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Contributed Paper

Crosslinking Effects on Alginate/Carboxymethyl Cellulose Packaging Film Properties

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ABSTRACT

We measured the effect of crosslinking with Ba^{2+}, Ca^{2+} and Zn^{2+} ions to sodium alginate (SA) mixed with carboxymethyl cellulose (CMC) film, prepared by solution casting. Although heavy metal ion crosslinked films had higher tensile strengths than neat SA/CMC films, the elongation at break, light transmission and swelling had decreased. In crosslinked films, film thickness and thermal stability also increased. Crosslinking with Ca^{2+} ion showed the optimum film properties. The effect of Ca^{2+} ion concentration between 1 to 4% w/v of $CaCl_2$ to SA/CMC film properties were further investigated. The 2% w/v of $CaCl_2$ had dominated the highest tensile strength compared to 3% and 4% w/v of $CaCl_2$. Light transmission, thickness and thermal stability were not affected. In conclusion, the 2% w/v $CaCl_2$ is the appropriated concentration for film preparation in packaging industry.

Keywords: bio-film, sodium alginate, carboxymethyl cellulose, ionic crosslinking

1. INTRODUCTION

Plastic films are now widely used in many applications [1,2], particularly in the food and packaging industry [1-3]. Commonly used films, from PP, PE, LDPE and HDPE, do not degrade naturally, because mostly they are derived from petrochemical sources [4]. When these plastics are consumed, large amounts of plastic waste, which is difficult to remove, are generated [4]. Although there are some degradable plastic from petrochemicals, *i.e.* PVA, PLA, PHA and PBS [2], they are often too expensive for the target application.

Therefore, films from natural materials, *e.g.* polysaccharides or alginates, are interesting, because they have lower costs whilst being degradable. Alginate is extracted from algal cell walls: it is composed of β-D-manumonicacid (M) and α-L-gluronic acid (G) [5-7]. Alginate is easily prepared, soluble, non-toxic and degradable by microorganisms [5-7]. However it is easily deformed and has low tensile strength and needs to be modified to improve film properties. Ionic Crosslinking with metal ions improves the mechanical and thermal properties of alginate [8, 9]. Qua Ling *et al.* [8] found that crosslinking with Al^{3+}, Ca^{2+}, Mn^{2+} and Zn^{2+} could be used to prepare alginate films, with suitable mechanical properties.

Carboxymethyl cellulose has been used to strengthen alginate stability film, because it has more stability, viscosity, binding ability, good water solubility and homogenous mixing with sodium alginate [6,10]. Zheng *et al.* [10] found that mixing carboxymethyl cellulose with alginate led to high gel strength and higher tensile strength and elongation at break.

However, the effect of ionic crosslinking on film properties of alginate, with carboxymethyl cellulose, has not yet been studies. Here, we discuss the properties alginate/carboxymethyl cellulose films, crosslinked with Ba^{2+}, Ca^{2+} and Zn^{2+} ions, as shown in Figure 1, and determined the optimum conditions for packaging applications.

2. MATERIAL AND METHODS

2.1 Materials

Sodium alginate (SA; alginic acid sodium salt, Food grade) and carboxymethyl cellulose (CMC; high viscosity, food grade) were purchased from Chemipan Corporation CO., Ltd. (Bangkok, Thailand). Barium chloride ($BaCl_2$; purity 99.5%, analytical grade), Calcium chloride ($CaCl_2$; purity 99.5%, analytical grade), Zinc chloride ($ZnCl_2$; purity 99.2%, analytical grade) and glycerol (minimum assay: 99.5%, Analytical grade) were purchased from Sigma-Aldrich Pte. Ltd. (Singapore). Deionized water (DW; pH 7.12) was prepared in our laboratories by distillation.

2.2 Film Preparation

1.5 g SA and 0.5 g CMC (3:1 ratio) was dissolved in 100 ml deionized water. 10% w/v glycerol was added: non-toxic glycerol was added for compatibility with SA/CMC solution and to enhance of the film. It was stirred and heated at 60 °C for 3 hr, then cooled to room temperature to remove air bubbles. The mixture solution was poured onto a 100 mm diameter acrylic plate (20 g solution per plate), oven dried (60 °C, 24 hr), and, finally, the films were cast into a rectangular container. For crosslinking of SA/CMC films with $BaCl_2$, $CaCl_2$ or $ZnCl_2$ solutions, the reaction pH should be in the range 5-7 (Kok and Wong) [7]. In our solutions, pHs were 5.23 (for $BaCl_2$), 5.27 (for $CaCl_2$) and 5.28 (for $ZnCl_2$). The film was further immersed in 2% w/v of the ionic solutions ($BaCl_2$, $CaCl_2$ and $ZnCl_2$) for 1 min. to check the effect of crosslinking agent concentration. The SA/CMC films were immersed in a range of 1%, to 4% w/v of $CaCl_2$ solution for 1 min.

2.3 Physical Properties

Specimen thickness was measured by a hand-held micrometer, with a precision of 0.01 mm. Six locations were randomly chosen on each sample and thickness recorded.

The film light transmission was measured by scanning the samples at wavelengths from 200 to 800 nm, using a spectrophotometer (UV-2600,

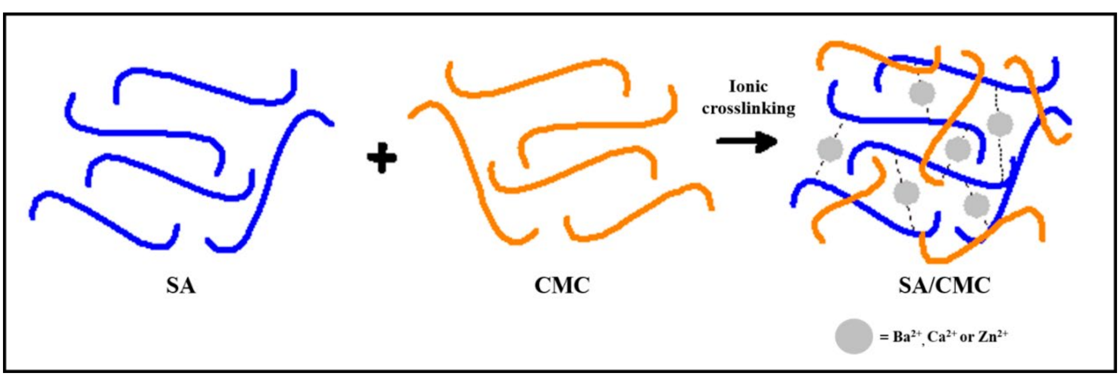

Figure 1. Schematic of the crosslinking reaction.

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2.4 Mechanical Properties

Tensile strength (TS), elongation at break (EB) of films were determined, following ASTM standard method D 882 - 09 (2009), using a Universal Testing Machine (Lloyd Instrument, Hampshire, UK) at room temperature, with 48 $\pm$ 5 % relative humidity. Ten 10 mm × 70 mm film samples, with the initial grip length of 50 mm were used. Each film was clamped and deformed under tensile loading using a 100 N load cell with the cross-head speed of 30 mm/min until the samples were broken. The maximum load and the final extension at break were used to calculate TS and EB.

2.5 Thermal Properties

Each film was tested using a differential scanning calorimeter (Perkin, Pyris 1 TGA, USA) from 25 - 500 °C at a heating rate of 5 degC/min. Nitrogen was used at a flow rate of 50 ml/min to create an inert atmosphere.

2.6 Swelling Measurement of Bio-film

Water absorption or swelling ratio of the films was measured using the gravimetric method. A known weight of the dry film was soaked in 100 ml deionized water for 60 min. Then, water in the container was separated from the swollen film using a paper filter. The swollen film was then weighed and the swelling ratio was determined from:

$$SR = (m_s - m_d) / m_d$$

where m_d and m_s represent mass of dried and swollen film, respectively.

3. Results and Discussion

3.1 Light Transmission Properties

From Figure 2, the neat SA/CMC film gave the highest light transmission at all wavelengths: cross-linking with Ba^{2+}, Ca^{2+} or Zn^{2+} ions significantly decreased the light transmission. The cross-linked region occurs at the carboxyl group of the SA regions and causes the higher density packing density which led to lower light transmission.

When the light transmission at 450 nm (blue light) was analyzed, it was found that the chlorophyll and carotenoid were crucially absorbed in SA part structure [8,11] (Table 1). Moreover, the Ca^{2+} cross-linked film had the highest light transmission compared to Zn^{2+} and Ba^{2+} cross-linked films. The percent of light transmission was as follow: $Ca^{2+} > Zn^{2+} > Ba^{2+}$ ions. Furthermore, the cross-linking ability of Ca^{2+} ion was also better than the other ions.

After $CaCl_2$ was selected to be the good cross-linking agent, the effect of concentration was further studied. At the wavelength of 200 to 800 nm, the cross-linked film bonded with 1% w/v of $CaCl_2$ had dominated the percent of light transmission more than other concentrations in all wavelength periods as shown in Figure 3. The concentration of 1% w/v of $CaCl_2$ caused to lower cross-linking bond between carboxyl group in the SA part. This was led to clear film and the highest percent of light transmission.

When the percent of light transmission was analyzed at wavelength of 450 nm, the increasing concentration of $CaCl_2$ for cross-linking bond caused to lower percent of light transmission (Table 1). The more concentration of $CaCl_2$ enhances the greater binding of cross-linked bond between Ca^{2+} and carboxyl group in the SA part. Moreover, the higher density packing was also effect to lower percent of light transmission.

3.2 Effect of Cross-Linking on Film Thickness

The film thickness before and after cross-linking were measured by immersion into $BaCl_2$, $CaCl_2$ and $ZnCl_2$ for 1 min. Each film was further dried in an oven at 50 °C for 12 hr and then measured thickness with micrometer. In Table 2 discloses film thickness change with various ions; Ba^{2+}, Ca^{2+} and Zn^{2+} ions after cross-linking. The cross-linked film increased film thickness compared to neat SA/CMC film. The cross-linking film brought

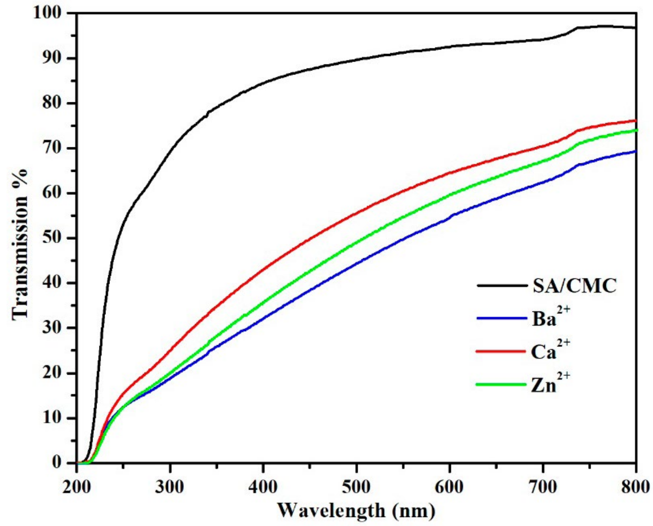

Figure 2. Transmission *vs* wavelength of films, without crosslinking (SA/CMC) and with Ba^{2+}, Ca^{2+} and Zn^{2+} ions.

Table 1. Light transmission of SA/CMC films cross-linked with different ions and concentrations by immersion for 1 min.

	Light transmission (%) [a,b]
SA/CMC	87.5 ± 0.8
Ba^{2+}	38.6 ± 0.9
Ca^{2+}	49.8 ± 0.6
Zn^{2+}	43.0 ± 0.2
1% $CaCl_2$	66.1 ± 0.9
2% $CaCl_2$	49.8 ± 0.6
3% $CaCl_2$	42.4 ± 0.5
4% $CaCl_2$	32.7 ± 0.8

[a] Mean of three replicates ± standard deviations.
[b] Mean light transmission at 450 nm.

to swollen state and stabilize the conformations of this state. The β-L-guluronate (G) or G-units in SA structure had significant swelling and film thickness. Moreover, the percent of film thickness after cross-linking with various ions had increasing arrangement ability as follow: Ca^{2+} > Zn^{2+} > Ba^{2+} ions.

The study of $CaCl_2$ concentration effected to film thickness by immersed in different $CaCl_2$ concentration (1 to 4% w/v) for 1 min was further investigated. Table 2 reveals that after cross-linking bond, the film was distinctly increased in thickness when the concentration of $CaCl_2$ was increased. At 4% w/v of $CaCl_2$ concentration,

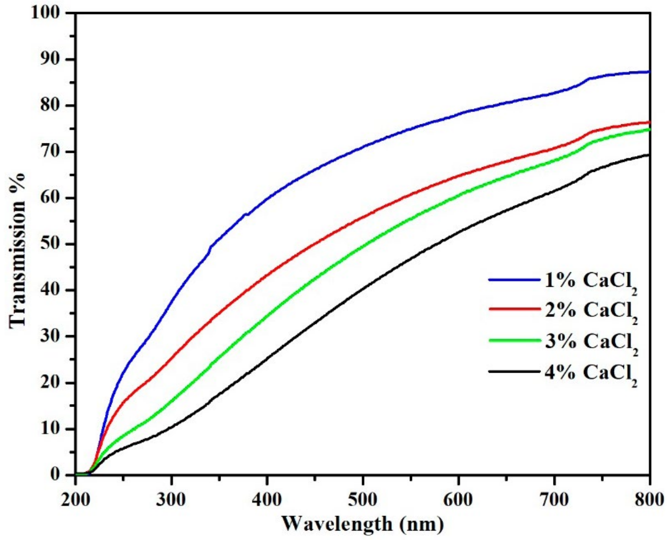

Figure 3. Transmission *vs* cross-linked Ca^{2+} concentration.

Table 2. Effect of cross-linking with different ions and concentration on thickness change by immersion in a solution for 1 min.

	Thickness before cross-linking (mm)[a]	Thickness after cross-linking (mm)[a]	Increment of thickness (%)
SA/CMC	0.104 ± 0.02	Non-crosslinking	0
Ba^{2+}	0.104 ± 0.03	0.115 ± 0.01	10.6
Ca^{2+}	0.104 ± 0.02	0.129 ± 0.03	24
Zn^{2+}	0.104 ± 0.01	0.122 ± 0.03	17.3
1% $CaCl_2$	0.103 ± 0.02	0.121 ± 0.01	17.5
2% $CaCl_2$	0.104 ± 0.02	0.129 ± 0.03	24
3% $CaCl_2$	0.104 ± 0.01	0.134 ± 0.01	28.8
4% $CaCl_2$	0.105 ± 0.03	0.145 ± 0.01	38.1

[a] Means of six replicates ± standard deviations.

Ca^{2+} ion has more diffusion ability into the SA structure and greatly caused SA cross-linked bond interaction between Ca^{2+} and carboxyl group. The more swelling and increasing thickness film had obviously appeared.

3.3 Mechanical Properties

The effect of different ionic crosslinking on the tensile strength and elongation at break at one minute cross-linked time was shown in Table 3. The effect of ionic crosslinking was significantly dominated on tensile strength and elongation at break, particularly the cross-linked agent of Ca^{2+} ion from $CaCl_2$ solution. It was revealed that the neat SA/CMC had tensile strength of 1.7 ± 1.0 MPa. When SA/CMC was cross-linked by Ca^{2+} ion, the tensile strength was increased to 9.1 ± 1.6 MPa. The tensile strengths of SA/CMC

Table 3. Mechanical properties of SA/CMC films cross-linked with different ions and concentrations by immersion in crosslinking solution for 1 min.

	Tensile strength (MPa)[a]	Elongation at break (%)[a]
SA/CMC	1.7 ± 1.0	70 ± 5
Ba^{2+}	4.9 ± 1.5	38.3 ± 7
Ca^{2+}	9.1 ± 1.6	69.2 ± 8
Zn^{2+}	6.5 ± 1.8	62.3 ± 6
1% $CaCl_2$	5.0 ± 1.4	80.7 ± 12
2% $CaCl_2$	9.1 ± 1.6	69.5 ± 10
3% $CaCl_2$	7.2 ± 1.4	53.9 ± 11
4% $CaCl_2$	6.5 ± 1.5	48.4 ± 10

[a] Means of ten replicates ± standard deviations.

were also increased when the cross-linking agent was changed to Ba^{2+} and Zn^{2+} ions. However, the tensile strengths of Ba^{2+} and Zn^{2+} ions were lower than Ca^{2+}. This could be explained by the various ion affinity effect [8,11]. In this research, the ion affinity interaction of Ca^{2+} ion was greater than Ba^{2+} and Zn^{2+} ions at same concentration, respectively. Pavlath et al. [11] studied the effect of Ca^{2+}, Cu^{2+} and Zn^{2+} ions on mechanical properties of SA films. The cross-linked film with Ca^{2+} ion had shown the highest tensile strength compared to Cu^{2+} and Zn^{2+} ions [11]. These were related to affinity and ionic bond strength with carboxyl group on SA chain [11]. All mentioned parameters have also more influenced to mechanical properties. In other aspect, the blended with CMC into film structure has been improved the flexibility of the film [6,10]. It is not involved to ionic cross-linking reaction because CMC has no carboxyl groups. Elongation at break of SA/CMC film cross-linked bond with Ba^{2+}, Ca^{2+} and Zn^{2+} ions was shown in Table 3. The cross-linked bond with Ca^{2+} has shown the highest elongation at break compared to the other ions. In case of Ba^{2+} and Zn^{2+} ions, the elongation at break was distinctly less than the cross-linked bond with Ca^{2+} ion according to chain mobility segment of SA polymer chain was decreased. This phenomenon is called lack of selectivity [8,12]. It causes the reduction of chain mobility and lower elongation at break.

After the appropriate cross-linked bond with Ca^{2+} was known and it had the highest tensile strength of SA/CMC film. The effect of different concentrations of $CaCl_2$ on tensile strength and elongation at break was further investigated. The concentration of Ca^{2+} ion was varied from 1% to 4%w/v $CaCl_2$ solution. It was found that the 2%w/v $CaCl_2$ cross-linking agent had shown the highest tensile strength. As the 3% and 4%w/v $CaCl_2$ cross-linking agent were gradually decreased tensile strength, respectively. This was shown in Table 3. The evidence was related to the cross-linked bond ability of Ca^{2+} ion with carboxyl groups in SA part. The higher the concentration of the $CaCl_2$ solution, the more cross-linking ability was appeared and led to restricted chain mobility with less free volume. The SA/CMC film was a stiff and has no strength (tensile strength reduction). In opposite way, the more concentration of $CaCl_2$ solution, the elongation at break was decrease because the carboxyl groups in SA structure had more cross-linked with Ca^{2+} ion. The stiffened phase in SA segment was no flexible even though CMC segment was exist. When the film was drawn, the SA phase had more stress, rapidly broken down and finally cracked phase between

SA and CMC. Elongation at break was decrease as a consequence.

The cross-linking ability of film bonding is depend only on carboxyl group in SA part. It is no related to CMC. The bonding occurs in the principal part of G-block. The longer G-block part could enhance to mechanical properties according to more cross-linking from ionic bridges between different chains. This is promoted SA part to form three-dimensional network call “egg-box” model. In promotes greater film strength structure as shown in Figure. 4 [5].

3.4 Thermal Properties

Thermal analysis of SA/CMC and SA/CMC film cross-linked with Ba^{2+}, Ca^{2+} and Zn^{2+} ions were shown in Table 4 and Figure 5. They were revealed that all films had thermal decomposition divided into three zones. For neat SA/CMC film, the first zone at 25-100 °C indicated the decomposition of surface water on SA and CMC [12,13,15,16]. Because the water molecule had bond forming capability with polar group of carboxyl and hydroxyl group on both surface water of SA and CMC, respectively [12,13,19]. Moreover, the weight loss was 19.9% during decomposition in the first zone. For the second zone the decomposition temperature was 100-200 °C. The decomposition of this zone came from volatile compounds and water molecule attached to the functional groups of alginate and initially non-removal CMC [12,14,15]. The other factor for the decomposition of this zone was occurred from the structures of carboxyl and hydroxyl groups inside SA and CMC, respectively [12-14], were destroyed from high thermal temperature of 65.8% weight loss. For the final zone was thermal decomposition of 200-900 °C. The organic compounds of SA and CMC [12] film appeared 13.8% weight loss. When the SA/CMC film was further crosslinked with Ba^{2+}, Ca^{2+} and Zn^{2+}, the three distinction zones were the same as neat SA/CMC film. However, there was less thermal decomposition, observed from lower weight loss every zone of thermal decomposition. The cross-linked films were then compared to each other. It was found that the Ca^{2+} cross-linking agent was dominated to less thermal decomposition compared to the ones, Ba^{2+} and

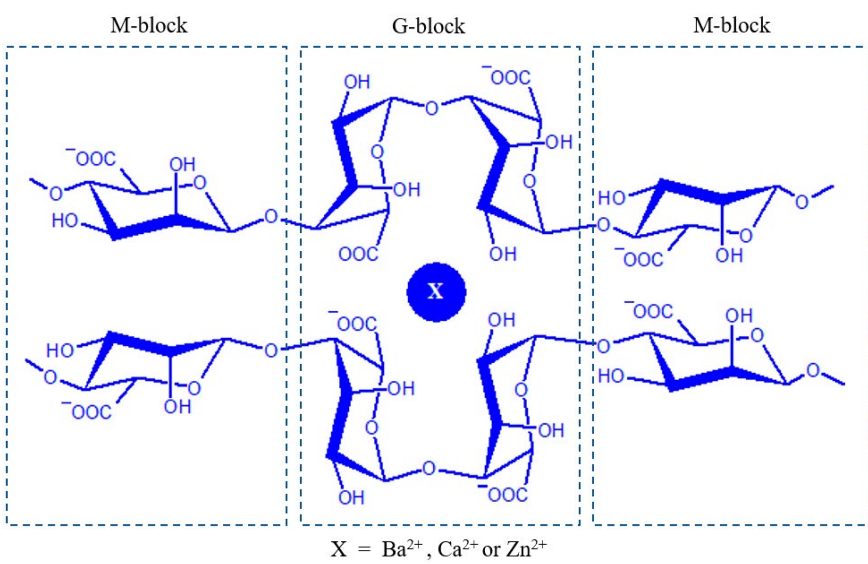

Figure 4. Interaction between cation and alginate G-block in the “egg-box model”.

Table 4. Mass loss of SA/CMC cross-linked films.

Sample	Weight loss at 25-100 °C (%)	Weight loss at 100-200 °C (%)	Weight loss at 200-900 °C (%)
SA/CMC	19.9	65.8	13.8
Ba^{2+}	19.2	63.5	11.9
Ca^{2+}	15.9	61	11.4
Zn^{2+}	16.5	62.9	11.7
1% $CaCl_2$	16.6	68.4	12.7
2% $CaCl_2$	15.9	61	11.4
3% $CaCl_2$	9.9	60.2	10.2
4% $CaCl_2$	5.8	60.2	10

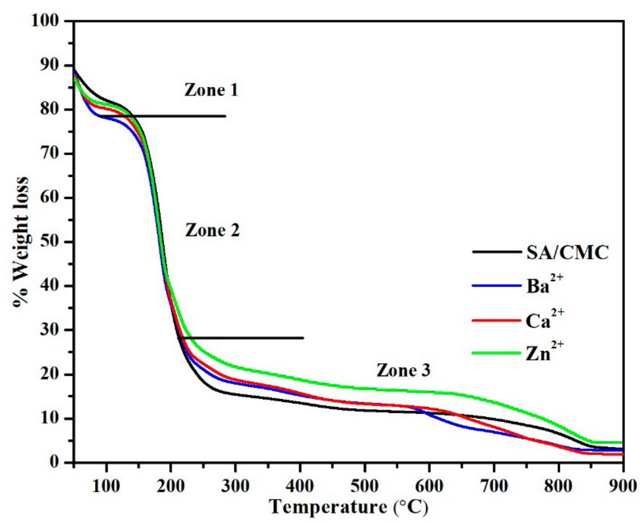

Figure 5. Thermograms: SA/CMC and crosslinked films crosslinked after immersion in 2% w/v crosslinking solution for 1 min.

Zn^{2+} ions. Furthermore, the weight loss of Ca^{2+} ion had least thermal decomposition. This was revealed that the cross-linked film with Ca^{2+} ion has the highest thermal stability film because of the stronger bond between Ca^{2+} ion and carboxyl group in SA structure [16].

The varied concentration of crosslinking agent of Ca^{2+} ions (1% - 4% CaCl2) was further investigated to thermal analysis of SA/CMC film. It was shown in Table 4 and Figure 6. The thermal diagram was still be in three zones as usual. The first zone of 25-100 °C, the second zone of 100-200 °C and the third zone of 200-900 °C were appeared, respectively. However, the weight losses were quite different. The higher concentration of $CaCl_2$, the lower the thermal decomposition of film was appeared. The reason for percent of weight loss was decreased when the concentration of $CaCl_2$ increased according to the more opportunity of Ca^{2+} ion for cross-linking bond between carboxyl

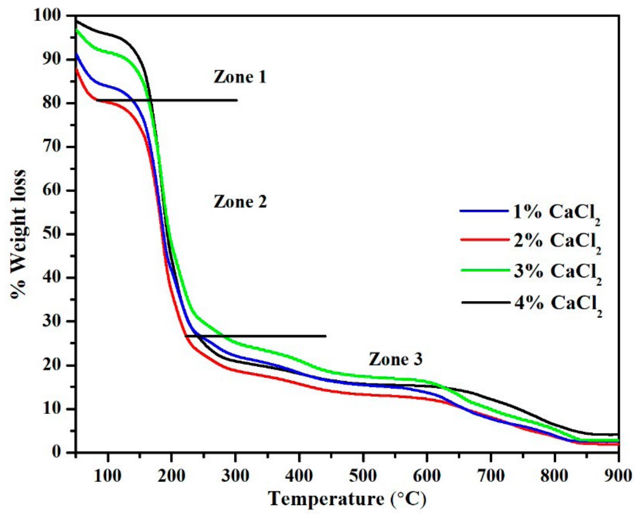

Figure 6. Thermal analysis of SA/CMC film cross-linked by differently immersed concentrations of $CaCl_2$ for 1 min.

Table 5. Swelling properties of SA/CMC and crosslinked films.

	Dry Mass (g)	Wet Mass (g)	Swelling Ratio	% Swelling
SA/CMC	3.41	6.65	0.95	95
Ba^{2+}	3.49	4.82	0.38	38
Ca^{2+}	3.48	4.06	0.16	16
Zn^{2+}	3.45	4.23	0.23	23
1% $CaCl_2$	3.44	5.12	0.48	48
2% $CaCl_2$	3.48	4.06	0.16	16
3% $CaCl_2$	3.49	3.96	0.13	13
4% $CaCl_2$	3.47	3.84	0.11	11

group in SA structure [16]. This caused SA/CMC structure having more cross-linking density and less free volume. Nevertheless, the surface water including water molecule on SA and CMC film had less amount bringing to lower percent of weight loss of thermal decomposition. Moreover, the SA structure cross-linked with more concentration Ca^{2+} caused strong bonding between carboxyl group leading to lower percent of weight loss and better thermal stability.

3.5 Swelling Properties

The more evidence for cross-linking reaction is swelling ratio of film. The film was immersed de-ionized water (pH = 7.12) for 24 hrs. The cross-linked film with Ba^{2+}, Ca^{2+} and Zn^{2+} ions had shown lower percent of swelling than neat SA/CMC film (Table 5). This is shown that the cross-linked bond occurred at carboxyl group region of G-block in SA part as shown in Figure 7. This causes insolubility or less absorption cross-linked

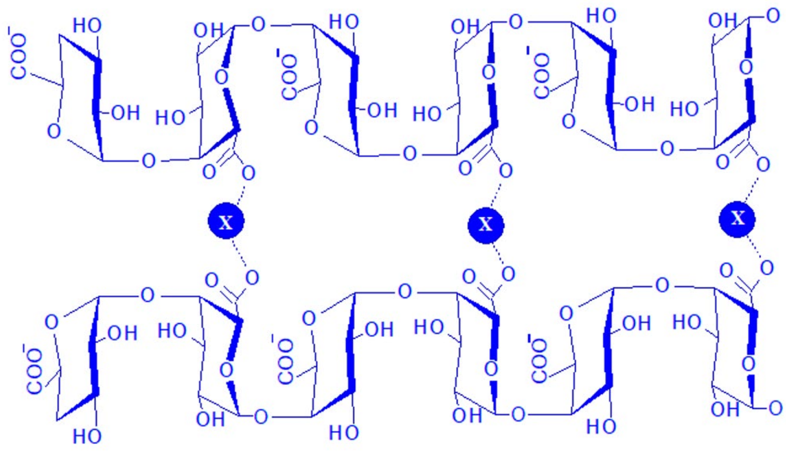

Figure 7. Diagram of ion crosslinking between SA chains.

film and lower percent of swelling compared to neat SA/CMC film.

When cross-linked bond with $CaCl_2$ solution at 1 - 4 %w/v was made, it was found that the more $CaCl_2$ concentration, the less swelling of film (Table 5). This was revealed that the effect of concentration had more influenced to the cross-linked bond ability. This was meant that the carboxyl group in SA had more cross-linked, led to less swelling for water absorption and caused the film structure changes with ionic cross-linking method.

4. Conclusions

The preparation of cross-linked SA/CMC film with ionic reaction was studied. The cross-linking Ca^{2+} ion at 2% w/v had more effect on film properties. In addition, the light transmission, film thickness, and tensile strength had also more significant effect than using of Ba^{2+} and Zn^{2+} ions. Furthermore, all thermal decomposition zones of Ca^{2+} cross-linking agent also indicated lower weight loss than Ba^{2+} and Zn^{2+} at same concentration. It was implied that the film possessed the optimum thermal stability. Moreover, the percent of swelling was decreased when using of Ca^{2+} ion for cross-linking agent. The density packing has obviously increased and brought to higher tensile strength. The optimum properties are specified on 2% w/v $CaCl_2$ which is suitable and efficient film for packaging industry.

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