

MECHANICAL STUDIES ON CHITOSAN/PVA BLEND WITH CALCIUM CHLORIDE AS IONIC CROSSLINKER

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Abstract— The present research aimed to enhance the flexibility of chitosan(CS)-Polyvinyl Alcohol(PVA) blend films crosslinking with Calcium chloride(CaCl_2).The blending of CS-PVA along with calcium chloride as Ionic crosslinking agent was confirmed by XRD. The mechanical property of the CS-PVA films was examined by universal mechanical tester (ASTMD). The % Elongation and Young's Modulus of the CS-PVA blend was enhanced from 17.16% and 0.98 Mpa after crosslinking with calcium chloride to 294.70% and 8.9 Mpa with decrease in tensile strength(TS), Thus the results indicate that the crosslinked CS-PVA blend films have great flexibility than CS-PVA blend alone hence promises to be a good material for the biomedical and food packaging applications.

Keywords— Chitosan-Polyvinyl Alcohol blend, cross linking, flexibility.

I. INTRODUCTION

Polymer blending is a method that is commonly used for providing desirable polymeric materials with combined properties suitable for particular applications. Investigation of blends of chitosan with synthetic and naturally occurring macromolecules has attracted much attention in the recently years in various occasions[1-5]. Blending of chitosan with synthetic polymers is a convenient method for preparation of synthetic biodegradable polymers having versatile properties such as good water absorbance and enhanced mechanical properties while maintaining biodegradability[6]. and chitosan [poly-b(1-4)-d-glucosamine], have recently been re-evaluated and found to be useful resources and functional materials [7-8]. However, their homopolymers are inadequate to meet the diversity of our demands for materials. Polymer blending is one of the most effective methods for providing new, desirable polymeric materials for practical applications. Chitosan blended with poly(vinyl alcohol)(PVA) have already been reported to have good mechanical properties [9] because of the specific intermolecular interactions between PVA and chitosan in the blends.

Ionic crosslinking is a simple and mild procedure. In contrast to covalent crosslinking, no auxiliary molecules such as catalysts are required [11], which is of great interest for medical or pharmaceutical applications. Indeed, ionic crosslinking can be ensured by the classical method of preparing a crosslinked network, namely by the addition of the crosslinker, either solubilised [13] or dispersed to the chitosan solution. These methods allow the formation of a homogeneous hydrogel by a random crosslinking reaction [14]. Other methods for ionic crosslinking of chitosan have also been developed to modulate hydrogel properties, such as drug release. Chitosan

can be crosslinked by simply dipping pieces of chitosan film into the crosslinker solution [15] or by adding the chitosan solution to the crosslinker solution[10,12,16] through a syringe for example. These latter methods induce the formation of systems that are similar to gel particles.

The objective of this study was to develop chitosan based film by blending and crosslinking with polyvinyl alcohol and calcium chloride in order to increase the flexibility as well as modulus of elasticity of chitosan biopolymer. This modified chitosan film may be a promising material in packaging applications, and particularly for food preservation and biomedical applications.

II. MATERIALS AND METHODS

Shrimp source Chitosan in a form of white flaks with a degree of deacetylation of 88.1% defined by UV method [17] was obtained from commercial source. Polyvinyl alcohol was purchased from Sigma Chemicals Co. (UK). Acetic acid (glacial 100%, pro analysis) was purchased from Merck (Germany). Calcium chloride dihydrate (granular, $M = 147.02 \text{ g mol}^{-1}$) was purchased from Merck (Germany). Ultra pure water (Elga-Prima Corp, UK) with a resistivity higher than $18 \text{ M}\Omega \text{ cm}^{-1}$ was used to prepare all solutions. All chemicals were used without further purification and freshly prepared solutions were always used in all experiments.

Synthesis of CS/PVA blend and its crosslinked films:

Chitosan was grounded and dried in an oven until a constant weight was observed. A 10 g L^{-1} solution of Cs was prepared by dissolving 5g of chitosan in 500 mL of acetic acid (0.1 M) followed by stirring and heating at 60°C for 14 to 16h. The solution was

filtered before being used to remove the undissolved particles. The PVA powder was dissolved in preheated ultra pure water followed by stirring at a temperature of 90°C for about 2 hours until clear solutions were obtained. To prepare the of CS-PVA blend, 50ml of Cs and 50ml of PVA solutions were mixed and stirred at 90°C for 30 min. to obtain homogeneous blended solutions. The pH of the solution was maintained at levels higher than pH~6 to avoid Cs precipitation. The obtained homogeneous of CS-PVA (50-50) solution was cast into a polystyrene Petri dish, after removing all trapped air bubbles. The cast solution was then allowed to dry in a vacuum oven at 60°C to form uniform and homogenous films.

The blended films were ionically crosslinked using the method described by Huang *et al.* [18]. The dried of CS-PVA (50-50) films were immersed in a different weight percentages of calcium chloride(CaCl_2) in aqueous ethanol solution, as shown in table 1. The crosslinking reaction was allowed to continue for 30-40 min at room temperature under continuous stirring. The crosslinked films were removed, and then placed under vacuum for drying.

Table 1: CHITOSAN/PVA blended films with different composition of ionic crosslinker.

Sl.no	Films designation	Calcium chloride (grams) (crosslinker)	Ethanol (ml)
01	CHITOSAN/PVA(50/50) blend	0.1	10
02	CS/PVA(50/50)	0.2	20
03	CS/PVA(50/50)	0.3	30
04	CS/PVA(50/50)	0.4	40
05	CS/PVA(50/50)	0.5	50

III. EXPERIMENTAL RESULTS

1: MORPHOLOGICAL STUDIES OF CS-PVA BLEND AND ITS CROSSLINKED FILMS:

Fig 1 shows the SEM images of surfaces of CS/PVA blended film and its corresponding crosslinked films with calcium chloride as ionic crosslinker. In fig 1of (a) shows smooth and homogenous surface with no straps or lumps unlike that of (b) and (c) where some lumps are seen .The surfaces of the blended film of CS/PVA are homogenous with no pores[19] ,this indicates the uniform distribution of Cs and PVA molecules throughout the films and is caused by the interaction of hydrogen bonds between the functional groups of the blended components (-OH and $-\text{NH}_2$ groups in chitosan and -OH groups in PVA).further, the images b and c shows that the crosslinking is achieved successfully as this completely modified the surface morphology of crosslinked of CS-PVA (50-50) blend.

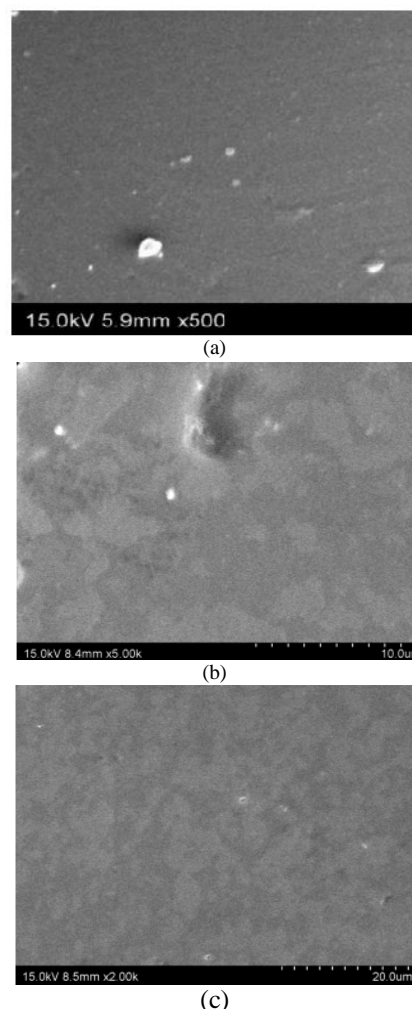


Fig 1: a) blend of CS-PVA 50-50 b) crosslinked CS-PVA blend with 0.2g CaCl_2 c) crosslinked CS-PVA blend with 0.4g CaCl_2 .

2: XRD STUDIES

X-ray diffraction gives very useful information on degree of samples crystallinity (crystallinity or amorphous nature) X-ray diffraction patterns of Chitosan-PVA blend (50-50) are shown in Fig 2. Chitosan exhibited the major crystalline peak at $2\theta = 20^\circ$ in agreement with the literature values [20]. Additional diffraction peaks are seen at the regions $2\theta = 37^\circ, 43^\circ, 64^\circ$ and 77° indicative of a clear structural changes as a result of blending with polyvinyl alcohol. On hydrolysis to alcohol, the intensity of all the peaks was enhanced, this may be due to the comparatively high crystalline nature of the chitosan-poly(vinyl alcohol) blend. This confirms that blending has been done .similarly the CS-PVA blend is crosslinked with 0.1,0.2,0.3,0.4 and 0.5g of calcium chloride(CaCl_2) which is shown below. These figures shows one broad peak at around 20° ,indicating that crosslinking has been done successfully.from It was concluded that, the CS-PVA blend has higher crystalline nature whereas the CS-PVA blend with Calcium chloride as crosslinking agent has amorphous nature and its crystallinity is decreases with increasing the crosslinker ratio to the CS-PVA blend.

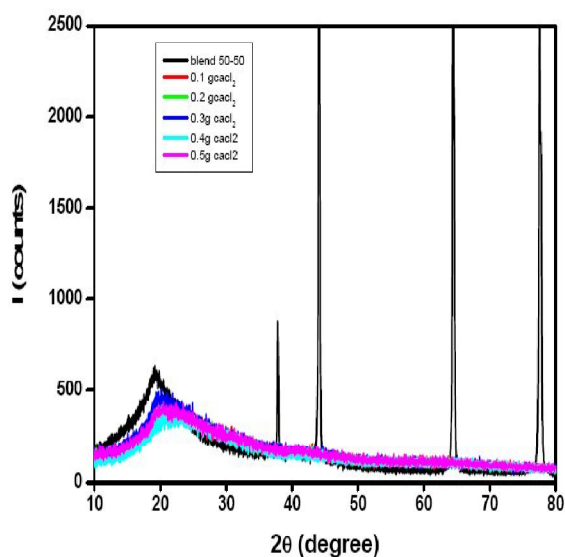


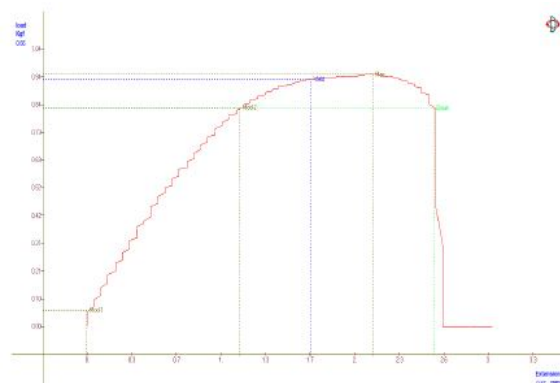
FIG 3: XRD graph of CS-PVA blend(50-50) and its corresponding crosslinked film with varying ratios of ionic crosslinker.

III. MECHANICAL PROPERTIES:

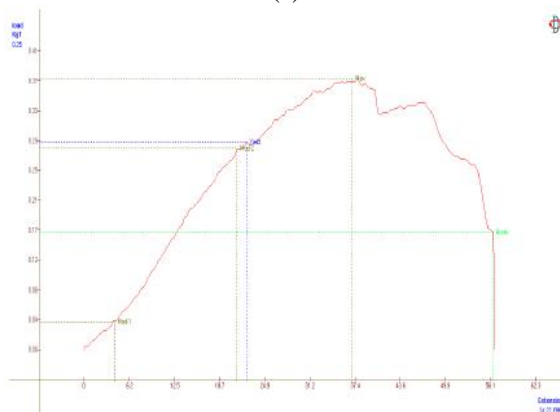
CS-PVA blend is able to increase the free volume between polymeric chains. In doing so, the ease of movement of polymeric chains with respect to each other is dramatically enhanced. In packaging, a plasticizer is a substance added to materials to impart flexibility, workability, and elongation. The addition of ionic crosslinker as plasticizer to the film is to overcome the film brittleness caused by extensive intermolecular force. The prepared new ductile materials with the addition of crosslinker calcium chloride, had very high Elongation % increased from 17.16% to 294.70% as well as Young's Modulus is increased from 0.10Mpa to 8.31Mpa while Tensile Strength is decreased from 8Mpa to 1.56Mpa which leads to effect the behavior of blend and can lead the intermolecular and intramolecular linkage of $-OH$ between CS and PVA molecules, as shown in Table 2. Usually the addition of calcium chloride as ionic crosslinker increased the Elongation% and Young's Modulus when compared with the CS-PVA blend alone[21]. The below graphs shows CS-PVA blend with different ratios.

Table 2: The values of Elongation %, Young's Modulus and Tensile strength,

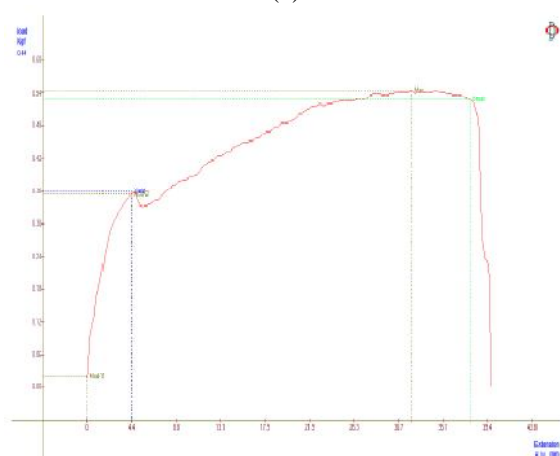
Specimen	Young's Modulus (Mpa)	Elongation %	Tensile strength (Mpa)
CS-PVA(50-50) blend	0.10	17.16	8.00
0.1g Cacl ₂	1.54	282.30	1.56
0.2g Cacl ₂	8.31	188.60	2.88
0.3g Cacl ₂	1.74	254.25	2.42
0.4g Cacl ₂	4.18	168.25	1.98
0.5g Cacl ₂	4.32	294.70	3.25



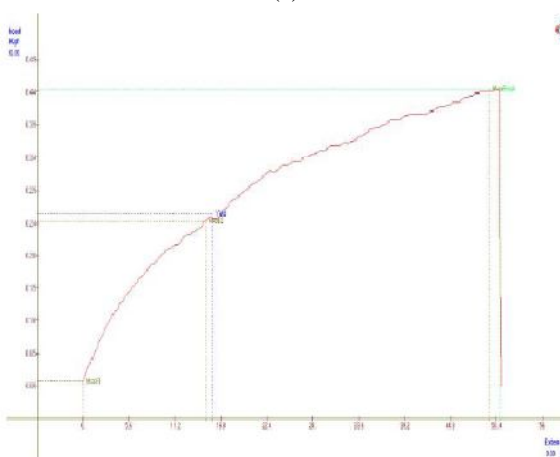
(a)



(b)



(c)



(d)

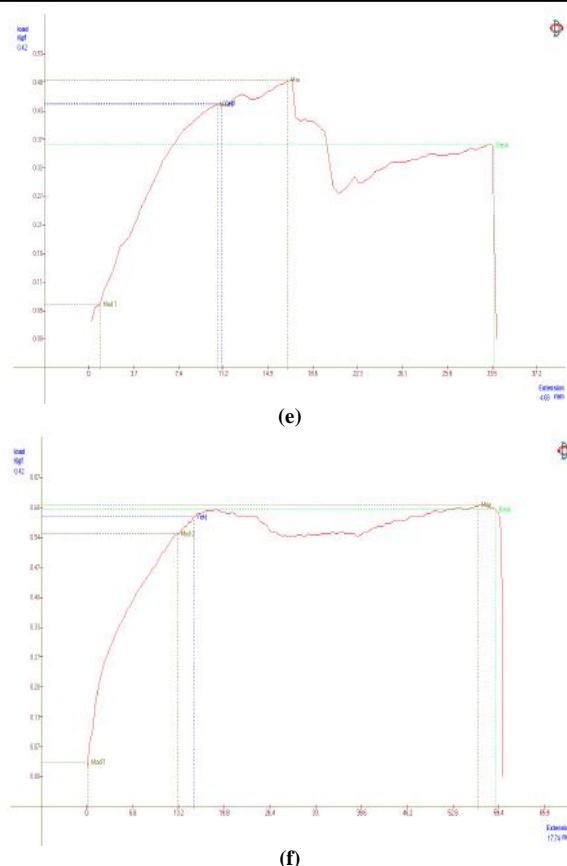


Fig 4. a) CS-PVA blend 50-50 b) crosslinking of blend with 0.1g CaCl_2 c) crosslinking of blend with 0.2g CaCl_2 d) crosslinking of blend with 0.3g CaCl_2 e) crosslinking of blend with 0.4g CaCl_2 f) crosslinking of blend with 0.5g CaCl_2 .

CONCLUSION

CS-PVA blend and its crosslinked films with ionic crosslinker calcium chloride is prepared. From SEM it is clear that CS-PVA blending along with its crosslinker is achieved successfully and XRD shows that the crystallinity of CS-PVA blend decreases as the crosslinker increases, hence indicating that the crosslinked films are amorphous in nature. The mechanical property of crosslinked films is successfully enhanced by increasing the elongation% and Young's modulus and decreasing TS values when compared to blend alone, as it shows that the degradation behavior can be improved with the addition of crosslinker. These blends and the crosslinked films have good adsorption capacity. Thus, chitosan-based films by blending and crosslinking with polyvinyl alcohol and calcium

chloride increases the flexibility as well as modulus of elasticity of chitosan biopolymer, hence promising to be a good material for biomedical and food packaging applications.

REFERENCES

- [1] Mucha M, *React Funct Polym.*, 1998, **38**, 19.
- [2] Srinivasa P C, Ramesh M N, Kumar K R and Tharanathan R N, *Carbohydr Polym.*, 2003, **53**(4), 431-438.
- [3] Shanmugasundaram N, Ravichandran P, Neelakanta P R, Nalini R, Subrata P and Rao K P, *Biomaterials*, 2001, **22**, 1943.
- [4] Chen X G, Wang Z, Liu W S and Park H J, *Biomaterials*, 2002, **23**(23), 4609-4614.
- [5] Sionkowska A, Wisniewski M, Skopinska J, Kennedy C J and Wess T J, *Biomaterials*, 2004, **25**(5), 795-801.
- [6] Engelberg I and Kohn J, *Biomaterials*, 1991, **12**, 292-304.
- [7] Li Q, Dunn ET, Grandmaison EW, Goodman MFA. *J Bioact Compat Polym* 1992;7:370.
- [8] Chandy T, Sharma CP. *Biomater Art Cells Art Org* 1990;18:1.
- [9] Miya M, Yoshikawa S, Iwamoto R, Mima S. *Kobunshi Ronbunshu* 1983;40:645.
- [10] F.L. Mi, S.S. Shyu, T.B. Wong, S.F. Jang, S.T. Lee, K.T. Lu, Chitosan polyelectrolyte complexation for the preparation of gel beads and controlled release of anticancer drug. II. Effect of pH-dependent ionic crosslinking or interpolymer complex using tripolyphosphate or polyphosphate as reagent, *J. Appl. Polym. Sci.* 74 (1999) 1093-1107.
- [11] X.Z. Shu, K.J. Zhu, W. Song, Novel pH-sensitive citrate cross-linked chitosan film for drug controlled release, *Int. J. Pharm.* 212 (2001) 19-28.
- [12] F.L. Mi, C.T. Chen, Y.C. Tseng, C.Y. Kuan, S.S. Shyu, Iron(III)-carboxymethylchitin microsphere for the pH-sensitive release of 6-mercaptopurine, *J. Controlled Release* 44 (1997) 19-32.
- [13] E. Ruel-Gariepy, A. Chenite, C. Chaput, S. Guirguis, J.-C. Leroux, Characterization of thermosensitive chitosan gels for the sustained delivery of drugs, *Int. J. Pharm.* 203 (2000) 89-98.
- [14] K.I. Draget, K.M. Varum, E. Moen, H. Gynnild, O. Smidsrod, Chitosan cross-linked with Mo(VI) polyoxyanions: a new gelling system, *Biomaterials* 13 (1992) 635-638.
- [15] X.Z. Shu, K.J. Zhu, Controlled drug release properties of ionically cross-linked chitosan beads: the influence of anion structure, *Int. J. Pharm.* 233 (2002) 217-225.
- [16] X. Shu, K.J. Zhu, A novel approach to prepare tripolyphosphate/chitosan complex beads for controlled release drug delivery, *Int. J. Pharm.* 201 (2000) 51-58.
- [17] M K . Cheung , Wan K P Y and Yu P H, *J Appl Polym Sci.*, 2002, 86,
- [18] Huang Y, Yu H and Xiao C, *Carbohydr Polym.*, 2007, **69**, 774.
- [19] R A A. Muzzarelli, and Rochetti R, *Carbohydr Polym.*, 1985, 5, 461-472
- [20] Engelberg I and Kohn J, *Biomaterials*, 1991, **12**, 292-304
- [21] kawakib j, Majeed and Mohanad I. *Kamil.issue* 11, 2013.

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