Radiation Modification of Natural Polymers

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**Cross-linking**

- Natural rubber latex
- Crosslinking of polysaccharides

**Degradation**

- Cellulose fibers obtained from wood pulp
- Degradation of polysaccharides

**Preparation of blends**

- Preparation of synthetic-natural polymer blends
Various research works have been performed on radiation vulcanization of natural rubber latex (RVNRL) since it possesses several advantages over sulfur vulcanization such as

- the absence of nitrosoamines compounds
- better transparency
- very low cytotoxicity
- and less rubber proteins that causes allergic response

Polyfunctional monomers which contain more than two polymerizable C= C double bonds in a molecule, and monofunctional acrylic monomers were used as vulcanization accelerators. Among the monofunctional monomers, n-butyl acrylate (n-BA) is the most effective vulcanization accelerator because it not only imparts much better physical properties at lower D<sub>v</sub> but also unreacted n-BA is not retained in the final product.

The low glass transition temperature of poly(n-BA) and a high probability of chain transfer reaction of n-BA during polymerization are closely related to its high sensitizing effect.
Many attempts were made to investigate an alternative accelerator to be used in radiation vulcanization of natural rubber latex (RVNRL).

Trimethylol propane tri-methacrylate (TMPTMA)
Phenoxy polyethylene glycol acrylate (polyfunctional monomer) (PPEGA)
Phenoxy ethyl acrylate (PEA),

Variation of tensile strength of NR vs dose

Variation of tensile strength of RVNRL prepared using TMPTMA at various doses of radiation.
Rayon is produced from viscose, a polymer made from cellulosic materials such as wood pulp. Cellulose fibers extracted from wood pulp can be converted to a thick liquid called viscose, which is used to make commercial products such as rayon fabrics and cellophane films.

The molecular weight of the natural cellulose is reduced by treatment with sodium hydroxide and heat. Then this material is dissolved in carbon disulfide to make viscose. Initial irradiation of the cellulose causes a reduction in molecular weight, and enables the rest of the process to be completed in less time with less chemical treatment.

This reduces the cost and also reduces the environmental pollution. The dose requirement is about 15 kGy.
Conventional Viscose Process

- Wood Pulp
- Alkalization (19% NaOH)
- Ageing (Heat, O₂)
- Xanthation (CS₂, 28-36%)
- Ripening (5-8% NaOH)
- Acid Bath
- Spinning
- Effluent Discharge
- H₂S, CS₂
- Stretching/Finishing
- Filament
- Staple Fibre
- Cord Casing
**Topic: Radiation Modification of Natural Polymers**

**POLYSACCHARIDES**

- **ALGINATES**
  Food stabilizer, gelling agent, encapsulation matrix, plant growth stimulator

- **CARRAGEENANS**
  Food processing, thickening agent, film forming, agriculture, horticulture, anti-HIV activities

- **CHITOSAN**
  Food processing, paper and textile industries, photographic processing, biomedical applications due to antifungal, antibacterial, antitumor activities as well as immuno-enhancing effects and protective effects against infection
Possible gelation mechanism of κ-carrageenan in aqueous solution: (----), ionic bonding; ( ), electrostatic forces of attraction.
Gigartina (France, Argentina/Chili, Morocco)
Chondrus (France, North Atlantic)
Iridaea (Chili)
Eucheuma (Philippines/Indonesia)
Natural polysaccharides from seaweeds (brown algae)

Alginate is phycocolloid

Consists of linear chains composed of two monosaccharides;
- D-mannuronic acid (mannuronate) (M)
- L-guluronic acid (guluronate) (G)

Sodium Alginate

D-guluronate (G)  D-mannuronate (M)
- Water-soluble gums sulfated polysaccharides
- 1,3 linked β-D-galactose and 1,4 linked α-D-galactose units.
- Anionic poly-electrolytes.
- Three main branches.
  - Kappa
  - Iota
  - Lambda

**Carrageenans**

- **κ-carrageenan**
- **ι-carrageenan**
- **λ-carrageenan**
The most essential medical applications of chitosan are as follows:
- Wound healing promoting dressings
- Dermatological agents
- Biodegradable carriers for slow release drugs
- Anticoagulant agents
- Optimological, dental and orthopedic agents
- Tumor cell metabolism reducing agents

Chitosan occurs in the shells of crabs, shrimps, prawns, lobsters, insects as well as some fungi wall cells.
DEGRADATION OF POLYSACCHARIDES

- Chemical
- Microwave
- Enzymatic
- Photolysis
- Ultrasound
- Radiation
Radiation cause the breakage of glycosidic bonds

Molecular weight, viscosity, gel strength decreases

Alginates were irradiated as solid state or in aqueous solutions
Alginate degradation under N₂ and O₂ conditions
Color Change of Irradiated Alginate

0 kGy  20 kGy  50 kGy
Appearance of mango treated with irradiated chitosan after 12 and 17 days storage

*Fresh mangoes were dipped into the irradiated chitosan solution (1%) and dried for surface coating.*
Rice was cultivated for 9 days in hydroponic solution with 20 ppm alginate irradiated in 4% solution

Alginate was irradiated at 100 kGy in 4% solution and rice was cultivated for 9 days

Effect of irradiated alginate on rice growth

(1) Without alginate
(2) 20 ppm alginate irradiated at 100 kGy in 4% solution
(3) 20 ppm alginate irradiated at 500 kGy in solid state.
Effect of concentration of degraded alginate on peanut growth. Alginate was irradiated at 100 kGy in 4% solution and peanut was sprayed with alginate solution for 15 days after 30 days cultivation.

Change in net photosynthesis of peanut plant by foliar spraying of irradiated alginate.

- ■: without alginate,
- ●: sprayed with irradiated alginate.
Rice was cultivated for 9 days in hydroponic solution with 100 mg/ml chitosan. From left, (1); control (without chitosan), (2); with unirradiated chitosan, (3)–(5); 20, 50 and 100 kGy-irradiated chitosan.

Effect of irradiated chitosan for rice growth

Change in rice growth with treatment of irradiated chitosan.
Rice and soybean plants were damaged at 2.5 mg/ml V (in VCl3).

These damages were reduced by application of radiation-degraded chitosan.

Bioimaging analyzer system (BAS) images of 48V in rice under V stress (10 mg/ml) with 50 mg/ml of irradiated chitosan.

Left: with chitosan
right: without chitosan.

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<th>Treatment</th>
<th>V content in seedling (µg/g dry wt.)</th>
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New topics

- A composite material for dietary applications
- Microgel particles (swelling)
- Radiation-modified chitosan (effective lipid+cholesterol binding)

**Lipid+cholesterol binding**

- Crosslinking
- Synthetic biocompatible polymer
- Microgels
- Matrix
- Fat-binding agent

Action
New topics

- Binding of lipids: ca. 20 g per 1 g of our composite substrate

- Preliminary animal studies under way (with positive results).
Polysaccharides undergo degradation by irradiation

Irradiation of polysaccharides at paste-like condition will led to crosslinking and form hydrogel.
Crosslinked CMC is suitable for healthcare products such as surgical operation mats for prevention of bedsores. High viscous solution of 20% CMC was pressed into a plastic bag and irradiated with 10 kGy. Such mats were tested by 68 patients in a hospital. No bedsores were observed in 64 patients and only red spots appeared on 4 patients immediately after surgical operation. This result reveals that the crosslinked CMC mat is extremely effective to prevent bedsores during surgical operation. This CMC gel mat is considered to disperse the body pressure and to maintain the best circulation of blood during operation.
Preparation of synthetic-natural polymer blends

- PVP-kappa carrageenan
- PVP-agar
- PVA-agar
- Chitosan-grafted N-isopropylacrylamide
- Chitosan/pHEMA membranes

Synthesis of antibacterial PVA/CM-chitosan blend hydrogels