradability

Graft chain of polyvinyl alcohol was obtained by grafting of vinyl acetate and saponification with alkaline solution. Figure 11 shows the biodegradability evaluated by biochemical oxygen demand (BOD) of the PHB grafted by vinyl acetate and PHB having the graft chains of polyvinyl alcohol. Grafting of vinyl acetate could lose the biodegradability of PHB.

After saponification, the biodegradability of PHB recovered in the considerable level. The grafting on PHB gave the new function of the external stimuli induced biodegradation. This technique can spread the application field of the biodegradable polymer in the agricultural and civil engineering materials.

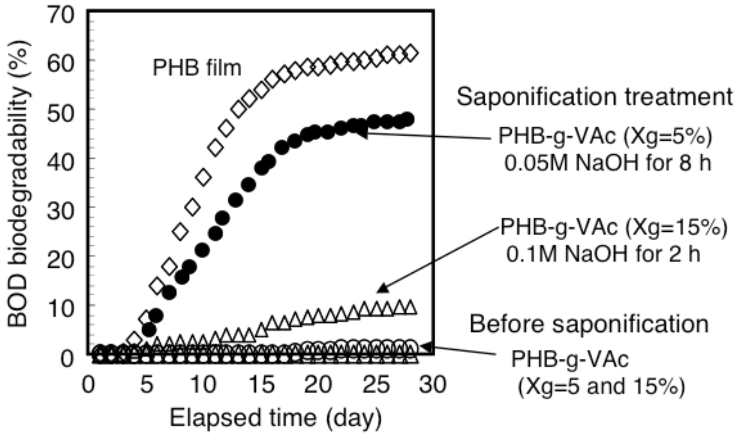


Fig. 11 BOD biodegradation profiles of PHB film grafted by vinyl acetate before and after saponification with alkaline solution, PHB-g-VAc: PHB film grafted by vinyl acetate, Xg: degree of grafting.

References

1) N. Seko, M. Tamada, F. Yoshii, "Current status of adsorbent for metal ions with radiation grafting and crosslinking technique", *Nucl. Instrum. Methods Phys. Res. B,* **236,** 21 (2005).
2) S. Jyo, T. Aoki, K. Kishita, M. Yamabe, M. Tamada T. Sugo, "Phosphonic acid fiber for selective and extremely rapid elimination of Lead (II)". *Anal. Sci*. **17** , Suppl. 201 (2001).
3) N. Seko, A. Katakai, S. Hasegawa, M. Tamada, N. Kasai, H. Takada, T. Sugo, K. Saito, "Aquaculture of uranium in seawater by fabric-adsorbent submerged system", *Nucl. Technol.*, **144** 274 (2003).
4) N. Seko, M. Tamada, N. Kasai, F. Yoshii, T. Shimizu, "Synthesis and evaluation of long braid adsorbent for recovery of uranium from seawater", *Proc. Civil Eng. Ocean*, **20** 611 (2004).
5) M. Tamada, N. Seko, N. Kasai, T. Shimizu, "Cost estimation of uranium recovery from seawater with system of braid type adsorbent", *Trans. At. Energy Soc. Japan*, **5** 358 (2006).
6) F. Yoshii, L. Zhao, R. A. Wach, N. Nagasawa, H. Mitomo, T. Kume, "Hydrogels of polysaccharide derivatives crosslinked with irradiation at paste-like condition", *Nucl. Instrum. Methods Phys. Res. B,* **208**, 320 (2003).
7) Y. Tokiwa, "Bioprocess and Biodegradable plastics", *J. Envir. Biotech*., **4,** 5 (2004) .
8) K. Bahari, H. Mitomo, T. Enjoji, S. Hasegawa, F. Yoshii, K. Makuuchi, "Radiation-induced graft polymerization of styrene onto poly-(3-hydroxybutyrate) and its copolymer with 3-hydroxyvalerate", *Angew. Makromol. Chem*., **250,** 31(1997).
9) Y. Wada, H. Mitomo, K. Kasuya, N. N. Nagasawa. Seko, M. Tamada, "Control of biodegradability of poly(3-hydroxybutyric acid) film with grafting acrylic acid and thermal remolding", *J. Appl. Polym. Sci*., **101,** 3856 (2006).
10) Y. Wada, N. Seko, N. Nagasawa, M. Tamada, K. Kasuya H. Mitomo, "Biodegradability of poly(3-hydroxybutyrate) film grafted with vinyl acetate: effect of grafting and saponification", *Radiat. Phys. Chem*. in press.

5.6 Radiation Processing Facilities and Services in Malaysia

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1. Introduction to Radiation Processing

Radiation processing technology is mostly based on the use of high energy ionizing radiation, mainly gamma rays from Co-60, high energy electrons (0.2 ~ 10 MeV) from electron accelerators and X-ray as a source of energy for different industrial applications. Irradiation can be defined as treating of substances with any form of electromagnetic radiation or high energy electrons. The radiation power needed for industrial processes is typically, between ten to a few hundreds kW. The scientific basis of radiation technology is the reactive chemical species produced by absorbed radiation resulting in changes in chemical, physical and biological properties.

1.1 Gamma Irradiation

Contrary to what most people believe, Co-60 is not a waste product of nuclear power plants. They are specifically produced for use in gamma irradiation plants. The Co-60 is produced by bombarding Co-59 with neutrons. As a result of additional neutron captured, the Co-59 becomes radioisotope Co-60.

$$n + \text{Co-59} \rightarrow \text{Co-60}$$

Radioisotope Co-60 is highly unstable and its decay process emits a beta-ray and two gamma-rays, resulting in the formation of stable isotope of nickel. The half-life of Co-60 is 5.27 years. A pellet of Co-60 has a useful life of 20 years by which time its activity is reduced to about 1/14th of the original. Long term storage will allow the activity of the pellet to decay to safe levels.

The gamma processing plant is designed for continuous operation. Material to be irradiated is put on a conveyor system which moves around the irradiation source. When irradiation is completed, the source is lowered. The cell is now safe for personnel because no radiation remains. When Co-60 rods are replaced, they are transferred from a shielded container to the storage position).

1.2 Electron Accelerator

Electron beam (e-beam) means the flow of electrons emitted from filament (cathode) as kinetic energy by moving in high electric field (Acceleration). Electrons are small negatively charged particles emitted by a hot tungsten filament. By having a large potential (voltage) difference between the cathode (the filament) and the anode, the electrons can be accelerated to almost the speed of light. The negatively charged electrons are accelerated, through a vacuum, towards the positive anode and are steered through a hole in the anode to form an intense electron beam. Materials to be treated are loaded on to a conveyor belt, pass under the electron beam and then unloaded. Accelerators, work on the same principle as a television tube. Beam current is an indication of the number of electrons being accelerated. Beam current in TV set is about several micro amps while in EBM, the beam current is a thousand times higher. According to the treatment to be carried out, the power of the electron beam may vary from 10 to several hundreds of kW, for energy of 5 to 10MeV.

1.3 X-Ray Generation

X-rays on the other hand, are produced when high energy electrons are stopped abruptly in a dense material such as tungsten, lead or gold. X-rays can penetrate deeper than electrons. This means they give up less of their energy in the product. Therefore the doses needed to kill pathogens will take longer than in an electron beam system. X-rays by their greater penetration allow more dense products to be irradiated such as catalogues and large boxes or bags of mail. The production of X-rays is very inefficient. At 1 MeV electrons, the production may yield only a percent or so of useful X-rays. At 10 MeV the yield may be as high as 10%. This means for a 100 kW electron beam system converting its output to X-rays, the power of the X-rays will be between 1 and 10 kW. If the system has 10 kW output the X-rays would be between 100 Watts and 1000 Watts.

2. Radiation Processing

In general the radiation processing applications fall into four main categories. These are (1) sterilization of products such as medical devices, food, packaging and waste materials to kill bacteria, (2) treatment of export bulk commodities such as tropical fruits to extend shelf life and kill quarantine pests such as fruit flies, (3) treatment of polymeric materials to modify their physical properties and (4) environmental preservation.

Currently, radiation sterilization is applied for surface decontamination of medical devices, mail sanitization, biohazard deduction and consumer goods.

The industrial applications of polymer processing in general consist of crosslinking, curing, grafting and degradation. Specific applications of polymer processing include radiation processing of polysaccharides for medical, pharmaceutical and agricultural uses, vulcanization of natural rubber latex, radiation processing of cellulose for viscose rayon industry, and hydrogels, advanced composites, new fiber materials for extreme conditions, pre-crosslinking of thermoplastics, advanced adsorbent materials, lithography.

Environmental applications of radiations have been developed in flue gas treatment, removal of volatile organic compounds from exhaust gases, drinking water treatment, decontamination of ground water, industrial wastewater treatment, municipal treatment and sludge treatment.

3. Radiation Processing Facilities & Services in Malaysia

3.1 Gamma facility

Table 1 lists gamma Irradiation Facilities in Malaysia.

Table 1 Gamma irradiation facilities in Malaysia

Plant	Location	Purpose of irradiation	Product
SINAGAMMA	Nuclear Malaysia	Service centre (Multipurpose irradiator)	Medical & non-medical
RAYMINTEX	Nuclear Malaysia	Latex irradiator	RVNRL
Sterilgamma	Rawang	Service Centre (Multipurpose irradiator)	Mostly medical product
Ansell	Mallaca	In-house irradiator	Medical products
Isotron	Kulim	In-house irradiator	Medical products

The radiation processing was first introduced in Malaysia when Ansell started using gamma irradiation sometime in 1984 to sterilize their in-house gloves. Subsequently, another gamma plant was commissioned at Nuclear Malaysia in 1989. The plant, SINAGAMA (Figure1), is the first irradiation service provider to cater all private sector radiation sterilization needs. Another irradiation service provider was commissioned by Sterilgamma in 1993. As recent as 1996, Nuclear Malaysia added another gamma plant in their technology park. This plant, RAYMINTEX (Figure 2), is essentially the semi-commercial plant that provides radiation vulcanization of natural rubber latex.

Fig. 1 SINAGAMA

Fig. 2 RAYMINTEX

3.2 Electron accelerator

Table 2 lists electron accelerators in Malaysia. The electron beam processing in Malaysia started in August 1991, with the operation of NHV EPS-3000 and Curetron 200 keV Cockcroft-Walton type accelerators at Nuclear Malaysia. These accelerators were primarily used between 1991 and 1994 to support R&D on medical product sterilization project (medical glove) radiation curing of surface coating and some activities on radiation modification of polymers. The e-beam irradiation centre, ALURTRON, was subsequently upgraded with additional facilities that accommodate R&D on heat shrinkable products, pilot-scale flue gas purification as well as handling machineries that cater commercial irradiation services such as wire and cables, tubes and hydrogels.

Currently the ALURTRON irradiation facility is the only electron beam irradiator to service the manufacturing industry in Malaysia, although there are several smaller machines installed in other parts of the country. These other machines are installed for in-house and specific application only. Although, there have been request for e-beam sterilization from medical product manufacturers, the machine at ALURTRON has insufficient energy to produce enough penetration power to sterilize their products in bulk packages.

Later, electron beam accelerators were also installed at other private companies such as Sumitomo Interconnects Sdn. Bhd. (2 units) and Seal Air Corporation Sdn. Bhd. (2 units). The accelerators at Sumitomo are solely used for in-house crosslinking of thin wire and cables. The machines at Seal Air Corporation (formerly WR Grace) are primarily used in the production heat shrinkable films. Other e-beam accelerator is shown in the Table 2.

Table 2 Electron Accelerators in Malaysia

Company	Machine Maker/Type/Model	Activity	keV/mA/kW
Sumitomo Electric Interconnect Products (M) Sdn Bhd, J. Bharu	NHV EPS-2000 EPS-250 EPS-800	Wire & cable	2,000/50/193.2 250/80/50 800/100/80
Meditop Corporation, Bangi	MHI	Sterilization of gloves	10,000/10/10
Continental Sime Tire SND BHD, P. Jaya	NHV EBC-C-300-35	Tire	300/350
Sk Polymer Technology, Kota Kemuning, S.Alam	ESI	Shrinkable Films	150/460/69
Seal Air Corp., Kuantan	ESI	Shrinkable Films 2 sets	550/60
Nuclear Malaysia	NHV CURETRON	R&D–Curing of Surface Coatings	200/20
	NHV ALURTRON	R&D & Services for crosslinking of tubes, heat shrinkable tubes, crosslinking of wire insulation	3,000/30

4. Summary

It is envisaged that radiation processing will continue to play an important role towards the progress and development of industry in Malaysia. Malaysian Government will continue to play an active role to support R & D in this field by providing the necessary infrastructure, facility, trained manpower and research funds. Additional e-beam accelerator is planned to be installed at Nuclear Malaysia in 2007. The medium energy electron beam accelerator (1 MeV, 50 mA) will be mainly use to evaluate the commercial viability for treating aqueous products such as wastewater.

5.7 Application of Radiation Processed Natural Polymers

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Abstract

Carboxymethyl cellulose (CMC) crosslinked at paste-like condition forms hydrogel. The hydrogel was applied as a coolant to keep flesh of vegetables and fish at low temperature. Shochu (Japanese liquor of 25% alcohol content) residue produced by fermentation of rice and sweet potato was rapidly converted to animal feed by water absorption of CMC dry gel. Poly(lactic acid) (PLA) crosslinked by irradiation in the presence of triallyl isocyanurate, TAIC was soaked in plasticizer to give softness. A maximum of 60 wt % plasticizer was incorporated in PLA resin and flexible PLA sheet was obtained.

1. Introduction

Radiation crosslinking is a useful technology to improve polymer materials. The crosslinked polyethylene and polypropylene were applied for wire and cable, foam and shrinkable tube. Recently, poly(tetrafluoroethylene) crosslinked at molten state was applied for O-ring 1). Furthermore, crosslinked poly(vinyl alcohol) hydrogel sheet was commercialized as a wound dressing 2).

We found that polysaccharides derivatives such as carboxymethyl cellulose (CMC), methycellulose and hydroxymethyl cellulose undergo crosslinking upon irradiation at paste-like high concentration condition 3). Furthermore, radiation degradable poly (lactic acid) PLA was successfully crosslinked by irradiation in presence of trially isocyanurate (TAIC) 4). Crosslinking of CMC and PLA resulted to materials with new properties and are expected for useful applications in various fields. In this presentation, applications of radiation crosslinked CMC hydrogel and modified PLA are reported.

2. Crosslinking of PLA and Its Application

2.1 Crosslinking of PLA

PLA predominantly undergoes degradation under direct irradiation. When the polymer is exposed to gamma-rays or electron beam, the mechanical and physical properties of the polymer decrease due to reduction of the molecular weight of the polymer. We employed polyfunctional monomers (PFM) to induce crosslinking of this degradable type polymer during irradiation. PFMs have been widely used as crosslinking agents for polyolefins. PFM was incorporated with PLA using a laboratory plastomill set at 20 rpm and 180℃ for 10 min. For electron beam irradiation, each sample was pressed in a hot press at 180℃ to form a sheet (150 mm X 150 mm, 0.1 mm thickness). The sheets were irradiated by electron beam from an accelerator with energy of 2 MeV and beam current of 1 mA, at a dose rate of 10 kGy/pass.

Six kinds of PFMs were incorporated to induce crosslinking of PLA[4]. It was found that TAIC was the most effective to lead crosslinking of PLA. As shown in Figure 1, TAIC concentration of 3 - 5% for PLA gave gel fraction of 80%. Crosslinking in the presence of TAI C improved heat stability of PLA.

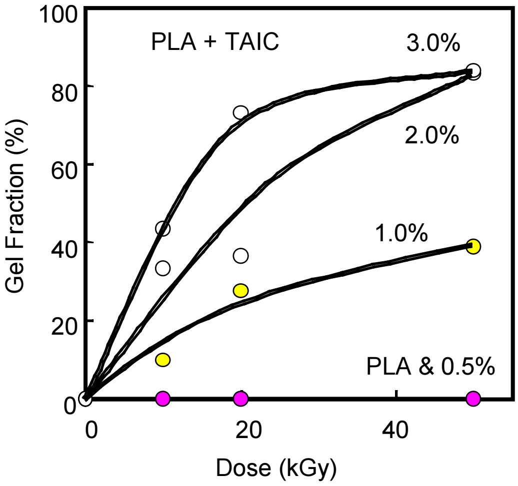

Fig. 1 Radiation crosslinking of PLA in the presence of TAIC

2.2 Application of crosslinked PLA for heat shrinkable tube and cup

Due to improvement of heat stability, crosslinked PLA is applied as a heat shrinkable tube. PLA is kneaded with TAIC and molded into tube by extruder at 180℃ then irradiated at 50 kGy. Irradiated tube expanded two times at 200℃ and expanded shape remained at room temperature. After that, expanded tube shrink up to original size by re-heating. The uncrosslinked sample can not be expanded over melting point (160℃). The crosslinked PLA was also applied for cup. PLA with 3% TAIC was molded into cups by extruder and irradiated to form crosslinked structures at 50 kGy. To evaluate heat resistance, boiling water was discharged in the unirradiated and the irradiated cups. The unirradiated cup deformed and changed to milky-like transparency but the crosslinked cup kept its original shape and transparency due to protection from crystallization by the crosslinked structure.

2.3 Modification of PLA by plasticizer

PLA has high transparency and hardness property. As mentioned earlier, heat stability of PLA was improved by crosslinking in EB irradiation in presence of TAIC. Further modification was carried out by adding plasticizer to give softness to PLA. The plasticizer was incorporated together with PLA and TAIC at 180 ℃. After irradiation, the compound was first pelletized to get chips (pellets) of PLA resin before molding. Plasticizer of 20 wt % remained intact in the PLA resin, but bleeding out was observed during molding for resins containing 30 wt % of plasticizer. Thus, to enhance concentration of plasticizer in PLA resin, crosslinked PLA was soaked in plasticizer at more than Tg. The plasticizer penetrated into crosslinked PLA. A maximum of 60 wt % plasticizer was trapped in PLA resin. Bleed (migration) test of 40 wt % plasticizer incorporated in PLA resin at 80℃ confirmed that bleeding of plasticizer from PLA resin is hardly observed even after 2 weeks. From these facts, it was deduced that plasticizer is fixed strongly in crosslinked network structure of PLA. It was found that softness and flexibility of crosslinked PLA can be controlled by concentration of plasticizer. Sheets of PLA with 40 wt % plasticizer prepared by injection molding has flexibility and does not break even when bending many times. Accordingly, soaking method to penetrate plasticizer in crosslinked PLA resin is effective to give flexibility for thin film and sheet.

3. Synthesis of CMC Hydrogel by Irradiation and Its Application

3.1 Radiation crosslinking of CMC

It is now well known that CMC irradiated in solid phase and in dilute aqueous solution (below 10%) undergoes degradation but we found that CMC undergoes crosslinking in irradiation at paste-like condition of high concentration. High concentration is better for crosslinking of CMC, as shown in Figure 2. Furthermore, it was found that crosslinking is affected greatly by degree of substitution (DS) of CMC.

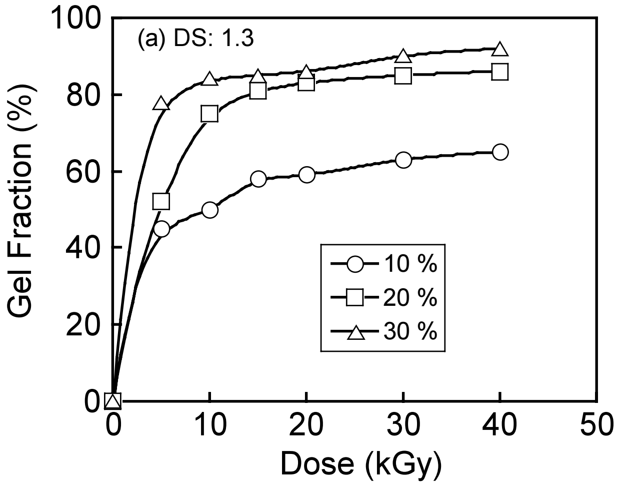

Fig. 2 Crosslinking of CMC at paste-like condition (DS 1.38)

3.2 Applications of CMC hydrogel

CMC hydrogel was applied as coolant. CMC gel coolant is a high quality product to cool fishes and vegetables. Another application of CMC hydrogel has been attempted for production of animal feeds. Japanese liquor, shochu (alcohol content, 25%) is produced by fermentation of rice and sweet potato. After production of shochu, a lot of shochu residues are formed. These residues, which contain about 90% water, are thrown away on the deep sea and rapidly gather molds. But throwing of shochu residues on the sea will be prohibited from end of March 2007. Thus, it is desired to find out new technology for reuse of shochu residues. A technology to utilize shochu residues for animal feeds was proposed. Corncob is added into rotary oven to absorb water in shochu residue. After that, the mixture is dried for 3 hours at 60 to 80℃. Dry powder feed for animal is obtained easily. In this case, 650 kg of corncob were required to treat 1 ton of shochu residue. CMC gel was added to reduce corncob. Required corncob reduced to 200 kg by addition of 0.2% (2 kg) CMC dry gel for every 1 ton of shochu residue. From these tests, it was confirmed that CMC dry gel is effective as water adsorbent for drying of shochu residue.

References

1) A. Setogawa, H. Nishi, Y. Yamamoto, H. Kusano, T. Asano, “Development of crosslinked PTFE and applied products”, *Hitachi Cable Review*, No. 21, 83-88 (August 2002).
2) F. Yoshii, K. Makuuchi, D. Darwis, M. T. Razzak, J. M. Rosiak, “Heat resistance poly(vinyl alcohol)”, *Radiat. Phys. Chem.*, **46**, 169 (1995).
3) F. Yoshii, L. Zhao, R. A. Wach, N. Nagasawa, H. Mitomo, T. Kume, “Hydrogels of polysaccharide derivatives crosslinked with irradiation at past-like condition”, *Nucl. Instrum. Methods Phys. Res. B*, **208**, 320 (2003).
4) N. Nagasawa, A. Kaneda, S. Kanazawa, T. Yagi, H. Mitomo, F. Yoshii, M. Tamada, “Application of poly(lactic acid) modified by radiation crosslinking”, *Nucl. Instrum. Methods Phys. Res. B*, **236**, 611 (2005).

5.8 Radiation Processing of Polysaccharides and Its Applications

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1. Introduction

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. 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 polymer in order to replace product based synthetic polymer. By doing this, we could safe our planet and have better live.

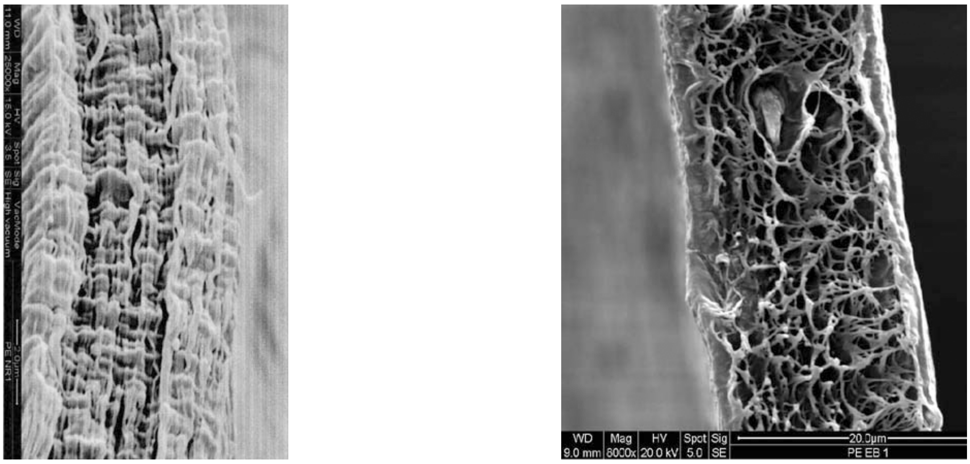
Polysaccharide has been characterized as natural polymer. However, only polysaccharide of chitosan, starch, cellulose, carrageenan and alginate has been given much attention in radiation processing research activity. Reason for this is that abundantly available, renewable and cheap. Radiation processing of these materials shown quite pronouncing results and achievements for various applications, for example as plant promoter and fertilizer in agriculture, wound dressing in medical, facial mask in cosmetic, slow release material in pharmaceutical and super-absorbent in industrial.

2. Radiation Technology

Radiation technology such as electron beam and gamma ray has been used on polymeric material either synthetic or natural in order to develop specific property on the polymer according to application. This ionizing radiation on polymer material will produce two majors reaction that is crosslinking and degradation. Both reactions will take place during irradiation but which will be dominant depend on various factor such as type and form of polymer, and irradiation parameters. Beside crosslinking and degradation, radiation can also be use to polymerize monomer or low molecular weight polymer by chain propagation process into polymer that has high molecular weight or long chain. In certain condition, radiation can produce copolymer by grafting process where polymer was grafted onto other polymer chain or backbone for example grafting of acrylic acid onto polyethylene film.

In the case of crosslinking process, ionizing radiation will produce radical on polymer chain and this excited radical will definitely react with other radical either on the same chain or different chain. This reaction will form inter-polymer network (IPN) in the shape of honeycomb within the polymer itself. The formation of IPN will enhanced the physical as well as chemical properties of the irradiated polymer. For example, non-irradiated polyethylene plastic bag has tensile strength and elongation, 58.38N/mm^2 and 1499 % respectively. After irradiation process, the tensile strength increase to 61.43N/mm^2 but the elongation or elongation decreased to 1306 %. The network formation, as shown in the Figure 1, explained changes on the physical properties of the PE plastic bag, where the network will increase strength but not elongation.

The size of network in the IPN could be controlled by varied the irradiation dose. For example, polyvinyl alcohol can only be crosslinked in aqueous solution form. The degree of crosslink was determined by irradiation dose as shown in Figure 2. It revealed that increasing irradiation dose will increase the density of network, as a result the hydrogel of PVA shrink which means reduction on pore size of network. This will push out the water that filled up the cavity of the network.



(a) Non-irradiated PE plastic bag *(b) Irradiated PE plastic bag*

Fig. 1 Scanning electron microscope of (a) non-irradiated and (b) irradiated PE plastic bag

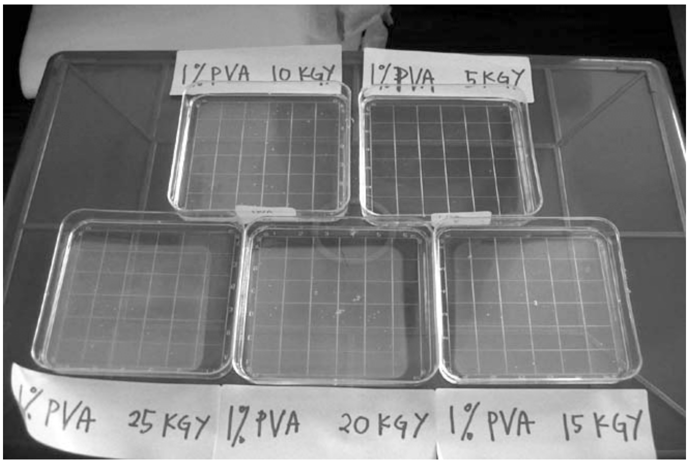


Fig. 2 Hydrogel of PVA at various irradiation doses

Ionizing radiation on polymer also caused degradation or chain scission especially for the natural polymer and some synthetic polymer such as polypropylene. This degradation will definitely reduce the molecular weight of polymer as a result it will have low viscosity when dissolve in solvent or low melt flow index (MFI) in molten stage. For example, 10 kGy irradiation dose will reduce more than half viscosity of starch in aqueous solution.

Electron beam and gamma irradiations on sago and cassava starches will cause leaching of amylose from the cooked starch. 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. This one of the reason why sago starch is more favorable to be used in making fish crackers than cassava starch.

3. Radiation Processing of Polysaccharide

Polysaccharide materials such as starch, cellulose, chitin/chitosan, carrageenan and alginate are abundantly available and cheap. Radiation and chemical modification of these materials will enhance and improve its property to be use in various field of application. Etherification process on starch and cellulose materials will convert starch and cellulose from non water-soluble into carboxymethyl starch (CMS) and carboxymethyl cellulose (CMC) that are water-soluble and have thickener or binder properties. This process can also be applied to other polysaccharide and gave same effect on the materials. 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. The degree of crosslink depends on concentration of CMS or CMC and 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 CMS/CMC in hydrogel.

Carrageenan same as starch and cellulose, will degrade when expose to irradiation. Non-irradiate carrageenan in gel stage has network with irregular pore size and structure but non-permanent gel. However, irradiated carrageenan/poly(vinylpyrrolidone) (PVP) blend will form hydrogel that has better regular pore size and network structure compare to non-irradiated carrageenan and irradiated PVP. This network structure also depends on irradiation dose. Increasing irradiation dose will increase degree of crosslinking, as a result the structure will be denser and pore size became smaller. This effect will reduce the swelling ability of the hydrogel. Beside irradiation dose, amount of carrageenan in the blend also gives an effect on swelling capability of the carrageenan/PVP hydrogel. Even though increasing amount of carrageenan in the blend will increase pore size of the network but irregular and breakable pore size. This type of network will reduce swelling capability of the hydrogel.

4. Application of Starch Based Polysaccharide

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 used as facial mask in skin care cosmetic application for treatment of acne and other skin problem. The sago hydrogel has also been tested and confirmed as medical device in wound dressing in medical device application. Since radiation degrade the sago starch as mention earlier, it will produce starch with more elastic property that can be used in production of bio-film and bio-foam sago starch. These products that can be used as packaging material, were biodegradable because of the nature of starch itself.

Hydrogels made of CMS/CMC have better swelling property than the sago hydrogel because of the carboxymethyl group present on the molecular chain. On top of that, its degree of swelling depend on the pH of medium in the following sequent neutral>alkaline>acid. The existent of carboxymethyl group will be an advantage for the hydrogel to be use in waste management. It can extract toxic metal or organic pollutant when introduce in water purification system. These hydrogel can also be used as wound dressing and bedsores mattress in medical application. The ability to absorb and control level of moisture in composting system, it has been introduced in decompose of animals excrement by microbe digestion and reduce cost of using sawdust in this process.

5. Conclusion

Radiation technology has shown it capability to improve and increase value added of natural polymer, in this case polysaccharide. It needs further explore the potential of this material in order to get full benefit of this development for our next generation and at the same time protect our environment.

5.9 Radiation Processed Polysaccharide Products

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Abstract

Radiation crosslinking, degradation and grafting techniques for modification of polymeric materials including natural polysaccharides have been providing many unique products. In this communication, typical products from radiation processed polysaccharides particularly plant growth promoter from alginate, plant protector and elicitor from chitosan, super water absorbent containing starch, hydrogel sheet containing carrageenan/CM-chitosan as burn wound dressing, metal ion adsorbent from partially deacetylated chitin were described. The procedures for producing those above products were also outlined. Future development works on radiation processing of polysaccharides were briefly presented.

1. Introduction

More than 30 years in the past, industrial applications of radiation processing technology has been mainly focused to 1) crosslinking of wire and cable, heat shrinkable tube and sheet, vulcanization of rubber and latex, 2) sterilization of medical supplies, cosmetics and pharmaceutical, 3) decontamination of food and more recently 4) treatment of flue gas and waste water. Radiation processing technology has been considered as a usefully unique tool for the production of new and value-added products. In addition, radiation processing technology is also considered as an environmentally friendly and energy saving technology. Most recently application of radiation processing technology for modification of natural polysaccharide such as alginate, chitin/chitosan, carrageenan, cellulose and starch has been the concerns for R&D work in many countries especially in the Asia region through IAEA/RCA/RAS 8/096 project, FNCA EB Workshop and bilateral co-operations. Radiation degradation of natural polysaccharides is to regulate low down the molecular weight and to produce oligosaccharides. Radiation processing of polysaccharide derivatives is not only to reduce the molecular weight and/or to produce oligomers but also to crosslink them into three-dimensional network especially for hydrogel material preparation. Furthermore modification of polysaccharides and their derivatives through radiation graft-polymerization with monomer will create a variety of products for different purposes of utilization. Natural polysaccharides with large quantity in nature and recycled material can be as a potential starting material source for treatment by radiation processing technology on industrial scale. In this communication, typical products from radiation processed polysaccharides particularly from alginate, chitin/chitosan, starch and carrageenan were presented and future development works were also briefly discussed.

2. Radiation Processed Polysaccharide Products

2.1 Plant-growth promoter from irradiated alginate

Alginate is a natural polysaccharide composed of two building blocks of monomer units, namely D-manuronic and L-gulucoronic acid attached through random 1, 4-glycoside linkages [1,2]. Alginates are extracted from brown seaweeds which contain from 18 ~ 40 % of the total plant expressed as alginic acid. The annual production of alginate is about 30,000 tons [2]. For most application such as for food and drink, pharmaceutical products, cosmetics, bioengineering, agriculture and other industries, alginates are sold for US$5 ~ 20/kg [2]. Oligoalginate, a degraded alginate, was reported to have several novel features such as plant growth promotion [3-5], plant elicitation [6] and bifidobacteria growth [7]. For radiation degradation, N. Nagasawa, et al. studied in detail by irradiation of sodium alginate in powder form and in solution with gamma ray Co-60 8). Interestingly, low energy electron beam (LEEB) can be applied for degradation of polysaccharides particularly for alginate in aqueous solution. Table 1 showed the results of molecular weight (MW) and MW distribution index (Mw/Mn) of alginate irradiated by gamma Co-60 radiation and LEED 9).

Table 1 Molecular weight of alginate irradiated by Co-60 and LEED

MW	Alginate powder	Alginate solution 5 %	
	0 kGy	Gamma Co-60 (10 kGy/h) 40 kGy	LEEB (250 keV, 10 mA) 35 min.
Mw	136,700	8,900	12,700
Mn	50,700	7,400	7,800
Mw/Mn	2.70	1.20	1.62

Based on results of the growth-promotion effect for plants and results of field test 10), a plant growth promoter product namely T&D (Permit No. 88/2000/QD-BNN) from irradiated alginate was commercialized for field application in Vietnam since 2000. The production procedure is briefly described as scheme 1.

Scheme 1
Brown seaweed (Sargassum) → extraction of alginate with Na_2CO_3 → sodium alginate solution 5 % (w/v) → irradiation (Co-60), 50 kGy → filtration → mixing with desired additives → product, plant growth promoter T&D.

By foliar spraying of T&D product with water dilution from 1/500 to 1/1000, the productivity of plants such as tea, carrot, cabbage, onion, groundnut and green vegetable was remarkably increased. In addition, the quality of agro-product was better improved through lower nitrate and higher total sugar content 10). Thus, the irradiated alginate product is suitable for the environmentally sustainable development of agriculture. Furthermore according to results reported by Relleve, et al. 11), irradiated carrageenan in some extent seems to be as effective as irradiated alginate for plant growth promotion. Carrageenan, water soluble and sulfated polysaccharides extracted from different species of marine red seaweeds of the class Rhodophyceae with annual production of about 50000 tons 12) may be one of the most potential starting polysaccharides for radiation processing application. Different grades of carrageenan are sold for 5 ~ 10 US$/kg.

2.2 Plant protector and plant elicitor (vaccine) from irradiated chitosan

2.2.1. Plant protector

Chitin, poly-β-(1→4) linked N-acetylglucosamine, is the second most abundant natural biopolymer on earth after cellulose. Chitosan, a deacetylated derivative of chitin is widely used as a flocculant, clarifier, fiber, film, plant disease resistance promoter, anti-cancer agent, wound healing agent and antimicrobial agent 13, 14). The production of chitosan is currently based on crab and shrimp shell discards. The world market of chitosan is approximately 2000 tons 15). Chitosan with different grades are sold at lowest price from 8-10US$/kg. For radiation degradation of chitosan, results of the studies by Mathuhashi and Kume 16), X. F. Liu, et al. 17) and L. Hai, et al. 18) indicated that antimicrobial activity of chitosan was enhanced for some certain extent by radiation. Accordingly, radiation is a very convenient tool for the modification of polymer materials including degradation of polysaccharides 19). Based on the above mentioned merits, the scheme 2 is applied for producing plant protector (fungicide) from irradiated chitosan.

Scheme 2
Chitosan flake → irradiation (Co-60), 50-100 kGy → dissolving in dilute organic acid (lactic) → filtration → mixing with desired additives → product, plant fungicides (Olicide, Goldrice).

Both fungicide products from irradiated chitosan namely Olicide (Permit No. 68/2002/BNN) used for vegetable and tea plant and Goldrice (Permit No. 49/03 SRN) used for rice were commercialized in Vietnam. Recently, an amount of 10,000 litters a newly developed product namely Stop (Permit No. 02/04 SRN) based on irradiated chitosan in complex with metal ion (Zn^{2+}, Cu^{2+}) used as nematocide for different plants such as melon, lettuce and dragon has been produced for market promotion. Besides anti-nematode effect, this product also functions effectively as fungicide for plants.

2.2.2. Plant elicitor (vaccine)

Oligochitosan has been reported to be as potent elicitor for modulation of plant resistance to diseases 3, 19, 20). It was known that the molecules that signal plants to begin the process of phytoalexin synthesis are called elicitors and phytoalexin are antimicrobial compounds 21). The study of Vander, et al. revealed that maximum elicitation was observed with chitosan of intermediate degree of deacetylation, (DD) 65 % 20). Furthermore, oligochitosan belong to, so called, exogenous elicitor and is recognized by plants more sensitively than endogenous ones for instance oligoalginate 6). Water-soluble chitosan or oligochitosan with degree of polymerization (DP) less than10 can be effectively produced with high yield (~80 %) and especially on large scale by irradiation of chitosan solution with dose of about 50 kGy 22). In addition to elicitation effect, oligochitosan also exhibits plant growth promotion effect remarkably 23, 24). The relationship between water- soluble chitosan yield and dose was typically presented in Figure 1. The procedure for production of plant elicitor from irradiated chitosan is described in Scheme 3. Thus oligochitosan produced by irradiation is very promising to apply in agriculture as elicitor (vaccine) for plants. This kind of product namely OSAN and RIZASA (Permit No. 395/06 ECR) was already commercialized in Thailand since 2002 and in Vietnam since April 2006 respectively.

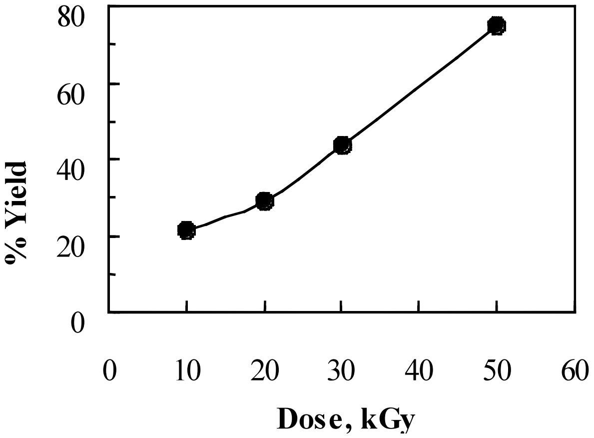

Fig. 1 Yield of water soluble chitosan produced by irradiation of 4 % chitosan solution

Scheme 3
Chitosan flake → dissolving in dilute organic acid (lactic) → irradiation (Co-60), 50 kGy → filtration → mixing with desired additives → product, plant elicitor (vaccine).

2.3 Supper water absorbent for soil conditioner

Radiation technology has been successfully used for crosslinking a number of water soluble synthetic polymer such as poly(vinylpyrrolidone) (PVP), poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), polyacrylamide (PAM) and poly(ethylene glycol) (PEG) and natural polymer derivatives such as carboxymethyl (CM) cellulose, CM-starch and CM-chitin/chitosan to produce hydrogel materials. Bakass, et al. reported that application of superabsorbent polymer improved the water- absorption capacity of the soil [25]. In spite of intensive study on production process, typically the study of Kiatkamjornwong, et al. on radiation grafting of acrylic acid/acrylamide onto CS[26], such a product of super water absorbent for agricultural application made by radiation crosslinking has been still not commercialized so far. The main reason may be due to high cost of production. In order to reduce the production cost, a simplified process for production of super water absorbent has been developed by our research group at the VINAGAMMA Center [27]. The procedure was briefly described as follows: an amount of 1 kg cassava starch was gelatinized by mixing in 8 litters water containing 1.16 kg KOH for 30 min. at room temperature. Then the gelatinized starch was neutralized with 2 kg acrylic acid and mixing was continued for another 30 min. The resulting gel was packed in PE bag and irradiated with Co-60 radiation at 5 kGy for crosslinking. Thus the obtained product, so-called super water absorbent in wet gel form was dried and grinded into fine powder (Scheme 4).

Scheme 4
Starch → gelatinization with KOH → neutralization with acrylic acid → irradiation (Co-60), 5 kGy → drying → grinding → product, super water absorbent

Some characteristics of the product such as water absorption, desorption and biodegradability in soil were shown in Figures 2 and 3.

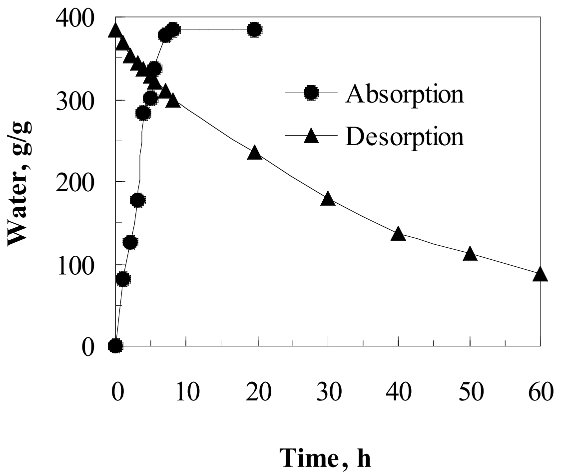

Fig. 2 Water absorption and desorption of sodium acrylate-g-starch

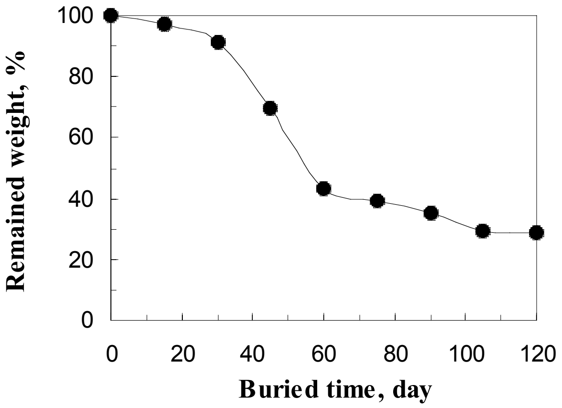

Fig. 3 Biodegradability of sodium acrylate-g-starch buried in soil

The estimated production cost was about 2 US$/kg (dried powder). Preliminary results of field test revealed that this super water absorbent product showed good effect to improve water and soil fertility. Large field experiment was already carried out and the product super water absorbent has been approved for field application.

2.4 Hydrogel as burn wound dressing

As mentioned above, hydrogels have been studied intensively using synthetic water soluble polymers (WSP) especially PVP and PVA [28, 29)]. Recently researches were focused on blending natural polysaccharides with WSP especially for medical application as burn wound dressing [30, 31)]. Owing to gelling at room temperature and haemostatic properties, kappa-carrageenan (KC) may be the most applicable natural polysaccharide in the formulation of hydrogel [31)]. Several hydrogel wound dressings were commercialized on market such as Vigilon (PEO), Geliperm (PAM & agar) [32)] especially radiation formed hydrogel from PVP/PEO and agar namely HDR and AQUA-GEL [28)]. The great advantage of radiation formed hydrogel is simultaneous crosslinking and sterilization of the product in a single step. Owing to the biocompatible features of polysaccharides particularly KC, two new formulations have been developed for radiation formed hydrogel as scheme 5.

Scheme 5
PVP/KC/PEG & PVA/KC/CM-chitosan aqueous solution → sheet casting at 60-70˚C (molding) → solidification by cooling to ambient temperature → sealing as final packages for dressing → irradiation, 25 kGy → product, hydrogel sheet dressing.

The contents (w/v) of the components in solution of the above two formulations were of 5/1.5/2.5 and 10/0.5/1 for PVP/KC/PEG & PVA/KC/CM-chitosan, respectively. Characteristics of hydrogel sheets are shown in Table 2 and Figure 4.

Table 2 Characteristics of hydrogel sheets

Parameter	PVP/KC/PEG	PVA/KC/CM-chitosan
Absorbed dose (Co-60), kGy	25	45
Thickness, mm	3.34	2.23
Tensile strength, kg/cm^2	0.97	0.23
Elongation at break, %	356	225
WVTR, g/m^2/24h	3480	2880
EWC, g/g	70	5.9

According to the reports of Queen, et al. [32)] and Razzak, et al. [29)], the desired water vapor transmission rate (WVTR) was in the range of 2000 ~ 2500g/m^2/24h. Thus the above radiation formed hydrogel sheets suited well with WVTR requirement. Table 2 indicated that hydrogel based on PVP/KC has higher tensile strength and the equilibrium water content (EWC) compared to that of hydrogel based on PVA/KC. It seems that suitable radiation formed hydrogel may be based on the mixture of PVP/PVA/KC together with biologically active additives such as CM-chitin/chitosan. Both hydrogel sheet products successfully passed clinical test and to be in the process of commercialization.

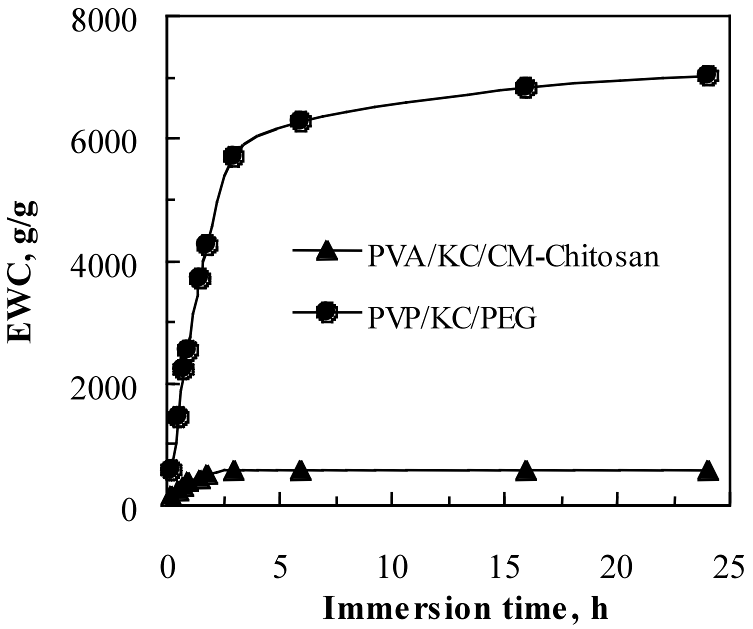

Fig. 4 Relationship between EWC (g/g) and immersion time (h)

2.5 Metal ion adsorbent from radiation grafting monomer onto chitin

As mentioned above, chitin with largely available quantity is of potential starting material to modify for application in different fields including for metal ion adsorbent [33, 34]. Chitosan, a deacetylated derivative of chitin exhibits higher metal ion adsorption capacity owing to the amino group content (-NH_2) [35]. However, chitosan is soluble in acidic media, therefore it restrains the practical use as metal ion adsorbent. Chitin even with low adsorption ability, but it is insoluble and stable in acidic media. Therefore it is desired to enhance the adsorptive property of chitin either through partially deacetylated (PD) process or grafting of monomer onto chitin or both. Gatot, et al. studied on radiation grafting of hydrophilic monomer onto chitin by pre-irradiation method (radiation peroxidized chitin) [33]. High grafting degree was attained in this process. However, high dose should be used and it was difficult to recover the excess monomer (unreacted monomer) in the grafting solution. The following procedure was carried out for producing novel adsorbent by the radiation grafting monomer onto PD-chitin (Scheme 6).

Scheme 6
Chitin flake → immerging in 30 % NaOH → PD-chitin (~DD40 %) → immerging in AAc solution, 20 % (v/v) → filtration → irradiation, 5 kGy → washing → neutralization with NaOH 1N → washing → drying → product, PD-chitin-g-PANa, metal ion adsorbent.

Typical adsorption isotherms of copper ion (Cu^{2+}) was shown in Figure 5. The equilibrium isotherms were well fitted by Langmuir equation with the constant KL = 15.5 and 19.4 (mg/g) for PD-chitin and PD-chitin-g-PANa, respectively [34]. This product can be produced on large scale with competitive cost and used as metal ion adsorbent for water purification as well as for other purposes such as for sorption of dyes and for immobilization of bioactive substances.

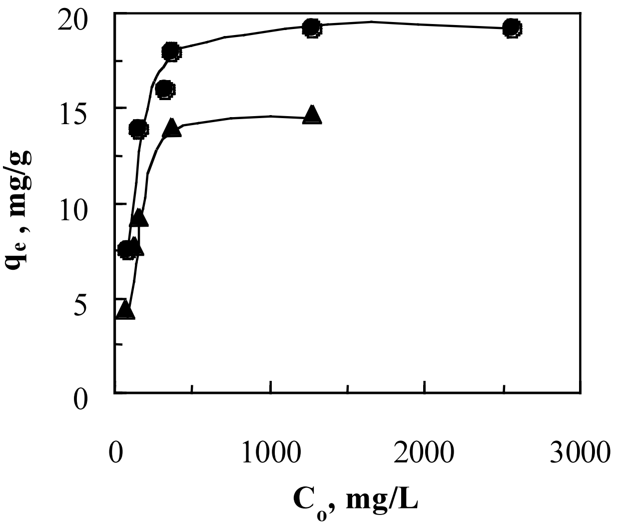

Fig. 5 Adsorption isotherms of Cu2+ on PD-chitin (▲) and PD-chitin-g-PANa (•)

3. Future Development

3.1 Irradiated chitin for animal feed additive and glucosamine production

3.1.1. Irradiated chitin for animal feed additive

Chitin is almost non-toxic. It was reported that chitin and its oligomers are a growth factor for bifidus bacteria in animal intestines [36]. Low molecular weight chitin and chitin-oligomer which can be produced on large scale by radiation degradation are expected to be a good source of chitinous supplement in animal feed such as hens, broiler and pig for improving intestinal bacterial flora and weight gain.

3.1.2. Irradiated chitin for glucosamine production

The use of glucosamine in combination with chondroitin sulfate was reported to have good effect in the management of osteoarthritis [37]. It was estimated that the glucosamine and chondroitin sulfate market exceeded five hundred million dollars in July 1998 and May 1999 [38]. The yield of glucosamine produced by HCl hydrolysis was increased from 40 % for chitin to 65 - 70 % for 50 kGy irradiated chitin. Thus irradiated chitin can be used for production of glucosamine with high yield.

3.2 Metal ion adsorbents and bioactive substance carriers

The use of radiation grafting for synthesis of metal ion adsorbent has been investigated by many authors [39~42]. Different synthetic polymers such as polyethylene, polypropylene were used for grafting. Natural polymers such as chitin, jute and coconut fibers may be of good trunk polymers for modification by radiation grafting. The resultant products can be used for metal ion adsorbents, sorption of dyes and immobilization of bioactive substance such as enzyme [43] and bacteria [44]. Further studies on modification of natural polymers for those above applications should be continued.

3.3 Hydrogel containing CM-chitin/chitosan as burn wound dressing

CM-chitin/chitosan are water- soluble derivatives of chitin. CM-chitin was known to be effective in promoting wound healing [45] and CM-chitosan was reported to have antibacterial activity [46]. Thus CM-chitin/chitosan might be useful additives in the formulation of hydrogel made by radiation crosslinking for burn wound dressing application. In addition, novel hydrogel can be prepared by irradiation of CM-chitin/chitosan solution with concentration from 10 % to 50 % [47]. However, further research work on the effect of wound healing of different type of CM-chitin such as low molecular weight, oligomers and crosslinked CM-chitin/chitosan in hydrogel sheet should be carried out.

3.4 Irradiated polysaccharides for development of human vaccines and drugs

It was reported that both polysaccharides and oligosaccharides have been used to make commercial vaccine, but oligosaccharides exhibits some distinct advantages [48]. Radiation degradation method together with adequate fractionation techniques is very promising to apply for preparation of pure oligosaccharides with large quantity for development of new and innovative glycoconjugate vaccines that attain a desired immunological performance. For instance, medical applications of dextran as plasma volume expander and blood flow improvement have been reported to be dependent on the size of molecular weight [49]. In fact, native dextrans were produced with a very high molecular weight. Therefore, depolymerization of native dextrans for clinical use must be carried out by acid hydrolysis or alternatively by radiation. Low molecular weight fraction with a narrow distribution will be potential starting material for vaccines and drugs development through conjugation process [48].

References

1) K. Clare, “Algin”, *Industrial gum-polysaccharides and their derivatives,* ed. by R. L Whistler, J. N. Bemller, Academic Press, New York, p. 105 (1993).
2) H. Ertesvag, S. Valla, “Biosynthesis and applications of alginates”, *Polym. Degradat. Stabil*., **59**, 85 (1998).
3) Y. Yonemoto, H. Tanaka, T. Yamashita, N. Kibatake, Y. Ishida, A. Kimura, K. Murita, “Promotion of germination and shoot elongation of some plants by alginate oligomers prepared with bacteria alginate lyase”, *J. Ferment. Bioeng*. **75** 68 (1993).
4) N. Q. Hien, N. Nagasawa, L. X. Tham, F. Yoshii, V. H. Dang, H. Mitomo. K. Makuuchi, T. Kume, “Growth-promotion of plants with depolymerized alginates by irradiation”, *Radiat. Phys. Chem*., **59**, 97 (2000).
5) L. Q. Luan, N. Q. Hien, N. Nagasawa, T. Kume, F. Yoshii, T. Nakanishi, “Biological effect of radiation-degraded alginate on flower plants in tissue culture”, *Biotechnol. Appl. Biochem*., **38,** 283 (2003).
6) C. Akimoto, H. Aoyagi, H. Tanaka, “Endogenous elicitor-like effects of alginate on physiological activities of plant cells”, *Appl. Microbiol. Biotechnol*., **52** 429 (1999).
7) H. Akiyama, T. Endo, R. Nakakita, K. Murita, Y. Yonemoto, K. Okayama, “Effect of depolymerized alginates on the growth of bifidobacteria”, *Biosci. Biotech. Biochem*., **56**, 355 (1992).
8) N. Nagasawa, H. Mitomo, F. Yoshii, T. Kume, “Radiation-induced degradation of sodium alginate”, *Polym. Degradat. Stabil*., **69,** 279 (2000).
9) F. Yoshii, et al., “Radiation degradation of marine polysaccharides by low energy electron beam”, *JAERI-Conf. 2003-016,* p. 42 (2003).
10) N. Q. Hien, L. Hai, L. Q. Luan, T. T. Hanh, N. Nagasawa, F. Yoshii, K. Makuuchi, T. Kume, “Radiation degradation of alginate and some results of biological effect of degraded alginate on plants”, *JAERI-Conf 2000-003*, p. 94 (2003).
11) L. N. Relleve, N. Nagasawa, L. Luan, T. Yagi, C. Aranilla, L. Abad, T. Kume, F. Yoshii, A. Dela Rosa, “Degradation of carrageenan by radiation”, *Polym. Degradat. Stabil.,* **87**, 403 (2004).

12) G. H. Therkelsen, "Carrageenan" in *Industrial gum-polysaccharides and their derivatives* ed. by R. L. Whistler, J. N. Bemller, Academic Press, New York, p. 145 (1993).
13) R. Shepherd, S. Reader, A. Falshaw, "Chitosan functional properties", *Glycoconjugate J.*, **14**, 535 (1997).
14) R. A. A. Muzzarelli, M. G. Peter, ed. by "*Chitin Handbook*", European Chitin Society, p. 359 (1997).
15) M. Toms, S. E. Harding, "*An introduction to polysaccharide biotechnology*", T. J Press (Padstow) Ltd., p. 144 (1998).
16) S. Matsuhashi, T. Kume, "Enhancement of antimicrobial activity of chitosan by irradiation", *J. Sci. Food Agric.*, **73**, 237 (1997).
17) X. F. Liu, Y. L. Guan, D. Z. Yang, Z. Li, K. D. Yao, "Antibacterial action of chitosan and carboxymethylated chitosan", *J. Appl. Polym. Sci.*, **79**, 1324 (2001).
18) L. Hai, T. B. Diep, N. Nagasawa. F. Yoshii, T. Kume, "Radiation depolymerization of chitosan to prepare oligomers", *Nucl. Instrum. Methods Phys. Res. B*, **208,** 466 (2003).
19) T. Kume, N. Nagasawa, F. Yoshii, "Utilization of carbohydrates by radiation processing", *Radiat. Phys. Chem.*, **63**, 625 (2002).
20) P. Vander, K. M. Varum, A. Dormard, N. E. El Gueddari, B. M. Moerschbacher, "Comparision of the ability of partially N-acetylated chitosans and chitooligosaccharides to elicit resistance reactions in wheat leaves", *Plant Physiol.* **118**, 1353 (1998).
21) A. G. Darvill, P. Albersheim, "Phytoalexin and their elicitors- a defense against microbial infection in plants", *Ann. Rev. Plant Physiol.*, **35**, 243 (1984).
22) W. S. Choi, K. J. Ahn, D. W. Lee, M. W. Byun, H. J. Park, "Preparation of chitosan oligomers by irradiation", *Polym. Degradat. Stabil.*, **78,** 533 (2002).
23) L. Q. Luan, V. T. T. Ha, L. Hai, N. Q. Hien, N. Nagasawa, F. Yoshii, T. Kume, "Study on the biological effect of irradiated chitosan on plants in tissue culture", *Advance in Chitin Science*, **5**, 468 (2002).
24) C. S. Upathum, "Radiation degradation of chitosan and its application for young orchid plant growth promotion", *Advance in Chitin Science*, **5**, 475 (2002).
25) M. Bakass, A. Mokhlisse, M. Lallemant, "Absorption and desorption of liquid water by a superabsorbent polymer: effect of polymer in the drying of the soil and the quality of certain plants", *J. Appl. Polym. Sci.*, **83**, 234 (2002).
26) S. Kiatkamjornwong, W. Chomsaksakul, M. Sonsuk, "Radiation modification of water absorption of cassava starch by acrylic acid/acrylamide", *Radiat. Phys. Chem.*, **59**, 413 (2000).
27) D. Binh, D. T. The, T. T. Canh, N. Q. Hien, V. T. K. Lang, P. T. T. Hong, N.D. Hang, "Study on application of radiation processing technology to produce superabsorbent polymer for soil conditioner" (to be published).
28) J. M. Rosiak, J. Olejniczak, "Medical applications of radiation formed hydrogels" *Radiat. Phys. Chem.*, **42**, 903 (1993).
29) M. T. Razzak, D. Darwis, D. Zainudin, S. P. Sukirno, "Irradiation of polyvinyl alcohol and poly vinyl pyrrolidone blended hydrogel for wound dressing", *Radiat. Phys. Chem.*, **62**, 107 (2001).
30) C. Aranilla, F. Yoshii, A. Dela Rosa, K. Makuuchi, "Kappa carrageenan polyethylene oxide hydrogel blends prepared by gamma irradiation", *Radiat. Phys. Chem.*, **55**, 127 (1999).
31) L. Abad, L. Relleve, C. Aranilla, A. Dela Rosa, "Properties of radiation synthesized PVP-kappa carrageenan hydrogel blends", *Radiat. Phys. Chem.*, **68**, 901 (2003).
32) D. Queen, J. D. S. Gaylor, J. H. Evans, J. M. Courtney, W. H. Reid, "The preclinical evaluation of the water vapor transmission rate through burn wound dressings", *Biomaterials*, **8**, 367 (1987).

33) T. G. Rekso, N. M. Surdia, L. R. Cynthia, A. Sadijah, “Study on irradiation grafting hydrophilic monomer onto chitin for ion exchange application”, *Advance in Chitin Science,* **5**, 333 (2002).
34) N. Q. Hien, D. V. Phu, N. N. Duy, H.T. Huy, “Radiation grafting of acrylic acid onto partially deacetylated chitin for metal ion adsorbent”, *Nucl. Instrum. Methods Phys. Res. B*, **236,** 606 (2005).
35) C. A. Eiden, C. A. Jewell, Y. P. Wightman, “Interaction of lead and chromium with chitin and chitosan”, *J. Appl. Polym. Sci*., **25**, 1587 (1980).
36) P. R. Austin, C. J. Brine, J. E. Castle, J. P. Zikakis, “Chitin: new facet of research”, *Science*, **212,** 749 (1981).
37) A. A. Brief, S. G. Maurer, P. E. Di Cesare, “The use of glucosamine and chondroitin sulfate in the management of osteoarthritis”, *J. Am. Aca. Orthopaedic Surgeons.,* **9**, 71 (2001).
38) K. J. Adebowale, D. S. Cox, Z. Liang, N. D. Eddington, “Analysis of glucosamine and chondroitin sulfate content in marketed products and caco-2 permeability on chondroitin sulfate raw material”, *JANA,* **3**, 33 (2000).
39) T. Siyam, H. A. Youssef, “Cationic resins prepared by radiation-induced graft copolymerization”, *Radiat. Phys. Chem*., **55**, 447 (1999).
40) E. A. Hegazy, H. A. A. El-Rehim, H. A. Shawky, “Investigations and characterization of radiation grafted copolymers for possible practical use in waste water treatment”, *Radiat. Phys. Chem*., **57**, 85 (2000).
41) N. Seko, A. Katakai, S. Hasegawa, M. Tamada, N. Kasai, H. Takeda, T. Sugo, K. Saito, “Aquaculture of uranium in seawater by a fabric-adsorbent submerged system”, *Nucl. Technol*., **144**, 274 (2003).
42) T. Shiraishi, M. Tamada, K. Saito, T. Sugo, “Recovery of cadmium from waste of scallop processing with amidoxime adsorbent synthesized by graft-polymerization”, *Radiat. Phys. Chem*., **66**, 43 (2003).
43) M. Hisamatsu, T. Yamada, “Partially deacetylated chitin as an acid-stable support for enzyme immobilization”, *J. Ferment. Bioeng*., 67, 219 (1989).
44) C. F. Degiorgi, R. A. Pizarro, E. E. Smolko, S. Lora, M. Carenza, “Hydrogel for immobilization of bacteria used in the treatment of metal-contaminated wastes”, *Radiat. Phys. Chem*., **63**, 109 (2002).
45) X. Zhao, K. Kato, Y. Fukumoto, K. Nakamae, “Synthesis of bioadhesive hydrogels from chitin derivatives”, *Int. J. Adhesion & Adhesives*, **21** 227 (2001).
46) X. L. Liu, Y. L. Guan, D. Z. Yang, Z. Li, K. D. Yao, “Antibacterial action of chitosan and carboxymethylated chitosan”, *J. Appl. Polym. Sci*., **79**, 1324 (2001).
47) L. Zhao, H. Mitomo, N. Nagasawa, F. Yoshii, T. Kume, “Radiation synthesis and characterization of the hydrogel based on carboxymethylated chitin derivatives”, *Carbohydrate Polym*., **51**, 169 (2003).
48) H. J. Jennings, A. R. Pon, “Polysaccharides and glycoconjugates as human vaccines” in *Polysaccharides in medicinal applications* (Ed. Dumitriu S.), Marcel Dekker, New York, p. 443 (1996).
49) A. N. De Belder, “Medical application of dextran and its derivatives” in *Polysaccharides in medicinal applications* (Ed. Dumitriu S.), Marcel Dekker, New York, p. 505 (1996).

5.10 Application of Chitin and Chitosan

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Chitin, one of the most abundant natural polysaccharides on the earth, is component of cell wall of fungi, cuticle components of insects and crustaceans. The chemical and crystalline structures of chitin are close to those of cellulose and C-2 hydroxyl group is only replaced by acetamide group in chitin. As chitin is cell wall component of fungi or viruses, plants, and cuticles of crustacean and Insects, they are containing chitin hydrolyzing enzymes in their self defense system. So that chitin is said to be biodegradable in animal body.

Chitin is reported to participate in the recovery of skin as wound dressing, in which chitin oligomers are the most effective to acceleration of epidermal cell recovery. Chitosan, on the other hand, is one of deacetylated derivatives is also reported to be biodegradable in animal body and to induce the recovery of fibroblast formation mainly by chitosan oligomer 1). The big advantage of chitosan is antimicrobial activity against fungi and viruses. The antimicrobial activity seems to be independent to the surface properties of fungi and viruses such as gram negative or gram positive as seen in the Table 1.

Table 1 Antimicrobial activities by chitosan
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)

But the antimicrobial activity is quite sensitive to the molecular size as shown in Figures 1 and 2. As shown in Figure 1 2), the chitosan oligomer with molecular weight less than 2,200 becomes rather enhancement of E. coli activity against almost complete suppression of bacterial activity by chitosan with molecular weight over 9,000. The antimicrobial activity by chitosan oligomers was assisted by the fluorescent study applying fluorescein isothiocianate (FITC) labeled chitosan oligomers as seen in Figure 2. The chitosan oligomer with low molecular weight permeated through cell membrane and high molecular weight fraction stacked on the cell wall of E. coli probably blocking of nutrition supply.

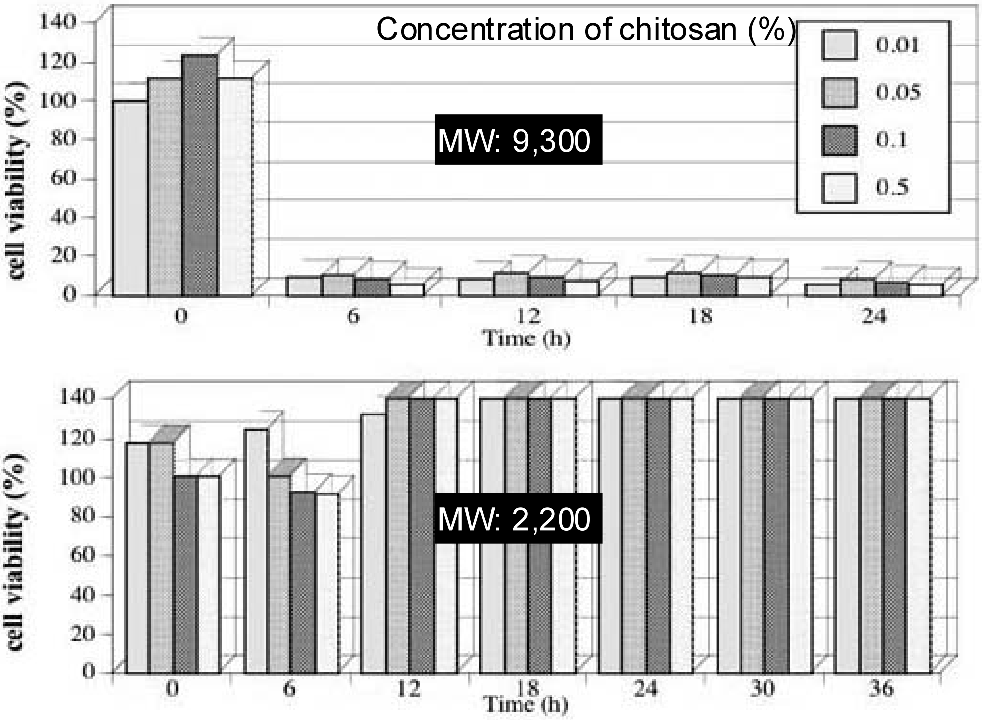

Fig. 1 Molecular weight and concentration dependencies of antimicrobial activity by chitosan oligomer on E. coli.

(A) Mw 9,300 *(B) Mw 2,200*

Fig. 2 Microscopic observation of FITC labeled chitosan oligomers

On the solubility of chitin or chitosan, chitin is known to be sparingly soluble in general solvents owing to rigid crystalline structure assisted by binary hydrogen bonding [3)], but chitosan becomes water soluble following the formation of salts with organic acids such as formic acid, acetic acid, propionic acid, glutamic acid, aspartic acid, ascorbic acid and so on [4)]. The solubility of chitin against calcium chloride dehydrate saturated methanol was found to depend on the degree of N-acetylation and the molecular weight seriously as shown in Figure 3.

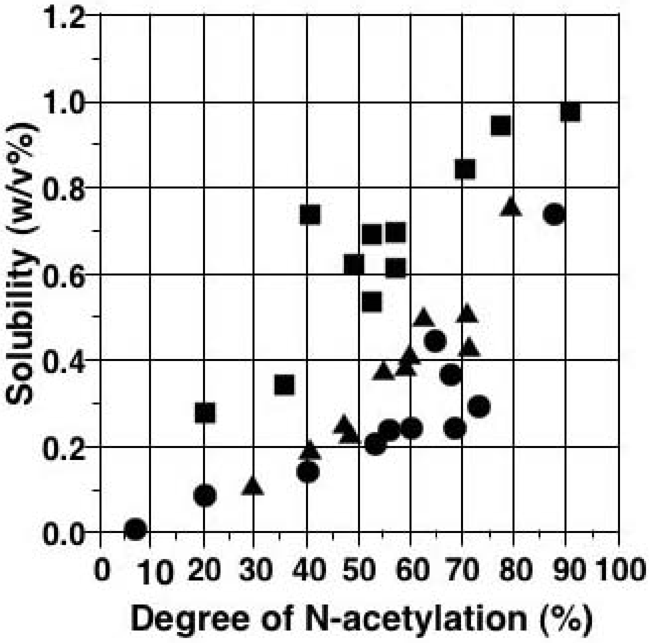

Fig. 3 Dependences of solubility against calcium chloride dehydrate saturated methanol on degree of N-acetylation and molecular weight of chitin

The dissolute chitin molecule becomes hydrogel following the precipitation by large excess of water and then dialyzed against deionized water extensively [5)]. Figure 4 shows the procedure of chitin sheet production.

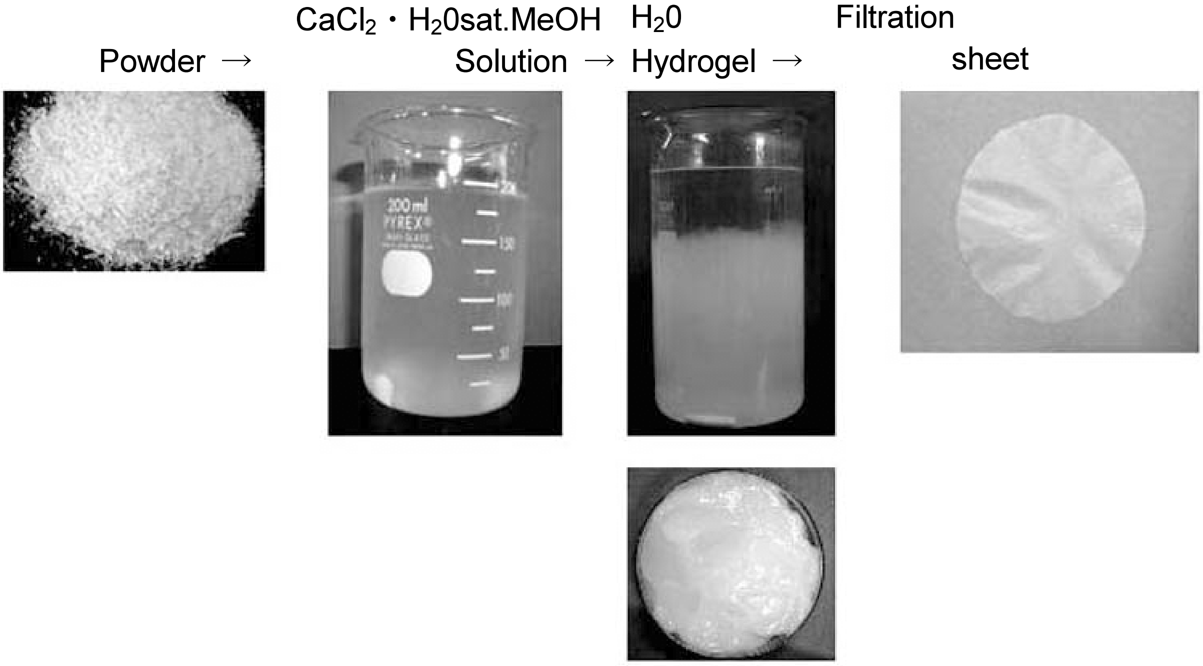

Fig. 4 Dissolution and precipitation procedures of chitin

The chitin hydrogel is highly water regainable and able to prepare the non-woven fabrics without any binder. The chitin non-fabrics tend to adsorb anionic compounds predominantly as those of chitosan. Figure 5 illustrates the adsorption behavior of chitosan against anionic and cationic dye.

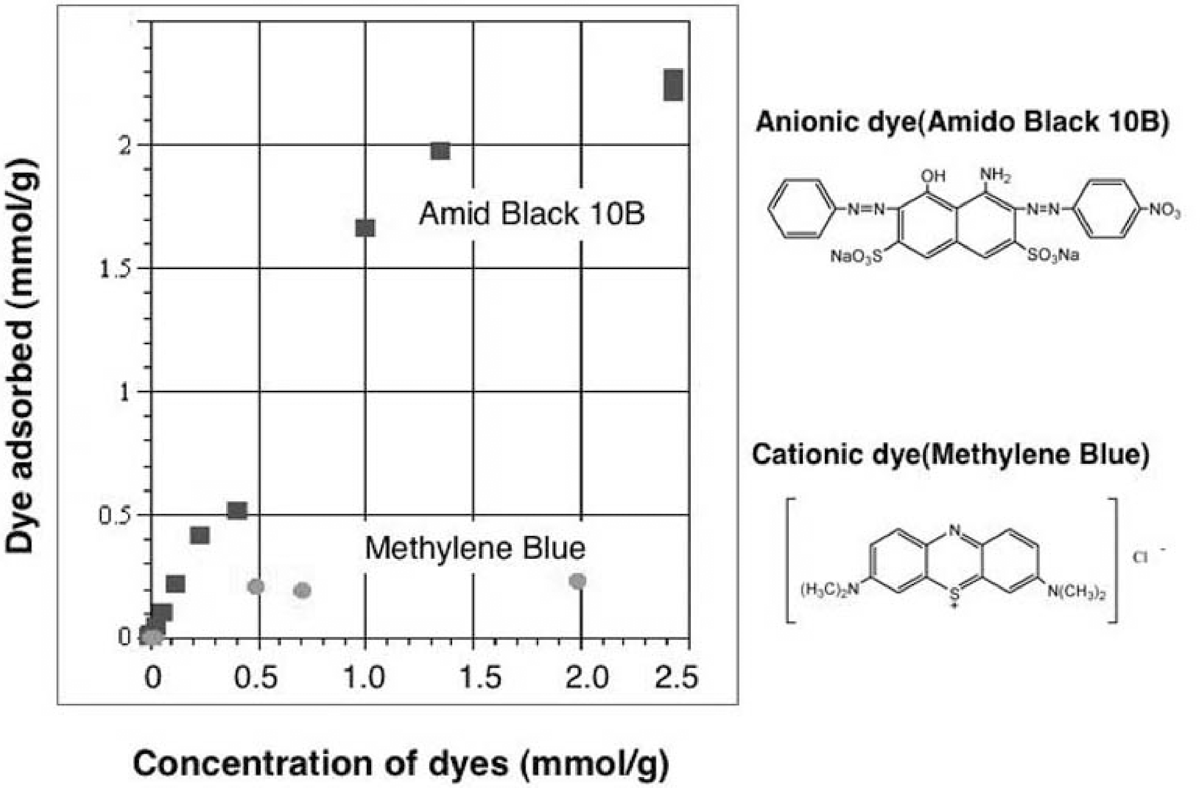

Fig. 5 Adsorption of dyes for chitosan woven fabrics

Another splendid property of chitin and chitosan is wound healing. The wound healing of chitin has been applied practically for long time and found to the acceleration of epidermal cell recovery mainly by the chitin oligomers. But the wound healing of chitosan was reported recently also mainly by chitosan oligomers 1). The wound healing by chitosan is the acceleration of fibroblast regeneration.

Since chitosan has an antimicrobial activity against fungi and viruses in addition to ion exchange property against cationic ions, biomedical applications have been investigated to apply regenerated chitosan products such as fiber, membrane and beads including chitosan coated alginate fiber 6). Figure 6 shows the manufacturing processes procedure of chitosan coated alginate fiber. Figure 7 shows the cut surface of the chitosan coated alginate fiber thus produced.

Chitosan beads were reported to be effective to remove radioactive materials from animal body by adsorption 7). Also chitosan beads were reported to adsorb heavy metals especially mercuric and copper ions 8). Chitosan aqueous acetic acid solution was also reported to work for the flocculation of organic materials from waste water of food industries 9).

Studies on the functionalization of chitin and chitosan are still going on to find novel applications, because fundamental studies on chitin and chitosan such as solvent system, regeneration and chemical modifications have started shortly before. We can expect radio active irradiation to apply of chitin and chitosan for various fields especially in the field of biomedical materials in near future.

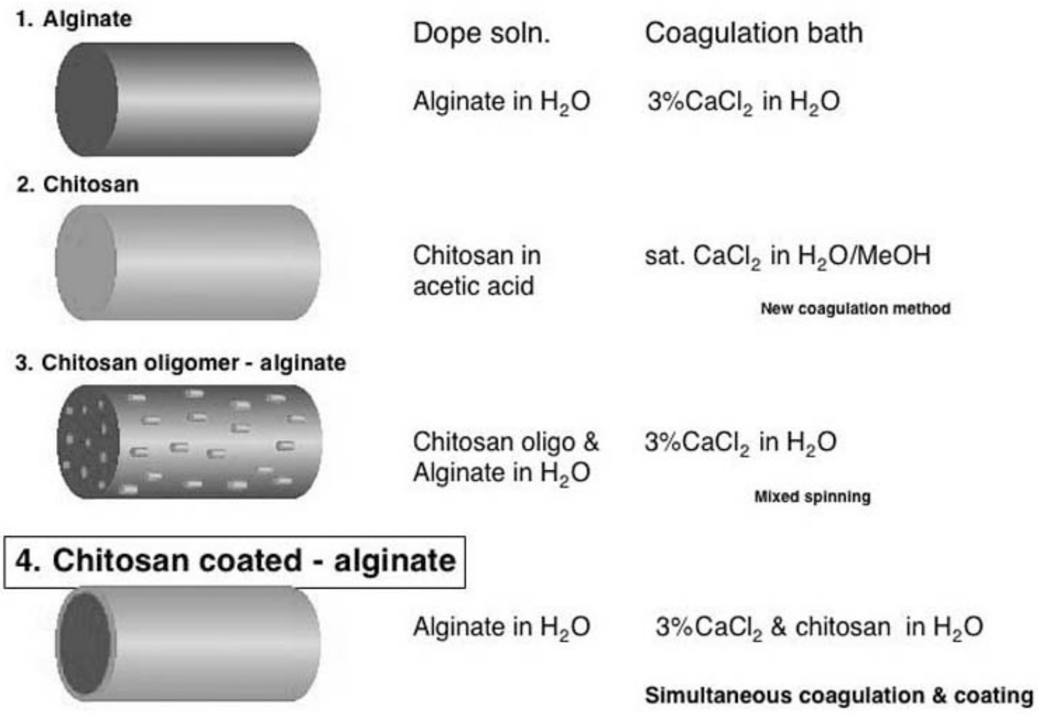

Fig. 6 Spinning conditions of chitosan related fibers

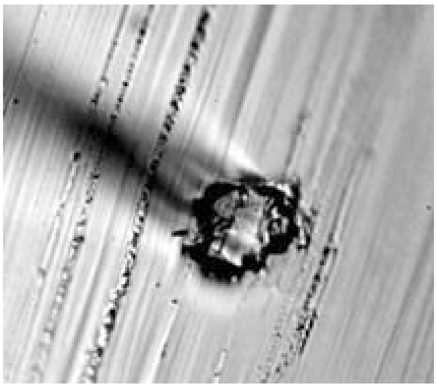

Fig. 7 Cut surface of chitosan coated alginate fiber (Chitosan part was stained by ninhydrin)

References

1) S. Minami, Y. Okamoto, K. Hamada, Y. Fukumoto, Y. Shigemasa, *"Chitin and Chitinases"* ed. by P. Jelles, R. A. A. Muzzarelli, Birkhauser, Basel, Boston, Berlin, p. 265 (1999).
2) S. Tokura, K. Ueno, S. Miyazaki, N. Nishi, *Macromol. Symp.*, **120**, 1 (1997).
3) H. Tamura, S. Tokura, *"Advances in Chitin and Chitosan"* ed. by H. Struszczyk, A. Domard, M. G. Peter, H. Pospieszny, Poznan, p.26 (224, 2005).
4) *"Chitin"* ed by R. A. A. Muzzarelli, Pergamon Press, Oxford, New York, Toronto, Pari, Frankfurt, p.104 (1977).
5) H. Tamura, H. Nagahama, S. Tokura, *Cellulose*, **13**, 357 (2006).
6) H. Tamura, S. Tokura, *Mat. Sci. & Appl. Chem.*, **A39**, 747 (2002).
7) R. A. A. Muzzarelli, R. Rochatti, G. Marangio, *J. Radioanal. Chem.*, **10**, 17 (1972).
8) R. A. A. Muzzarelli, A. Isolati, *Air & Soil Poll.*, **1**, 65 (1971)
9) Sato, M, *"Application of Chitin and Chitosan"* ed. by Japanese Chitin/Chitosan Society, Gihodo Press, p. 210 (1990).

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・m^{-1}=1[(b)]
立体角	ステラジアン[(a)]	sr[(c)]		m^{2}・m^{-2}=1[(b)]
周波数	ヘルツ	Hz		s^{-1}
力	ニュートン	N		m・kg・s^{-2}
圧力，応力	パスカル	Pa	N/m^{2}	m^{-1}・kg・s^{-2}
エネルギー，仕事，熱量	ジュール	J	N・m	m^{2}・kg・s^{-2}
工率，放射束	ワット	W	J/s	m^{2}・kg・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}・kg・s^{-3}・A^{-1}
静電容量	ファラド	F	C/V	m^{-2}・kg^{-1}・s^{4}・A^{2}
電気抵抗	オーム	Ω	V/A	m^{2}・kg・s^{-3}・A^{-2}
コンダクタンス	ジーメンス	S	A/V	m^{-2}・kg^{-1}・s^{3}・A^{2}
磁束	ウエーバ	Wb	V・s	m^{2}・kg・s^{-2}・A^{-1}
磁束密度	テスラ	T	Wb/m^{2}	kg・s^{-2}・A^{-1}
インダクタンス	ヘンリー	H	Wb/A	m^{2}・kg・s^{-2}・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}・m^{-2}・cd=cd
照度	ルクス	lx	lm/m^{2}	m^{2}・m^{-4}・cd=m^{-2}・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}・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}・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}・kg・s^{-1}
力のモーメント	ニュートンメートル	N・m	m^{2}・kg・s^{-2}
表面張力	ニュートン毎メートル	N/m	kg・s^{-2}
角速度	ラジアン毎秒	rad/s	m・m^{-1}・s^{-1}=s^{-1}
角加速度	ラジアン毎平方秒	rad/s^{2}	m・m^{-1}・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・s^{-3}
熱容量，エントロピー	ジュール毎ケルビン	J/K	m^{2}・kg・s^{-2}・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}・s^{-2}・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}・s^{-2}・K^{-1}
熱伝導率	ワット毎メートル毎ケルビン	W/(m・K)	m・kg・s^{-3}・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}・kg・s^{-2}
電界の強さ	ボルト毎メートル	V/m	m・kg・s^{-3}・A^{-1}
体積電荷	クーロン毎立方メートル	C/m^{3}	m^{-3}・s・A
電気変位	クーロン毎平方メートル	C/m^{2}	m^{-2}・s・A
誘電率	ファラド毎メートル	F/m	m^{-3}・kg^{-1}・s^{4}・A^{2}
透磁率	ヘンリー毎メートル	H/m	m・kg・s^{-2}・A^{-2}
モルエネルギー	ジュール毎モル	J/mol	m^{2}・kg・s^{-2}・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}・kg・s^{-2}・K^{-1}・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}・s・A
吸収線量率	グレイ毎秒	Gy/s	m^{2}・s^{-3}
放射強度	ワット毎ステラジアン	W/sr	m^{4}・m^{-2}・kg・s^{-3}=m^{2}・kg・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}・sr)	m^{2}・m^{-2}・kg・s^{-3}=kg・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)×10^{-19}J
統一原子質量単位	u	1u=1.6605402(10)×10^{-27}kg
天文単位	ua	1ua=1.49597870691(30)×10^{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	１a=1 dam^{2}=10^{2}m^{2}
ヘクタール	ha	１ha=1 hm^{2}=10^{4}m^{2}
バール	bar	１bar=0.1MPa=100kPa=1000hPa=10^{5}Pa
オングストローム	Å	１Å=0.1nm=10^{-10}m
バーン	b	１b=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・s/cm^{2}=0.1Pa・s
ストークス	St	1 St =1cm^{2}/s=10^{-4}m^{2}/s
ガウス	G	1 G ˆ10^{-4}T
エルステッド	Oe	1 Oe ˆ(1000/4π)A/m
マクスウェル	Mx	1 Mx ˆ10^{-8}Wb
スチルブ	sb	1 sb =1cd/cm^{2}=10^{4}cd/m^{2}
ホト	ph	1 ph=10^{4}lx
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=3.7×10^{10}Bq
レントゲン	R	1 R = 2.58×10^{-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=1.002×10^{-4}nm
ガンマ	γ	1γ=1 nT=10^{-9}T
ジャンスキー	Jy	1 Jy=10^{-26}W・m^{-2}・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 = 2×10^{-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 µ =1µm=10^{-6}m

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