Preparation of radiation crosslinked superabsorbent hydrogel using carboxymethylcellulose

by

S.M.N.D Kumari

Thesis submitted to the University of Sri Jayewardenepura for the award of the Degree of Master of Science in Polymer Science and Technology on 13th of August 2008

DEDICATION

I dedicate this thesis to my parents, husband, brother, teachers and all my family members who helped me in my academic achievements.

"The work described in this thesis was carried out by me under the supervision of Mr.J.T.S Lal Motha and a report on this has not been submitted in whole or in part to any University or any other institution for another Degree or Diploma".

2008 08 12 Date

Signature of candidate

"I certify that the above statement made by the candidate is true and that this thesis is suitable for submission to the university for the purpose of evaluation".

Date Date

Signature of supervisor

12/08/2008

Dr Laleen Karunanayake BSc (SIP), PhD (North London) Senior Lecturer Department of Chemistry finite sets of any language appropriet

LIST OF ABBREVIATIONS

AAc :Acrylic acid

Ws: Swollen weight

CMC: Carboxymethylcellulose

Temp: Temperature

Carboxymethylchitin

Wd: Weight of the insoluble gel

CMCTS: Carboxymethylchitosan

CMS: Carboxymethylstrach

cP :centi poise

DS: Degree of Substitution

FT-IR: Furere Transmission Infra Red

γ : gamma

Gf%: Gel fraction

Wi: Initial weight of dried gel

LDPE: Low density polyethylene

MAA: Methacrylic acid

PEO: Polyethylene oxide

PEG: Polyethylene glycol

PVA: Polyvinyl alcohol

PVP: Polyvinylpyrrolidone

KMnO₄: Potassium permanganate

SEM: Scanning Electron Microscopy

SR: Swelling Ratio

LIST OF FIGURES

	Page
Fig.1.1. Structures of synthetic polymers	3
Fig.1.2. CMC molecular structure	4
Fig.1.3. Types of carrageenans	7
Fig.1.4. Agar structural unit	8
Fig.1.5. Alginate structural unit	8
Fig.1.6. Structural units.(a)Chitin, (b) Chitosan.	9
Fig.2.1.Gamma Irradiator	13
Fig.2.2. (a) wound dressing, and (b) gel protector.	17
Fig.2.3. Synthesis of amidoxime adsorbent with radiation induced	18
grafting.	
Fig.2.4. (a) Sago foams, and (b) Sago film.	19
Fig.2.5. Radiation crosslinking of CMC	21
Fig.2.6. Non bedsore prevention mat of CMC.	22
Fig.2.7. CMC gel coolant.	23
Fig.2.8. Face mask hydrogel.	25
Fig.3.1.CMC powder.(a) 0.9 DS CMC (b) 0.76 DS CMC.	28
Fig.3.2.CMC sample preparation. (a) CMC paste, and (b) CMC paste	28
in PE bags.	
Fig.3.3. Swollen CMC hydrogels in water and 0.9% NaCl	30

Fig.4.1. Effect of concentration on crosslinking of CMC	35	
Fig.4.2. Effect of degree of substitution on crosslinking of CMC	35	
Fig.4.3. Effect of the sealing method for the Gf%	36	
Fig.4.4. Viscosity of irradiated CMC in different concentrations and DS	37	
Fig.4.5. Swelling of irradiated 5%,10% CMC in distilled water and	38	
0.9% NaCl solution		
Fig.4.6. Effect of Degree of Substitution SR of CMC	38	
Fig.4.7. Swelling of different DS CMC in distilled water and	39	
0.9% NaCl solution		
Fig.4.8. Effect of concentration of inorganic salts for SR of CMC	39	
Fig.4.9. The relationship between pH and SR of different DS of CMC	40	
Fig.4.10. Effect of swelling temperature on SR of CMC	41	
Fig.4.11. Relationship between swelling time and SR of CMC	41	
Fig.4.12. Non irradiated, 0.76 DS CMC powder	42	
Fig.4.13 Irradiated 20%, 0.76 DS CMC at 50 kGy	42	
Fig.4.14. Non irradiated 0.9 DS CMC powder	43	
Fig.4.15. Non irradiated 0.76 DS CMC powder	43	
Fig.4.16. Transverse section of irradiated 0.9 DS CMC at 60kGy	43	
Fig.4.17. Transverse section of irradiated 0.76 DS CMC at 60kGy	44	
Fig.4.18. Surface of irradiated 0.9DS CMC at 60kGy	44	
Fig.4.19. Surface of irradiated 0.76DS CMC at 60kGy	44	

LIST OF TABLES

	Page
Table.4.1. Formulations for the prepared hydrogels	33
Table.4.2. Average swelling values, Gf% with water and 0.9% NaCl	33
of 5% CMC	
Table.4.3. Average swelling values, Gf% with water and 0.9% NaCl	33
of 10% CMC	
Table.4.4. Average swelling values, Gf% with water and 0.9% NaCl	34
of 20%, 0.76 DS CMC	
Table.4.5. Average swelling values, Gf% with water and 0.9% NaCl	34
of 20%, 0.9 DS CMC	
Table.4.6. Gf% of 20%, 0.76 DS CMC in different sealing methods	36
Table.4.7. Average viscosity of 5%,10%, 0.76 DS CMC	36
Table.4.8. Average viscosity of 20%, 0.76 DS and 0.9 DS CMC	37
Table.4.9. Viscosity of different states of CMC irradiated at 30kGy	37
Table.4.10. Average swelling values with various concentrations	39
of NaCl,CaCl ₂	
Table.4.11. Average SR of different DS CMC with different pHs	40
Table.4.12. Average swelling values with different temperatures	40
Table.4.13. Changing of SR with the time	41

CONTENTS

				Page
	List of abbrev	viations		iii
	List of figures	.		iv
	List of tables			vi
	Acknowledge	ments		xii
	Abstract			xiv
		Chapter 1	Introduction	
1.1	Superabsorbe	nt Hydrogel		1
1.2	Types of hydr	rogels		1
	1.2.1	Homoplymer hydro	ogels	1
	1.2.2	Copolymer hydrog	els	2
	1.2.3	Multipolymer hydr	rogels	2
	1.2.4	Hybrid hydrogels		2
1.3	Hydrogel for	ming absorbent poly	rmers	3
	1.3.1	Synthetic polymers	3	3
	1.3.2	Natural polymers		3
		1.3.2.1 Carboxym	ethylcellulose	3
		1.3.2.1.1	Molecular structure	4
		1.3.2.1.2	Preparation and properties	5
		1.3.2.1.3	Functionality	5
		1.3.2.1.4	Applications of CMC	6

		1.3.2.2 Carrageenen	7
		1.3.2.3 Agar	7
		1.3.2.4 Alginate	8
		1.3.2.5 Chitin/ Chitosan	8
1.4	Properties of	hydrogels	9
	(Chapter 2 Processing methods of hydrogel	
2.1	Chemical proc	eessing	10
2.2	Radiation prod	cessing	10
	2.2.1	Ionozing radiation	11
	2.2.2	Types of Ionizing radiation	11
	2.2.3	Source of ionizing radiation	12
		2.2.3.1 Radioisotopes	12
		2.2.3.1.1 Cobalt source	14
		2.2.3.1.2 Monitoring dose	14
		2.2.3.2 Electron Accelerator	14
		2.2.3.3 X- ray	15
	2.2.4	Radiation Unit	15
		2.2.4.1 Radio activity	15
		2.2.4.2 Radiation dose	16
		2.2.4.3 Dose rate	16

2.3	Radiat	ion pro	cessing applications	16
		2.3.1	Formation of hydrogels	16
		2.3.2	Curing monomers and oligomers	17
		2.3.3	Coloration of gem stones	17
		2.3.4	Radiation grafting	17
		2.3.5	Crosslinking of polymers	18
		2.3.6	Degradation of polymers	19
		2.3.7	Formation of Bio degradable packing materials	19
		2.3.8	Sterilization of medical products	19
		2.3.9	Agricultural applications	20
		2.7.10	Food irradiation	20
	2.4	Applic	eations of radiation crosslinked CMC hydrogels	20
		2.4.1	As super absorbent materials	21
		2.4.2	As bedsore prevention mats	22
		2.4.3	As fertilizer	22
		2.4.4	As wound covers	23
		2.4.5	As gel coolant	23
		2.4.6	As metal absorbent	23
		2.4.7	As physical barriers for preventing surgical adhesions	24
		218	As face mask	24

Chapter 3 Experimental procedure

3.1	Instruments	27
3.2	Materials and chemicals	27
3.3	Sample preparation	28
3.4	Irradiation	29
3.5	Gel fraction	29
3.6	Swelling studies of hydrogel	29
3.7	Viscosity of CMC	30
3.8	Scanning Electron Microscopy (SEM)	31
3.9	FT-IR analysis	32
	Chapter 4 Results, discussion and conclusion	
4.1	Results	33
	4.1.1 Swelling studies	33
	4.1.2 FTIR analysis	42
	4.1.3 Morphology of gel structure	43
4.2	Discussion	45
	4.2.1 Crosslinking of CMC	45
	4.2.2 Degaradation of CMC	46

	4.2.3	Swelling of CMC hydrogel	47
		4.2.3.1 Swelling in distilled water	47
		4.2.3.2 Effect of salt solution on swelling	48
		4.2.3.3 Swelling variation with pH	49
		4.2.3.4 Effect of tamperature for swelling	50
		4.2.3.5 Swelling changing with the time	50
	4.2.4	FTIR analysis	51
	4.2.5	SEM morphology	52
4.3	Conclusion		53
4.4	Further Studie	rs ·	53
	References		54
	Appendices		59
	1. Swellin	ng values	59
	2. Viscosi	ty changes of irradiated CMC	63
	3. Radiati	on units	63
	4. FTIR g	raphs	64

ACKNOWLEDGEMENTS

First I would like to express my sincere thank to Dr.Laleen Karunanayake as my Master's course coordinator of the Department of Chemistry, University of Sri Jayewardenepura, Sri Lanka for the encouragement, guidance and help given to me throughout my research project.

I would like to offer my heartiest thanks to Mr.J.T.S Lal Motha, Sectional Head of Material Technology Section (MTS) in Industrial Technology Institute (ITI) as my project supervisor for the advice, guidance and facility provided during my research project.

I wish to express my sincere thanks to all of the staff members who are working at MTS in ITI and specially to Research Officer Ms. D.A De Silva. Also I wish to express my special thanks to Research Officer Mr. S. Malavipathirana who is working at Chemical and Microbiology Laboratory (CML), ITI for giving me the instructions and guidance throughout my course work.

Also I give my sincere thanks to staff members of Atomic Energy Authority (AEA),Orugodawatta, and specially to Mrs.Samantha Kulathunge, Head of Radiation Processing Section, Scientific Officer Mr.Ruwan De Silva and Mr. Malinda for their invaluable service, advice, generous support and training giving me for the project.

Also I give my thank to all the staff members working in Food Technology Section at ITI for giving their facility to seal the samples and I would like to give my thank for library staff members, ITI for giving me computer and reading facilities throughout my project.

Finally special thank goes to my parents, husband, colleagues and family members for their generous help towards my academic achievement at all times.

ABSTRACT

Radiation crosslinking of Carboxymethylcellulose (CMC) with a Degree of Substitution (DS) of 0.76 and 0.9 was the subject of the investigation. This radiation crosslinked CMC can be used as a substitute for conventional hydrogels. CMC was irradiated in solid state and aqueous solutions at various irradiation doses. DS and the concentration of the aqueous solution had a remarkable effect on the crosslinking of CMC. Irradiation of CMC in solid state and low concentrated aqueous solution has low crosslinking whereas 20% CMC gave the highest gel fraction. CMC with a DS of 0.9 caused for higher crosslinking than that with DS of 0.76 with the same concentration.

It was apparent that high DS and high concentration in an aqueous solution were favorable for high crosslinking of CMC. It is assumed that high radiation crosslinking of CMC was induced by the increase mobility of its molecules in water and by the formation of CMC radicals from the abstraction of hydrogen atoms from macromolecules in the intermediate products of water radiolysis.

The effect of various parameters such as concentration of different inorganic salts, pH, swelling temperature, swelling time on the swelling ratio in water were investigated in detail. 0.9 CMC hydrogel swelled by 120g of water per gram of dry gel at 60kGy applied dose and 0.76 by 110g of water per gram of dry gel. Swelling tests of CMC hydrogels in salt concentrations and media of various pHs showed that swelling values decreased with the increase of salt concentration and was high at the neutral pH media. Radiation crosslinked Na-CMC showed good water absorption below 50°C,

whereas it became solution when heated more than 60°C. Equilibrium swelling time of the Na-CMC was also investigated by a kinetic study and the equilibrium swelling was reached after 16 hours.

The effect of the sealing condition on crosslinking of CMC was investigated. Vaccum sealed CMC samples showed higher swelling values and gel fraction than that of the samples sealed by polythene sealer. Irradiation of CMC even in 5%,10% aqueous solution and solid state resulted in degradation, hence viscosity decreases. More concentrated solution of 20% CMC was taken high viscosity due to the crosslinking by radiation.

FTIR spectra revealed, radiation crosslinking reaction of CMC occurred in side chains of CMC molecules due to the presence of –OH, -CH₂ and R-O- CH₂-COO whereas radical formed in –CH-O-CH- of main chain of CMC molecule lead easily to the chain scission. Scanning electron micrographs show highly porous structure of the gel. Therefore large amount of water will absorb to them and retain even under pressure.