



## Emerging applications of radiation-modified carrageenans



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### ABSTRACT

The Philippines supplies almost half of the world's processed carrageenan as ingredient for different applications. In order to maintain the country's competitive advantage, R&D on radiation processed carrageenan with various potential applications had been undertaken. PVP-carrageenan hydrogels for wound dressing had been developed. A carrageenan-based radiation dose indicator can detect radiation dose of as low as 5 kGy. Irradiated carrageenan has also been tested as plant growth promoter. Irradiated carrageenans have been found to contain some antioxidant properties which increase with increasing dose and concentration. Carboxymethyl carrageenans had also been developed that shows promising effect as super water absorbent for soil conditioner in plants.

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### 1. Introduction

The Eucheuma seaweed, which produces carrageenan, is a red algae grown in culture farms located mostly in Eastern Visayas and Mindanao part of the Philippines. The Philippines is the world's major producer of farmed Eucheuma and Kappaphycus seaweeds currently supplying about 40% of the raw material requirements for carrageenan production. The Seaweed Industry of the Philippines (SIAP) has pioneered the world's seaweed farming and processing as early as 1970. SIAP produces almost half of the world's processed seaweeds (carrageenan) as ingredient for different applications such as food, pet food, personal care, and pharmaceutical products [1]. This data easily make the Eucheuma seaweed and the Philippine processed carrageenan as priority export products of the country. Some 70% of all carrageenan products are utilized by the food industry. Of the remaining commercially used products, the major applications are in the cosmetics and personal care industries [2]. The Philippines should maintain its competitive advantage through R & D that will diversify the applications of carrageenan and open new markets for carrageenan.

Carrageenans are hydrophilic polymers that comprise the main structural polysaccharides of numerous species of seaweed e.g., Eucheuma, Chondrus, Gigartina, Fucellaria [3]. They are composed of D-galactose units linked alternately with  $\beta$  (1,3)-D-galactose-4-

sulfated and  $\alpha$  (1-4)-3,6-anhydro-D-galactose. These sulfated galactans are classified according to the presence of the 3,6-anhydrogalactose on the 4-linked residue, and in the number and position of the sulfate group. The repeating units of the principal gel formers, kappa-, iota- and lambda-carrageenans are shown in Fig. 1. From the structural point of view, the carrageenans have vast potential for non-food applications such as matrices for controlled drug delivery systems, immobilized enzyme systems, and for wound dressing.

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 [4]. Radiation processing is a very convenient tool for imparting desirable effects in polymeric materials and it has been an area of enormous interest in the last few decades. The Philippines through the Philippine Nuclear Research Institute (PNRI) for the past years has taken much effort in pursuing studies on the radiation modification of carrageenan for the conversion of these abundant natural resources into useful value-added products. This paper presents the progress and highlights of activities related to the application of radiation modified carrageenans.

### 2. Potential applications of radiation-modified $\kappa$ -carrageenan

#### 2.1. Poly(vinyl pyrrolidone) – $\kappa$ -carrageenan hydrogels for burn/wound dressing

Various water soluble polymers like poly(vinyl pyrrolidone) (PVP), poly(vinyl alcohol) (PVA) and poly(ethylene oxide) (PEO)

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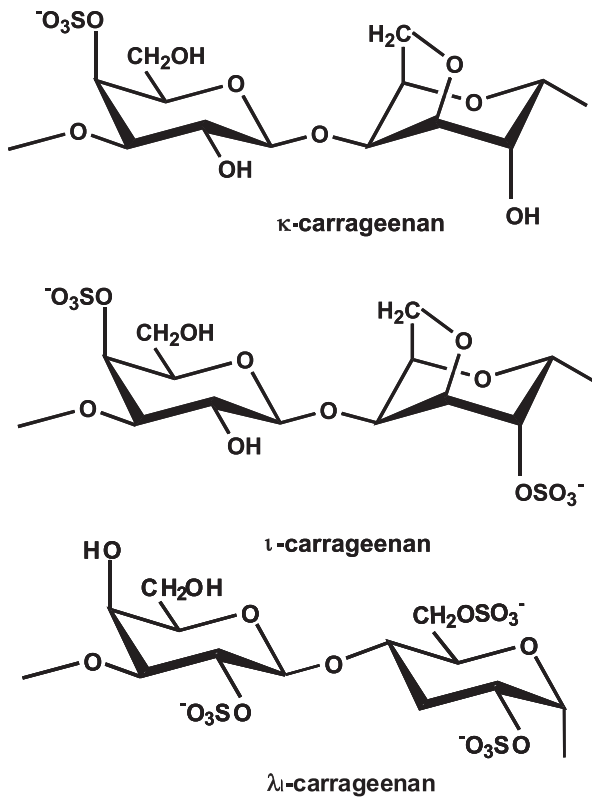


Fig. 1. Idealized structure of κ-, ι- and λ-carrageenan.

have been used successfully as a basic material for the manufacturing of hydrogel wound dressing. They show usually good biocompatibility. A combination with natural polymers such as agar

improves the physical–mechanical properties such as tensile strength, swelling and gel fraction. A method of preparing these hydrogels was first patented in 1989 (US Patent No. 4,871,490) [5]. The method consists of a combination of poly(vinyl pyrrolidone), poly(ethyleneglycol) and agar crosslinked and sterilized simultaneously by radiation. Parallel to the sterilization is the formation of a permanent three-dimensional network. There are already some commercialized hydrogel wound dressings under the trade names Vigilon, Ivalon, Aqua gel and Kik gel, Cli-gel, Burn caring, P-Chitosan, Hiezel, etc. which are using the same technique. Hydrogel made up of a blend of PVP and κ-carrageenan is now also a fully developed technology. The presence of carrageenan greatly improved the mechanical property (tensile strength) and swelling capacity of the hydrogel. In fact, both properties are much higher than the PVP-agar hydrogel [6]. Physico-mechanical properties of the PVP-carrageenan hydrogel indicated an  $F_{max} > 1000$  gf, Gel Fraction  $> 50\%$ , and Degree of Swelling  $< 40$ .

Clinical trials done to patients (a total of 61 patients) with grade 2–4 decubitus ulcers indicated that the decrease in size of the ulcers for those covered with hydrogel dressing was significantly higher than those of the control (Fig. 2). The mean decrease in the size of the wound for the control group was  $0.37\text{ cm}^2$  against that of the experimental group with  $0.84\text{ cm}^2$  ( $p = 0.012$ ). There was no statistically significant difference in both initial and post treatment infection scores. ( $p = 0.44$  and  $p = 0.42$  respectively). Thus, the study showed that PVP-carrageenan hydrogel prepared by gamma irradiation is superior to saline gauze in treating decubitus ulcers. In addition, the convenience of having to change the hydrogel dressing only every four days may ease the pain of the patient and turn out to be more economical than the daily change requirement of the traditional wet dressing (see Fig. 2).

The PVP-carrageenan hydrogel dressing has passed clinical trials as wound dressing for diabetic ulcers and burn dressings and has a patent under the Philippine Patent Office (No. 1-2000-02471) and is now ready for commercialization [7].

### PVP-carrageenan hydrogels as Bedsore dressing

#### Mean decrease in ulcer size after 12 days treatment

	Mean Initial Ulcer Size (cm <sup>2</sup> )	Mean Decrease in ulcer size (cm <sup>2</sup> )
Control group	21.75 ± 11.26	0.37
PVP-carrageenan hydrogel	21.36 ± 10.75	0.84

#### Infection score after 12 days treatment

	Mean Initial Infection Score	Mean Post Tx Infection Score
Control group	0.41	0.15
PVP-carrageenan hydrogel	0.43	0.18



Fig. 2. Clinical trials of PVP-carrageenan hydrogels in diabetic ulcers.

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