Synthesis and Characterization of Superabsorbent Hydrogels Based on Natural Polymers: Kappa Carrageenan

Charity Mampho, Sadanand Pandey, James Ramontja, Elvis Fosso-Kankeu, Frans Waanders

***Abstract*—** This study demonstrates the synthesis of κ-carrageenan-cl-poly (DMAA) hydrogel by using N_1N_1 Dimethyl acrylamide (DMMA) monomer, MBA as crosslinker and APS as initiator by involving free radical co-polymerization and crosslinking reaction technique at 70 °C for 4 h. The obtained κ-carrageenan-cl-poly (DMAA) hydrogel was washed and soaked in the acetone to remove the unreacted DMMA (homopolymer). The obtained hydrogel was dried at 60°C temperature to a constant weight. The infrared spectra (FTIR), X-ray diffraction analysis (XRD), Scanning electron microscopy (SEM), and the value of swelling degree of obtained κ-carrageenan-cl-poly (DMAA) hydrogel showed that κ-carrageenan was able to be crosslinked using DMAA and MBA in presence of initiator. APS concentration less than 0.05 g was not able to crosslink hydroxyls group of carrageenan. The optimised hydrogel swelling degree in water media was found to be 2740%. The κ-carrageenan-cl-poly (DMAA) hydrogel was found to be pH sensitive.

***Index Terms*—** κ-carrageenan; N_1N_1 Dimethyl Acrylamide; Crosslinker; Hydrogel, Swelling.

I. INTRODUCTION

Hydrogel or highly swelling polymers are hydrophilic, three-dimensional (3D) networks that can absorb water in amounts from 10% up to thousands of times their dry weight. These hydrogels are extensively used in various applications such as hygienic products, foods, cosmetics, agriculture, medical and pharmaceutical **[1-5].** Because of multiple uses of hydrogel, there is increase in the worldwide production of hydrogel. Nowadays, the worldwide production of hydrogel is more than one million tons in year. Hence, the synthesis and characterization of superabsorbent hydrogels is the main goal of several research groups in the world **[6, 7].**

The properties of the swelling medium (e.g., pH, ionic strength and the counter ion and its valence) affect the swelling characteristics **[3].** Hydrogels that respond sharply and reproducibly to the medium conditions are referred to as "responsive", "smart" or "intelligent". Among these, pH-sensitive hydrogels have been extensively investigated for their potential use in site-specific delivery of drugs to specific regions of the gastrointestinal tract and have been prepared for the delivery of low molecular weight protein drugs **[8, 9].**

Nowadays, preparation of hydrogels based on natural polymers especially polysaccharides, have been explored extensively. Compared to synthetic polymer, the polysaccharides-based hydrogels exhibited several advantages. They are more renewable, more biodegradable and cheaper because the raw materials are locally abundant. The biocompatibility of polysaccharides is characteristic of a material of great interest, mainly on biomedical applications. The carrageenan are a group of linear sulfated polysaccharides, present in the cell structure of rodophyceae algae. Besides this source, gigartinaceae produce Kappa (κ) and Lambda (λ) carrageenan, while solieriaceae produce Kappa and Iota (i) carrageenan. All carrageenan have high molecular mass and are formed of alternating units of D-galactose and 3,6-anhydro-Dgalactose (3,6-AG) joined by a-1,3 and b-1,4-glycosidic bonds **[10-13].** The main differences between the types of carrageenan are the position and number of ester sulfate groups (3,6-anhydroD-galactose-n-sulfate). The content of 3,6-anhydro-D-galactose (3,6-AG) determines the characteristics among the carrageenan types and higher levels of ester sulfate imply smaller gelling force and lower solidification temperature **[10,14, 15].** The structure of κ-carrageenan are shown in **(Figure 1).** The presence of hydroxyls and sulfate groups in carrageenan structure cause the carrageenan tend to be hydrophilic. For improving the stability in aqueous, the carrageenan structures must be chemically crosslinked to produce hydrogel structure.

In this work, we synthesize and characterize new superabsorbent composites based on Kappa (κ) carrageenan in the presence of monomer (N_1N_1 Dimethyl acrylamide) by using N,N'-methylenebisacrylamide and ammonium persulfate as cross linker and initiator respectively. The swelling properties of obtained hydrogel at different pH media were also studied.

Elvis Fosso-Kankeu is with the School of Chemical and Minerals Engineering of the North West University, Bult area-Potchefstroom-South Africa

Charity Mampho is with the School of Chemical and Minerals Engineering of the North West University, Bult area-Potchefstroom-South Africa.

Frans Waanders is with the School of Chemical and Minerals Engineering of the North West University, Bult area-Potchefstroom-South Africa.

Sadanand Pandey is with the Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa.

James Ramontja is with the Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa.

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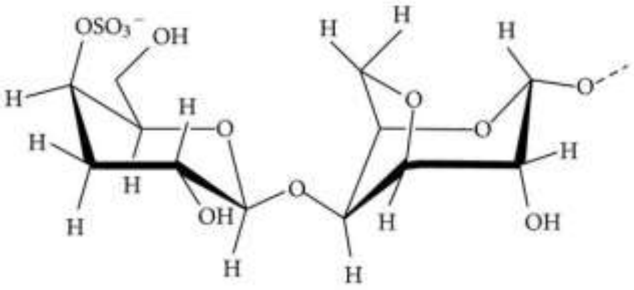

Fig. 1 Structure of κ-carrageenan.

II. MATERIALS AND METHOD

A. Materials

κ-carrageenan biopolymer was obtained from sigma (UK). The N_1N_1 Dimethyl acrylamide (DMAA, 99 %,) monomer was obtained from Aldrich (Netherlands) and were used without further purification. Ammonium persulfate (APS), 99% (Merck, Germany), the cross linker, N, N-methylenebisacrylamide (MBA), 99% (Aldrich, UK). All other reagents used were of analytical grade.

B. Synthesis of κ-carrageenan-cl-poly (DMAA) hydrogels

A polymer matrix composed of κ-carrageenan-cl-poly (AA) was prepared by using MBA as crosslinker and APS as initiator in hot air oven. The grafting of N_1N_1 Dimethyl acrylamide (DMAA) monomer onto Kappa (κ) carrageenan in the presence of MBA cross linker by free radical co-polymerization technique. In synthesis of κ-carrageenan-cl-poly(DMAA) hydrogels, 2 g of κ-carrageenan was homogenously dissolve in beaker containing deionized water and stirred for 2 h (speed of stirrer was 200 rpm). Then 6ml of N_1N_1 Dimethyl acrylamide (DMAA) were added in dissolve κ-carrageenan solution and stirrer for 20 minutes. Thereafter 0.4 g of MBA (dissolved in 2 mL of distilled water) were added into solution containing κ-carrageenan solution and dissolve completely. Finally, KPS initiator (0.6 g in 2 mL water) was transferred into solution containing κ-carrageenan solution. The reaction mixtures were kept at 70 °C for 4 h. The final volume was kept 180ml. After the reaction, the synthesized κ-carrageenan -cl-poly (DMAA) hydrogels were subjected to precipitations with acetone to completely remove the uncross-linked polymer from the copolymers.

The synthesized nanocomposites hydrogels were cut into small pieces of ~10 mm in length and were dried in an oven at 60 °C to constant weight.

C. Measurement of swelling

The swelling of hydrogel was determined gravimetrically. For this purpose the dried sample (0.05 g) was immersed totally in distilled water (10 ml) and allowed to reach equilibrium at room temperature. The equilibrium swelling (ES) of the hydrogel was determined according to the following Equation. (1):

$$\% \, S = \frac{Wf - Wi}{Wi} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where W_f is the final weight taken after the sample has swollen and W_i is the initial weight before swelling.

where W_f is the weight of swollen gels at predetermined time t, and Wi is the initial weight of samples. Samples were immersed in fresh buffer solution after weighting. Also, the test was carried out in triplicate and the calculated swelling ratios were reported in the mean values to maximize the accuracy.

D. Effect of Swelling with time

To study the rate of absorbency of the hydrogel, certain amount of sample (0.05 g) was immersed in 10 ml distilled water. At various time intervals, the swelling of the hydrogel was measured according to the earlier mentioned Equation. (1).

E Scanning electron microscopy (SEM)

The surface morphology of the κ-carrageenan and κ-carrageenan-cl-poly(DMAA) hydrogels samples was examined by a scanning electron microscopy (SEM), (TESCAN, VEGA SEM) under a 20 kV electron acceleration voltage by carbon coating of samples.

II. RESULTS AND DISCUSSION

A. Hydrogel synthesis and swelling studies

To study the behaviour of κ-carrageenan-cl-poly (DMAA) hydrogels in different pH, swelling study were also carried out in buffer solution of pH 4 and 8. It was found that by increasing the medium pH, swelling ability of κ-carrageenan-cl-poly(DMAA) hydrogels increases, i.e., in pH 4, i.e acidic medium , κ-carrageenan-cl-poly(DMAA) hydrogels equilibrium swelling (ES) capacity was found to be 1370%; however, equilibrium swelling (ES) capacity in pH 6.3 i.e (neutral medium) and pH 8 i.e (alkaline medium) was found to be 2400% and 2740 %, respectively. It was observed that with increase in time from 60 to 420 min, there is continuous increase in % swelling from 1510 to 2740%, thereafter it attain equilibrium **(Figure 2)**..

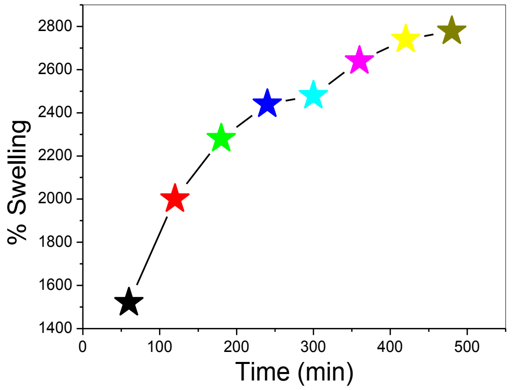

Fig. 2. Swelling behaviour of κ-carrageenan-cl-poly (DMAA) hydrogels with time in basic medium.

This behaviour can be explained as follows: synthesized κ-carrageenan-cl-poly (DMAA) hydrogels are prepared in pH of distilled water (pH 6.25 ± 0.25), and since the pKa of the carboxylic acid in the polysaccharide is almost 4.6, ionization of the carboxylic acid groups occurs (COO–) [16]. Electrostatic repulsion force caused by the hydrogen bonds break down and this will lead to more water penetrating into the network. Therefore, the synergistic effect of negative-charges and hydrogen bonds justifies the water uptake behavior in the intermediate pH [17]. At lower pH values, protonation of the –COOH groups results in formation of more hydrogen bonds between the –COOH groups in κ-carrageenan-cl-poly (DMAA) hydrogels hydroxyl groups. Therefore a more compact hydrogel structure with restricted movement and relaxation structure result in less swelling, reaching equilibrium swelling faster and less flexible network in acidic environment. On the other hand, in alkaline medium, ionization of -COOH groups occurs in which these functional groups produce an electrostatic repulsion among polymer chains that expands the network allowing more water to penetrate the κ-carrageenan-cl-poly(DMAA) hydrogels network [18,19].

B. Characterization of the synthesized hydrogel

One of the most important properties that must be considered is the hydrogel microstructure morphology. The surface morphology of the samples was investigated by scanning electron microscopy. **Figure 3** shows SEM micrographs of the κ-carrageenan at 500x (a), 1000x (b), 2000x (c), and κ-carrageenan-cl-poly(DMAA) hydrogel at 500x (d), 1000x (e), 2000x (f). The SEM of κ-carrageenan shows rough uneven surface **(Figure 3a-c).** The grafting of DMAA onto κ-carrageenan brings about considerable changes in morphology of κ-carrageenan. The κ-carrageenan-cl-poly (DMAA) hydrogel **(Figure 3d-f)** shows leaf like morphology and appears to have smooth homogeneous surface.

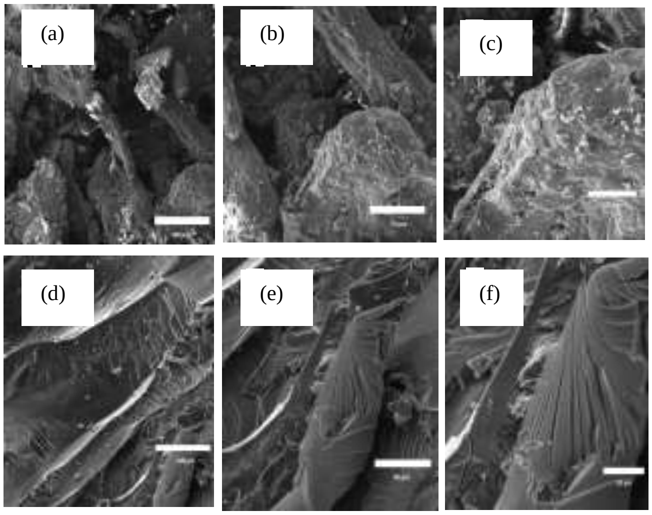

Fig. 3 SEM micrographs of the κ-carrageenan at 500x (a),1000x (b), 2000x (c), and κ-carrageenan-cl-poly(DMAA) hydrogel at 500x (d),1000x (e), 2000x (f).

III. CONCLUSION

K-carrageenan-cl-poly (DMAA) hydrogels containing κ-carrageenan and DMAA could be made by simultaneous graft copolymerization and crosslinking by conventional technique. The synthesised graft copolymers and gels have been characterized by SEM analysis and considerable changes were observed on the morphology of κ-carrageenan as a result of grafting. Dynamic swelling studies have been carried out for the swelling process have been evaluated. Swelling behavior of the hydrogel under different pH conditions was investigated. K-carrageenan-cl-poly (DMAA) hydrogels equilibrium swelling (ES) capacity was found to be 1370%; however, equilibrium swelling (ES) capacity in pH 6.3 i.e (neutral medium) and pH 8 i.e (alkaline medium) was found to be 2400% and 2740 %, respectively. Thus from the results, kappa carrageenan hydrogels were found to be pH sensitive. The obtained hydrogels were unstable at low pH in aqueous environments. Because of the above significant properties, κ-carrageenan-cl-poly (DMAA) hydrogels can be exploited for drug delivery and wastewater treatment in near future.

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REFERENCES

[1] Y. Osada and R. Khokhlov, "Polymer Gels and Networks." Marcel Dekker, Inc. New York, 2005.

[2] H. Li, J. Yang, X. Hu, J. Liang, Y. Fan and X. Zhang, "Superabsorbent polysaccharide hydrogels based on pullulan derivate as antibacterial release wound dressing, *J. Biomed. Mater. Res*., *A*., vol. 98, no. 31, 2011. https://doi.org/10.1002/jbm.a.33045

[3] S. Thakur, S. Pandey, A. Omatayo, "Development of a sodium alginate-based organic/inorganic superabsorbent composite hydrogel for adsorption of Methylene blue." *Carbohydrate Polymer.* vol. 153, pp 34-46, 2016. https://doi.org/10.1016/j.carbpol.2016.06.104

[4] W.E. Hennink and C.F. van Nostrum, "Novel crosslinking methods to design hydrogels." *Adv. Drug Deliv. Rev.*, vol. 54, no. 13, 2002. https://doi.org/10.1016/s0169-409x(01)00240-x

[5] Y. Chen, Y.F. Liu, H.M. Tan and J.X. Jiang, "Synthesis and characterization of a novel superabsorbent polymer of N,O-carboxymethyl chitosan graft copolymerized with vinyl monomers." *Carbohyd. Polym.*, vol. 75, no. 287, 2009..

[6] J.P. Zhang, Q. Wang and A.Q. Wang, "Synthesis and characterization of chitosan-g-poly(acrylic acid)/attapulgite superabsorbent composites." *Carbohyd. Polym.*, vol. 68, no. 367, 2007.

[7] Y. Dai, P. Li and A. Wang, "Intelligent drug delivery system of intelligent high polymer materials." *Prog. Chem.*, vol. 19, no. 362, 2007.

[8] H.Y. Zhou, Y.P. Zhang, W.F. Zhang and X.G. Chen, "Biocompatibility and characteristics of injectable chitosan-based thermosensitive hydrogel for drug delivery." *Carbohyd. Polym*., vol. 83, no. 1643, 2011.

[9] R.A. Pedroso, I.M. Demiate, "Evaluation of the influence of starch and carrageenan on the physicochemical and sensory characteristics of cooked turkey ham." *Food Sci. Technol.* vol. 28, pp. 24–31, 2008. https://doi.org/10.1590/S0101-20612008000100005

[10] T. Jayaramudu, G.M. Raghavendra, K. Varaprasad, R. Sadiku, K. Ramam, K.M. Raju, "Iota-carrageenan-based biodegradable Ag0

nanocomposite hydrogels for the inactivation of bacteria." *Carbohydr. Polym*. vol. 95, pp. 188–194, 2013.
https://doi.org/10.1016/j.carbpol.2013.02.075

[11] V.D. Prajapati, P.M. Maheriya, G.K. Jani, H.K. Solanki, "Carrageenan: a natural seaweed polysaccharide and its applications." *Carbohydr. Polym*. vol. 105, pp. 97–112, 2014.
https://doi.org/10.1016/j.carbpol.2014.01.067

[12] L. Li, R. Ni, Y. Shao, S. Mao, "Carrageenan and its applications in drug delivery." *Carbohydr. Polym*. vol. 103, pp. 1–11, 2014.
https://doi.org/10.1016/j.carbpol.2013.12.008

[13] V.L. Campo, D.F. Kawano, D.B. Silva Jr., I. Carvalho, "Carrageenans: biological properties, chemical modifications and structures analysis: a review." *Carbohydr. Polym.* vol. 77, pp.167–180, 2009.
https://doi.org/10.1016/j.carbpol.2009.01.020

[14] A.L. Daniel-da-Silva, R. Lóio, J.A. Lopes-da-silva, T. Trindade, B.J. Goodfellow, A.M. Gil, "Effects of magnetite nanoparticles on the thermorheological properties of carrageenan hydrogels." *J. Colloid Interface Sci*. vol. 324, pp. 205–211, 2008.
https://doi.org/10.1016/j.jcis.2008.04.051

[15] A. Pourjavadi, Sh. Barzegar, F. Zeidabadi, "Synthesis and properties of biodegradable hydrogels of k-carrageenan grafted acrylic-acid-co-2-acrylamido- 2-methylpropanesulfonic acid as candidates for drug delivery systems." *React. Funct. Polym.* vol. 67, pp. 644–654, 2007.
https://doi.org/10.1016/j.reactfunctpolym.2007.04.007

[16] M.F.A. Taleb, H.L.A. El-Mohdy, and H.A.A. El-Rehim, "Radiation preparation of PVA/CMC copolymers and their application in removal of dyes." *Journal of Hazardous Materials*. vol. 168, no. 1, pp. 68–75, 2009.
https://doi.org/10.1016/j.jhazmat.2009.02.001

[17] S. Gorgieva, and V. Kokol, "Synthesis and application of new temperatureresponsive hydrogels based on carboxymethyl and hydroxyethylcellulose derivatives for the functional finishing of cotton knitwear." *Carbohydrate Polymers*. vol. 85, pp. 664-673, 2011.
https://doi.org/10.1016/j.carbpol.2011.03.037

[18] J. Chen, M. Liu and Sh. Chen, "Synthesis and characterization of thermoand pH-sensitive kappa-carrageenan-g-poly(methacrylic acid)/poly(NN diethylacrylamide) semi-IPN hydrogel." *Materials Chemistry and Physics*. vol. 115, pp. 339–346, 2009.
https://doi.org/10.1016/j.matchemphys.2008.12.026

[19] S. Francis, M. Kumar and L. Varshney, "Radiation synthesis of superabsorbent poly(acrylic acid)–carrageenan hydrogels." *Radiation Physics and Chemistry*. vol. 69, pp. 481–486, 2004.
https://doi.org/10.1016/j.radphyschem.2003.09.004

The corresponding author is currently an Associate Professor in the School of Chemical and Minerals Engineering at the North-West University (Potchefstroom). He is an NRF rated researcher who has published journal articles, book chapters and book.

Prof Elvis Fosso-Kankeu has been the recipient of several merit awards.