
Microwave Copolymerized Carboxymethyl Cellulose-Chitosan Hydrogel

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Abstract – Copolymerization is a method used to connect different chains of polymers to form a hybrid macromolecule with modified properties of both polymers. Copolymerization can be done with different methods, one of which is microwave irradiation. Some naturally-occurring polymers are known to have excellent biocompatibility, biodegradability, and absorption. They are modified to become hydrogels or superabsorbent polymers that retain a huge amount of water. Microwave radiation initiates copolymerization. This study copolymerized carboxymethyl cellulose with chitosan using microwave radiation for 3, 6, and 9 minutes with carboxymethyl cellulose microwaved for 3 minutes as control. The findings of this study showed that the CMC-Chitosan hydrogel yielded lower gel content compared to the control group which is the CMC hydrogel. The polymer irradiated for 9 minutes is the most efficient in terms of absorbency. All in all, the three experimental set-ups had exhibited ideal absorption values, with a slower de-swelling ratio.

Introduction. – Hydrogels or superabsorbent polymers are materials that exist in gel state in the presence of water and absorb large amounts of liquid. They are used in the agricultural field to reduce irrigation water consumption and to increase the water retention of soil [1–3]. Hydrogels can also be used for contact lenses and wound dressings [4].

Cellulose forms the cell wall of plants and is an abundant superabsorbent material that is biodegradable and renewable from which carboxymethyl cellulose (CMC) can be synthesized. The synthesis of this derivative is necessary to overcome the poor reactivity of cellulose that makes it difficult to transform into other materials [5, 3]. According to a study [6], the presence of CMC in a hydrogel provides the hydrogel itself with electrostatic charges anchored to the network, which doubles its swelling capacity.

Copolymerization is a common method for the modification of surfaces of polymers and important to improve the physical or chemical properties of polymers [7]. Chitin is commonly synthesized from crustacean shells from which chitosan can be derived. Chitosan a highly-hydrophilic polymer is non-toxic, biocompatible, biodegradable that makes it a good choice for hydrogel preparation. Ultraviolet (UV) radiation can be used to crosslink or link the polymer chains of cellulose-based polymers to improve the properties of the molecule, however UV crosslinker ma-

chines are difficult to acquire. Microwave, on the other hand, is present in almost every household and establishes fast, cost effective, and environmentally friendly way of copolymerization [8].

Carboxymethyl cellulose can be copolymerized with chitosan via microwave radiation to produce a hydrogel efficient in retaining water for agricultural purposes. The efficiency of the synthesized polymer will be based on its gel content, absorbency, and de-swelling ratio or rate of water release [9].

Methods. – This study aimed to synthesize a superabsorbent polymer from carboxymethyl cellulose crosslinked with chitosan via microwave radiation. The gel content, water absorbency, and de-swelling ratio of the polymer were tested. The CMC microwaved for 3 minutes served as the control whereas the different durations of microwave irradiation of CMC and Chitosan (3, 6, and 9 minutes) served as the independent variables.

Materials. Commercially available Carboxymethyl Cellulose of edible grade was obtained. Chitosan was also bought. Since chitosan is water insoluble, 2 lactic acid aqueous solution was added.

Microwave Copolymerization of Chitosan. This copolymerization method was taken from the Microwave Initiated Synthesis and Application of Polyacrylic Acid

Grafted Carboxymethyl Cellulose of Mishra *et al.*[10]. Fives grams of CMC was dissolved in 100 ml distilled water. Fifteen grams of Chitosan dissolved in a 100 mL solution before it was added to the CMC solution. Constituents were mixed in the reaction vessel (500 mL beaker). The reaction vessel was subsequently placed on the turntable of a microwave oven. Microwave irradiation using American Home AMW-6510W with operation frequency of 2450 MHz at a power of 700 W was performed for 3, 6, and 9 minutes. Periodically, the microwave irradiation was paused (as the reaction mixture started to boil, i.e. at 65 C) and was cooled by placing the reaction vessel in cold water. This was to avoid competing homopolymer formation reaction or the reaction between CMC-CMC molecules and chitosan-chitosan to the minimum and also to prevent any thermal damage to the backbone polymer chain. The reaction vessel and its contents were cooled and kept undisturbed for 12 h to complete the polymerization.

Evaluation of Superabsorbent Polymer. To determine the gel content of the hydrogel, the polymers were cut and any non-copolymerized Chitosan or CMC formed by competing homopolymer formation reaction were removed from the copolymer synthesized by washing it with a methanolwater mixture (36 mL:4 mL). The hydrogel was dried at 100C for 6 hours. The remaining part or the insoluble and crosslinked parts were dried and weighed [11]. The equation to determine the gel content is shown in Equation 1

$$Gelcontent = (W_o/W_1) * 100 \quad (1)$$

where W1 is the weight of the insoluble part of the sample (after the extraction) and W0 is the weight of dried hydrogel before extraction.

The absorbency of the hydrogel or the volume of water the polymer can absorb was determined as follows: 1 g of hydrogel was immersed in 200 mL distilled water at room temperature (30 2C) and the weight was measured every hour for five hours. The tea bag was allowed to drain for 10 min or until the excess water stopped dripping. The equation for the swelling capacity or absorbency is shown in Equation 2

$$Absorbency = (W_2 - W_1/W_1) \quad (2)$$

where W1 and W2 represent the weight of the dry polymer and the swollen gel, respectively. The rate of absorption was obtained by determining the absorbance at consecutive time intervals.

The hydrogel was swollen until it reached its equilibrium absorption capacity or steady uptake of water which will be taken in a beaker placed in a tray with holes and kept at room temperature (30 2C), which resulted to the spontaneous escape of the absorbed water or the de-swelling of the polymer. The weight of the polymer was taken every five hours for 30 hours. The equation for the de-swelling

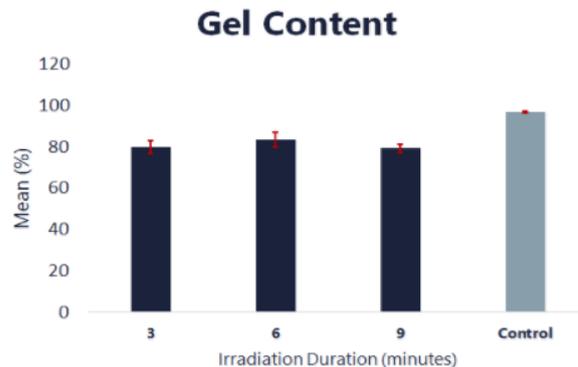


Fig. 1: Gel Content

ratio is shown in Equation 3

$$Deswelling = W_t/W_{t0} \quad (3)$$

where Wt and Wto are the weight of the sample at deswelling time (t) and initial weight of the fully swollen hydrogel, respectively.

Chemicals used were put in closed containers before disposal. Used glasswares and equipments were washed with dishwashing liquid and rinsed thoroughly. The polymers were placed in a sealed container and disposed and all wastes were segregated.

An ANOVA statistical analysis using PAST (Paleontological Statistics Software) with a level of confidence of 0.05 was performed to compare the means of the gel-content, absorbency, and de-swelling ratio of the polymers crosslinked at varying durations.

Results. – The gel content of CMC-Chitosan hydrogels microwaved for different periods were determined with CMC microwaved for three minutes as control. The gel content mean values in Fig. 1 of the CMC-Chitosan hydrogels were adjacent to each other. Using Tukeys pairwise comparison, it showed that there is no significant difference between the CMC-Chitosan hydrogels. However, in One-Way ANOVA, the calculated p value of the gel content ($p=2.28 \times 10^{-8}$) is less than 0.05, indicating that there is a significant difference between the CMC-Chitosan hydrogel groups and the CMC hydrogel group.

The absorbance values of CMC-Chitosan hydrogels microwaved for different periods were determined every hour with the CMC microwaved for three minutes as control. This was done hourly for five hours to depict a trend of the absorbency. Fig. 2 shows that as the time of irradiation increases, the absorbency also increases. The highest absorbency is the hydrogel irradiated for nine minutes, and the least absorbency is the control. This shows that the combination of CMC and Chitosan is more effective than CMC alone.

Using One-way ANOVA, the calculated p value ($p=2.08 \times 10^{-8}$) shows that there is a significant difference between all the variables including the control.

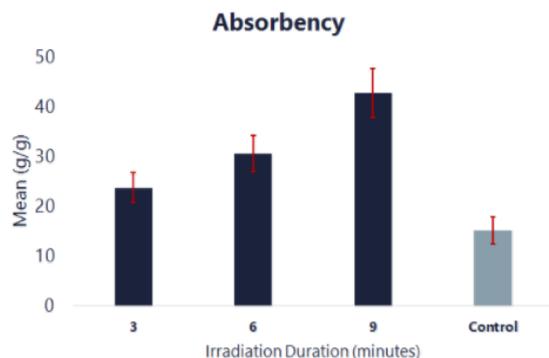


Fig. 2: Absorbency

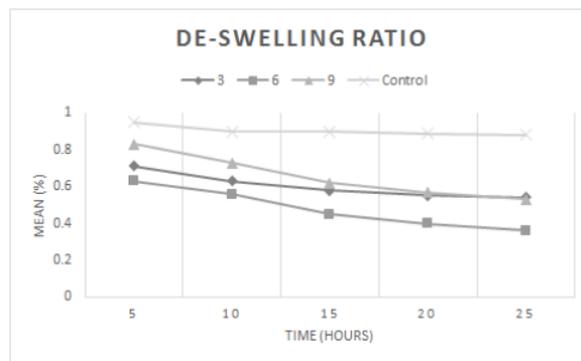


Fig. 3: De-Swelling Ratio

Fig. 3 is the trend of the de-swelling ratio of the hydrogels with different irradiation durations. The control and the hydrogel irradiated for three minutes are slow to release adsorbed water and the hydrogels with high absorbances, those irradiated for 9 minutes and 6 minutes, have fast de-swelling rates. The two slowest de-swelling rates have almost parallel trends and so do the two fastest de-swelling rates.

Discussion. – Copolymerization is the process of modifying the properties of hydrogel. In this study, microwave irradiation was used to copolymerize CMC with chitosan. When small polar molecules like water are microwaved, the whole molecule rotates and this rotation produces heat. There is no breakage of bonds because the whole molecule is rotating. On the other hand, if macromolecules like polysaccharides are copolymerized using microwave radiation, the polar bonds (O-H bonds) along with the other bonds (e.g. C-C bond) show rotation. The partial rotation of the molecules lead to breakage of the polar bonds. This process leads to free radical sites formation where copolymerization takes place. Connecting another polymer on CMC results to a copolymer that is mostly 2-O- and 6-O- linked. This is explained by the neighboring side chains on the cellulose backbone. Because of lack in free space, the mobility of the segments are greatly reduced and molecules are inhibited to penetrate this layer. This was consistent with the study of El-Mohdy (2014) in which the Fourier Transform Infrared Spectroscopy proved the copolymerization of 2-Acrylamidoglycolic Acid with CMC on the CMCs hydroxyl group -CH₂COO in the C2 position. Chitosan has a primary amino group (C2) and a primary (C3) and a secondary free hydroxyl groups (C6) that gives it a considerable opportunity for chemical modification. Depending on the reaction conditions (temperature and pH) the reaction can take place on the amino group, on the hydroxyl groups or on both. Depicts the chemical modification of chitosan in a neutral media wherein the only modification happens at the primary amino group. In the study of Jayakumar et al., thioglycolic acid crosslinked with chi-

tosan via amide bond formation mediated by 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide. The result is consistent with the illustration above that showed that copolymerization chitosan in an acidic media results to a major substitution on the amino group. The pH value of the CMC-Chitosan copolymer was 7.12 which means that the crosslink happened at CMCs hydroxyl group -CH₂COO at C2 and at chitosans primary amino group (C2). To determine the percentage of the copolymerized hydrogel, gel content was evaluated. Gel content is the measure of the degree of copolymerization between polymers, which means that the higher the gel content, the more flexible and durable the hydrogel. In the study by Sutradhar et al. (2015), the gel content of hydrogel prepared from CMC-acrylamide increases as the irradiation dose increases, however, its absorbency decreased with the increasing dose. This is due to the cross-linked density in the polymer. The more dense the copolymerization the lesser vacant space there is in the network for free solvent to enter. In contrast to UV irradiation and other thermal curing techniques, microwave induced copolymerization is more effective in terms of lesser reaction time and does not need an additional radical source to induce copolymerization. Compared to UV irradiation it is also more effective in an ambient oxygen atmosphere, where the inhibitory effect of oxygen could affect the recombination of free radicals. In this study, the gel content of the control is significantly higher than the hydrogels with CMC-Chitosan. This means the copolymerization worked better with CMC alone because the resulting product managed to have significantly higher absorbance values compared to that treated with Chitosan. This may be because of the numerous polar molecules along the CMC chain compared to the Chitosan chain. These polar molecules will be candidates for hydrogen bonding when microwave irradiation takes place. The absorbency of the hydrogel determines its swelling property. Absorbency denotes the amount of fluid which a given amount of hydrogel can absorb. The absorption of the combination of CMC and Chitosan is significantly higher than the absorption of hydrogel-forming microwave were evaluated. It shows that the longer the hy-

drogel is exposed to the radiation, the greater its swelling capacity, but for every material, there is a limitation. A Hydrogel with high absorption are efficient for agricultural use since it retains the moisture in the soil for a longer period of time, preventing the plants from drying. High absorptivity is also valued for its use in diapers because it will allow more urine to be stored. If the synthesized hydrogel will be used for the aforementioned examples, it is optimal to use a CMC-Chitosan hydrogel irradiated for nine minutes. De-swelling ratio is the percentage of the remaining hydrogel after releasing the absorbed water for a time interval. In this study, the control had the slowest de-swelling rate. The de-swelling behavior of the swollen hydrogels might be affected by various environmental factors such as temperature, humidity and also by other factors such as size of the polymer, chemical composition, crosslinking density of the polymer, thickness of the hydrogel, mechanical strength of the hydrogel, gel content 15. In this study, the de-swelling of the control has the slowest rate. This could be because the control has the highest gel content meaning the crosslink inside the polymer is dense. These small spaces make the diffusion of water molecules out of the hydrogel surface slower leading to a high de-swelling percentage. Hydrogels are used in personal hygiene products, one of which are diapers. Controlling content leakage is crucial to diapers because it reduces the risk of fecal contamination and thus the potential for the spread of illness. The de-swelling ratio should be adjusted to the hydrogels minimum for it to be efficient for reducing leakage in diapers. Therefore, hydrogels irradiated for six and nine minutes are not optimum for diapers because of their high de-swelling ratios. De-swelling ratio is also important for the use of hydrogels in drug delivery systems since it determines the rate of release of the drug from the hydrogel that encapsulates it. Copolymerizing chitosan unto CMC can increase the efficiency of the hydrogel for drug-release due to the Chitosans hydro-solubility. It is a useful polymer for mucosal drug delivery because it adheres to mucosal surfaces. It also has other properties such as pH sensitivity, biocompatibility and low toxicity 16. Moreover, chitosan is metabolized by certain human enzymes, especially lysozyme, and is biodegradable 17. If the drug placed within the hydrogel needs to be quickly diffused, it is optimum to the CMC-Chitosan hydrogels irradiated for six and nine minutes since they have the highest de-swelling ratios. If the drug needs to be released in slow amounts, the CMC hydrogel or the CMC-Chitosan hydrogel irradiated for three minutes may be chosen. These are all based on the irradiation duration alone but further variations such as changing the CMC-Chitosan ratio can be done to the hydrogels to modify their de-swelling properties to fit the application. CMC-Chitosan hydrogels copolymerized through microwave irradiation have lower gel content than the CMC hydrogel. Longer irradiation time results to a polymer with higher absorbency and faster de-swelling rate. In terms of absorbency, the hydrogel microwaved for nine minutes is the

most efficient.

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REFERENCES

- [1] BARBUCCI, R. and MAGNANI, A. and CONSUMI, M., Swelling Behavior of Carboxymethylcellulose Hydrogels in Relation to Cross-Linking, pH, and Charge Density. *Macromolecules*, Vol. **33** 2000, p. 7475-7480.
- [2] NNADI, F. and BRAVE C., Environmentally friendly superabsorbent polymers for water conservation in agricultural lands. *Journal of Soil Science and Environmental Management*, Vol. **2** 2011, p. 206-211.
- [3] PITALOKA AB and SAPUTRA AH and NASIKIN M, Water Hyacinth for Superabsorbent Polymer Material *Applied Sciences Journal*, Vol. **22** 2013, p. 747-754.
- [4] CAL E and KHUTORYANSKIY VV, Biomedical applications of hydrogels: A review of patents and commercial products *European Polymer Journal*, Vol. **65** 2015, p. 252-267.
- [5] MUSFIROH I and HASANAH AN, The Optimization of Sodium Carboxymethyl Cellulose (NA-CMC) Synthesized from Water Hyacinth (*Eichhornia crassipes* (Mart.) Solm) *Cellulose eearch Journal of Pharmaceutical, Biological and Chemical Sciences*, Vol. **4** 2013, p. 1092.
- [6] SANNINO A and DEMITRI C and MADAGHIELE M, Biodegradable Cellulose-based Hydrogels: Design and Applications *Materials*, Vol. **2** 2009, p. 353-373.
- [7] KHAN F and AHMAD SR, Graft copolymerization and characterization of 2-hydroxyethyl methacrylate onto jute fiber by photoirradiation *Journal of Applied Polymer Science*, Vol. **101** 2006, p. 2898-2910.
- [8] GUPTA, D. and BELDAR A. and TANK, R, Suspension copolymerization of styrene and divinylbenzene: formation of beads *Journal of Applied Polymer Science*, Vol. **101** 2006, p. 3559-3563.
- [9] AHMED EM, Hydrogel: Preparation, characterization, and applications: A review *Journal of Advanced Research*, Vol. **6** 2015, p. 105-121.
- [10] MISHRA V and KUMAR R., Graft copolymerization of Carboxymethylcellulose: An overview *TCR*, Vol. **4** 2012
- [11] GONCALVES A, Synthesis and characterization of high performance superabsorbent hydrogels using bis[2-(methacryloyloxy)ethyl] phosphate as crosslinker *Express Polymer Letters*, Vol. **10** 2015, p. 248-258.
- [12] SUTRADHAR SC, KHAN MR, RAHMAN MM, DAFADAR NC, The Synthesis of Superabsorbent Polymers from a Carboxymethylcellulose/acrylic Acid Blend Using Gamma Radiation and its Application in Agriculture *Journal of Physical Science*, Vol. **26** 2015, p. 23-39.
- [13] ARANAZ I and HARRIS R and HERAS A, Chitosan Amphiphilic Derivatives. Chemistry and Applications *Current Organic Chemistry*, Vol. **14** 2010, p. 308-330.
- [14] JAYAKUMAR R and PRABAHARANA M and REIS R and MANO J, Graft copolymerized chitosan present status and applications *Elsevier*, Vol. **62** 2005, p. 142-158.

- [15] DOGO, Y and OKAY, O., Swelling/Deswelling Kinetics of Poly(N- isopropylacrylamide) Hydrogels Formed in PEG Solutions *Wiley InterScience* 2005.
- [16] HIRANO, S and NAGAO, N, Effects of chitosan, pectic acid, lysozyme, and chitinase on the growth of several phytopathogens *Agricultural and Biological Chemistry*, Vol. **53** 1989, p. 3065-3066.
- [17] MUZZARELLI, R. A. and ROCHETTI, R. and STANIC, V. and WECKX, M., Methods for the determination of the degree of acetylation of chitin and chitosan *Chitin Handbook* 1997, p. 101-119.