FNCA2009 Electron Accelerator Application Workshop
- Radiation Processing of Natural Polymers –

Summary of FNCA Member Countries' Reports and IAEA/RCA Report

Part A. Summaries of Country Reports on Radiation Processing and Application of Chitosan

(1) Bangladesh (Dr. Emdadul. Md. Haque, BAEC)

Bangladesh produces shrimp and prawn about 750,000 metric ton per annum and it is increasing every year. So there is a reason to extract chitosan from the waste shell of shrimp/prawn. Method for the extraction of chitosan from the locally available waste shell has been established. The molecular weight was determined by measuring viscosity of chitosan solution before and after irradiation at various doses. Biodegradable chitosan films were prepared with 2-Hydroxy ethyl methacrylate (HEMA) using various formulation and curing under UV source or irradiating with gamma rays. The chitosan solution obtained under FNCA was applied in local vegetable and chili as plant growth promoter. Positive results were found by the application of chitosan.

(2) China (Prof. Youjiu Zhang, Soochow University)

The presentation discussed about different pre-treatment methods for degradation of chitosan via radiation to produce water soluble oligomers. Chitosan samples in solid state, treated with 5% and 24% H_2O_2, immersed in water and treated with sensitizer were irradiated at different doses. Samples treated with 24% H_2O_2 and with sensitizer exhibited the most significant effect in degradation of chitosan. Research on the synergistic effect of ozone on degradation of chitosan showed that molecular weight of chitosan decrease remarkably with increasing the pretreatment time and concentration of ozone. A study on the application of irradiated chitosan as radiation protector was conducted by determining survival rate of BRL cells treated with 4 Gy gamma exposure and chitosan. The higher survival rate and lower SubG1 peek of the irradiated cells was acquired under low-molecular weight chitosan (LMWC). After treated with 50μg/mL of LMWC and 4Gy 60Co γ irradiation, survival rates of BRL cells was increased from 66.5%±0.19% to 87.5%±0.16% in 48h ($P < 0.05$), and the peak of SubG1 was decreased from 51.9%±2.1% to 16.9%±1.3% in 24h ($P < 0.05$). The results indicate that low molecular weight chitosan has excellent radiation protection effects to normal rat liver cell line (BRL).

(3) Indonesia (Dr. Gatot Trimulyadi Rekso, BATAN)

Irradiation method is effective for reducing the molecular weight and viscosity of chitosan. The IRKA irradiator facility at PATIR-BATAN could be used for pilot production of oligochitosan with maximum capacity of 1000 L/batch. Results of field test application of oligochitosan on chilli plant showed increase in productivity around 0.25 kg/plant. The antimicrobial property of irradiated chitosan was also evaluated for possible use in food preservation. Initial study showed effective growth inhibition of *staphylococcus aureus* and *echerichia coli*.

(4) Japan (Dr. Fumio Yoshii, ICPD-JAEA)

Field test of oligo-chitosan prepared byγ-ray irradiation to evaluate as a plant growth promoter was carried out. Five percent (5%) chitosan solution in acetic acid was irradiated and resulting solution was diluted 500 times using water. The dilute solution was sprayed on plant leaves such as potherb mustard, brassica, crown daisy and turf. Results show effectiveness of oligo-chitosan as PGP on these plants. Furthermore, oligochitosan was effective to prevent damage of fusarium in cyclamen during summer season. From these results, oligo-chitosan under the brand name oligo-glucosamine-L (OG-L) was commercialized in Japan.

(5) Malaysia (Dr. K. Bin Hashim, Nuclear Malaysia)

Pilot scale production of oligochitosan was carried out by continuous flow gamma radiation. Total production was about 1,440 litres. Oligochitosan was characterized in terms of colour, pH, viscosity and molecular weight. Storage study has shown that oligochitosan solution degraded during storage, based on the result of viscosity and pH.

The germination study on rice seed showed that soaking rice seed in 200pmm oligochitosan for 24 hours give the highest average growth percentage of rice seed on compared with soaking in water or in water followed with soaking in 200ppm oligochitosan. Further study comparing oligochitosan with commercial growth promoter, *VitaCambah* on seed growth revealed that low molecular weight oligochitosan promote better growth for rice seed and it needs low concentration to give same effect as higher molecular weight oligochitosan.

Field trial of oligochitosan as plant growth promoter and elicitor on rice was carried out in collaboration with FELCRA (M) Bhd. on 24 hectares rice plantation. In this study, eight treatments (T1-T8) with triplicates for each treatment had been identified. Data compilation had been carried out in respect to fungus blast, rice check, crop cutting survey, analysis on soil, nutrient analysis of paddy plant and rice yield for each plot. Study indicated that rice yield depended on germination treatment with oligochitosan, spray treatment with oligochitosan and other factors such as soil condition, nutrient up take, insect infection and plant growth.

(6) The Philippines (Ms. Charito. T. Aranilla, PNRI)

The second phase of the project on semi-commercialization of PVP-Carrageenan hydrogels has been completed. Major outcome include (1) development of manufacturing process; (2) optimization of parameters for radiation processing; (3) production of 10,000 pieces for free distribution in hospitals; (4) development of QA/QC system protocol; (5) initiation of market acceptability test; and (6) establishment of six trial centers in Northern Luzon. The project enters into phase 3 where the objectives are to conduct product stability/shelf-life determination studies on products produced in a BFAD approved semi-controlled sterile facility (Class 100,000) and to transfer technology to Biotecos Co. through a licensing agreement.

In order to facilitate the application of radiation processed oligochitosan and oligocarrageenan, a research program entitled "Plant bio-stimulants and elicitor from radiation-modified natural polymers" was created and proposed to the Department of Science and Technology for funding. This program is in collaboration with two experts from the Philippine Rice Research Institute and the National Crop Protection Center, UP Los Banos. The objectives of the program are to develop plant-growth promoting/elicitor products from radiation-modified chitosan and carrageenan for commercialization, to study effect on application to *Spathoglottis* and *Dendrobium* orchids, elucidate growth promotion mechanisms on rice and to evaluate biological efficacy as inducers of resistance against bacterial and viral pathogens on rice and bitter gourd.

(7) Thailand (Dr. Phiriyatorn Suwanmala, TINT)

The field test of oligochitosan as plant growth promoter on rice was carried out in collaboration with Pathum Thani Rice Research Center, Phathumthani, Thailand. Four treatments were done with randomized complete block design (RCBD). For each replication of each treatment, rice seeds were planted in a 4m x 6m plot. The foliar spraying with irradiated chitosan were done three times, at 20 days after sowing, at tillering phase and at panicle initiation phase, respectively, at a rate of 400 ml/plot. Rice plant treated with fertilizer and irradiated chitosan gave the highest number of grain yield.

The field test of oligochitosan as elicitor on rice conducted at Pathum Thani Rice Research Center, Phathumthani, Thailand. The foliar sprayings with irradiated chitosan were done three times, at 20, 30 and 40 days after transplanting. At booting and heading stages, rice plant treated with irradiated chitosan had lower percentage of Bacterial Blight (BB) than control. The percentage of Sheath Blight (ShB) at heading stage and dough stage decreased with decreasing concentration of irradiated chitosan, i.e from 80 to 20 ppm.

(8) Vietnam (Mr. Le Hai, VAEI)

Plant growth promoters T&D-4DD from irradiated alginate and plant protectors/elicitor OLICIDE-9DD and elicitor from crustacean shell have been achieved and commercialized. Derivatives of chitin/ chitosan (CM-chitin and CM-chitosan) have been successfully studied and are still being developed. Glucosamine in hydrochloride and sulfate forms have been prepared by hydrolysis and deacetylation of irradiated chitin. The results indicated that glucosamine yield increased from irradiated chitin.

Studies on the production of super water absorbent have been successfully carried out in VINAGAMMA and Nuclear Research Institute. Two products namely GAMMA-Sorbs and Agro gel were applied and commercialized.

Studies on radiation modification of polyvinyl alcohol by grafting with acrylamide and N-vinyl pyrrolidone showed that the rheological property was stable at high pressure, temperature and salinity conditions. Currently, the studied polymers were utilized to enhance oil recovery. A research contract on the application of radiation processed polymers for oil recovery in oil wells have been flooded with water is being started in 2010.

Part B. Summaries of Country Reports on Radiation Processing and Application of Starch/Polysaccharides for Super Water Absorbent (SWA)

(1) Bangladesh (Dr. Emdadul. Md. Haque, BAEC)

Super water absorbent was prepared from acrylamide and kappa-Carrageenan solution by the application of radiation. Characteristic properties such as soiling behavior, gel content etc. were determined. The superabsorbent hydrogel shows the equilibrium swelling in the range ~2500 to ~3300%. Super water absorbent was also prepared using acrylamide and HEMA. Equilibrium swelling was in the range ~1200 to ~1600%. This will be applied in agricultural fields.

(2) Indonesia (Mr. Erizal, BATAN)

Non-toxic superabsorbent hydrogels were synthesized from aqueous solution containing 5 % polyethylene oxide (PEO) with different concentrations of alginate (0.5-2.0%) irradiated at the doses of 20, 30, and 40 kGy by gamma radiation. The gel fraction, swelling kinetics and the equilibrium degree of swelling (EDS) of the hydrogels were studied. It was found that the incorporation of even 2 % alginate (sodium salt) increases the EDS of the hydrogels from 20 ~320 g/g. At a dose of 20 kGy, PEO-alginat hydrogels with high gel fraction (~80 %) and very high EDS (~ 320 g/g) were syntehsized. The hydrogels were also found to be sensitive to ionic solution of NaCl. The PEO-alginate hydrogels can be considered as potential biomaterial in health care.

A series of superabsorbent hydrogels were prepared from acrylamide (AAM) and potassium acrylic (KA) by gamma irradiation technique at room temperature. Solutions of 15% potassium acrylate and containing different concentrations of AAM (10-16%) were irradiated by gamma rays (20-40 kGy). The copolymers were characterized by FTIR. The gel fraction, kinetics swelling and the equilibrium degree of swelling (EDS) were studied. Under optimum conditions (dose 20 kGy and concentration of AAM 10 %), poly(AAM-co-KA) hydrogel with high gel fraction (~100%) and very high EDS (~420 g/g) were prepared. The capacity of hydrogel to adsorp metal ion Cu 2+ and ion Fe3+ were investigated. At optimum conditions (10 minutes), the hydrogel can adsorp ion Cu 2+ up to 95 %, and for adsorption of ion Fe3+ was reached up to 55 % at 80 minutes observation. This hydrogel can be considered as candidate for soil conditioning and ion metal absorbent.

(3) Japan (Dr. Fumio Yoshii, ICPD-JAEA)

Crosslinking and biodegradability of carboxymethyl-starch (CMS) and carboxy-methyl cellulose (CMC) were studied for application as super water absorbent. Swelling capacities of CMC and CMS hydrogels were 450 g/g dry hydrogel and 340 g/g dry gel, respectively. These values are comparable to swelling capacity of 350 g/g dry gel of commercial product composed of polyacrylic acid (PAAC). Biodegradation of CMS hydrogels showed biodegradability of about 40% for a composting period of about two weeks.

(4) The Philippines (Ms. Charito. T. Aranilla, PNRI)

Synthesis and radiation crosslinking of carboxymethyl-k-carrageenan (cmkc) was successfully achieved to obtain crosslinked hydrogels. Crosslinking of cmkc showed dependence on degree of substitution (DS), concentration and radiation dose. Highest gel content was about 76% exhibited by CMkC-3S hydrogel with a DS of 1.66. The hydrogels exhibited different degrees of swelling in water, saline and PBS solutions. Highest water absorption was exhibited by 30% CMkC-2S (without sol part) irradiated at 30 kGy and gave a value of 200g/g hydrogel for a period of 10 minutes and 400 g/g for a period of 30 minutes.

(5) Thailand (Dr. Phiriyatorn Suwanmala, TINT)

The superabsorbent was synthesized from polyacrylic acid-grafted cassava starch. Various factors were investigated in order to determine the optimum conditions for the grafting polymerization. The criteria were emphasized by the optimum conditions of important parameters to give a maximum amount of water absorption. The sand mixed with 0.1 wt% hydrogel can absorb more water than the sand without hydrogel. After seven days the sand without hydrogel had nearly given off all water, while the sand with 0.1% wt hydrogel still retained 50% water. The germination percentage of seeds with 0.5 wt% hydrogel was also higher than that of the seeds without hydrogel. After 15 days, soil

with 0.5 wt% hydrogel showed a favourable effect on weights of leafages and roots of plants. The experimental results showed that the superabsorbent may have considerable effect on seed germination and young plant growth.

(6) Vietnam (Mr. Le Hai, VAEI)

Super water absorbent prepared from acrylic acid with cassava costs of about 2,000 USD/ton but modification by adding bagasse or coconut fiber powder resulted to significant reduction on cost of about 20% (1,600USD/kg). Field tests for the modified SWA were done on coffee, tea, pepper. Good soil humidity was maintained and crop yield increased by 20%. The field tests on dragon, orange, rubber cassava, orchid are on-going. Cooperation with companies, farm owners and the Departments of Science & Technology of provinces were carried out for expansion and promotion to market.

Part C. Summary of the Presentation on the IAEA/RCA Project Activities on Radiation Processing of Natural Polymer (Dr. Khairul Zaman Hj Mohd Dahlan)

Under the IAEA/RCA Program for 2009 – 2011, RCA member states have formulated a project entitled "Supporting Radiation Processing of Polymeric Materials for Agricultural Applications and environmental Remediation", RAS/8/109. The objective of the project is to enhance agricultural production and mitigate environmental pollution using radiation technology. In many RCA member states, agricultural sector is still the main and important economic sector of the country and it is also related to food security. However, the member states are very concerned on the shortage of water resources due to the increase in urbanization for development, industrialization and absence of stringent environmental laws and high cost of fertilizer that may affect the agricultural productivity in the region. In relation to this, several radiation-processed products such as super-water absorbent and plant-growth promoter produced by radiation degradation of natural polymers such as alginate, chitosan, carrageenan and starch have been identified that will contribute towards overcoming the above concerned. Natural polymers were selected as the starting materials because they are renewable and abundant. The willingness of some member countries that have successfully developed radiation-processed products for agricultural use to share the knowledge and transfer the technology to other member countries in the region is also the main deciding factor in the formulation of regional project cooperation.

In addition, to mitigate environmental pollution, radiation technology will also be used to treat wastewater and to produce adsorbents of toxic metal and other pollutants for improving the quality of wastewater and industrial effluent management enabling the water to be recycled and reused for agriculture purposes.

Solid waste, in particular plastic and rubber waste, is also an environmental problem as they are not biodegradable and is difficult to dispose off. The ability of radiation processing to degrade and crosslink polymers could provide an alternative way of reprocessing, recycling and reutilizing plastic and rubber waste.