

Effect of Ionic Crosslinking on Thermal Stability of Chitosan-Polyvinyl Alcohol Polymer Blend

Firdos Jahan¹, R.D. Mathad²Scholar, Department of Post Graduate Studies and Research in Physics, Gulbarga University, Kalaburgi, India¹Professor, Department of Post Graduate Studies and Research in Physics, Gulbarga University, Kalaburgi, India²

ABSTRACT: The present research aimed to enhance the thermal stability of chitosan(CS)-Polyvinyl Alcohol(PVA) blend crosslinking with Calcium chloride(CaCl_2).The blending of CS-PVA along with calcium chloride as crosslinking agent was confirmed by Fourier Transform Infrared Spectroscopy (FTIR) .The morphology of the film surface were investigated by Scanning Electron Microscopy (SEM). The thermal property of the CS-PVA film was examined by Differential Scanning Calorimetry (DSC) .The melting temperature (T_m) of the CS-PVA blend was enhanced from 165°C after crosslinking to 278°C .Thus the results indicate that the crosslinked CS-PVA blend films have good thermal stability than CS-PVA blend, and promises to be a good material for the biomedical and food packaging applications.

KEYWORDS: Chitosan-Polyvinyl Alcohol blend, Calcium Chloride, and Ionic crosslinking of films.

I. INTRODUCTION

In the recent decades there has been a considerable interest in polymer blends owing to their potential applications [1, 2]. In terms of scientific research the field of the synthetic polymer blends had experienced an enormous growth in recent years. Blending and alloying of polymers with other polymeric components had a significant development [3-5]. One of the main advantages of blending the polymer at the various compositions was the achievement of the change in properties of the final product. Polymer blends can be obtained with a range of properties depending on their chemical nature of the polymer mixed and more precisely on the polymer-A-polymer-B interactions [6].

Chitosan (CS) is derived from chitin found in the exoskeleton of insects, shells of crustaceans or various fungi, and is a linear, crystalline polysaccharide which composed of β -(1 \rightarrow 4) linked N-acetyl-Dglucosamine(Poly-(1-4)-2-Amino-2-deoxy- β -D-Glucan),Chitin and chitosan have tremendous applications in the biomedical field due to their good biocompatibility, biodegradability, and capacity to form membranes, beads, fibers, scaffold and gels [7-12]. Chitosan inhibits the growth of a wide variety of fungi, yeasts, and bacteria. Chitosan also represents interesting properties such as excellent film forming capacity and gas and aroma barrier properties at dry conditions, which makes it a suitable material for designing food coatings and packaging structures [13].chitosan has a wide range in packaging applications, and particularly for food preservation applications [14]. Recently, a chitosan–starch film has been prepared using microwave treatment which may find potential application in food packaging [15].

Poly (vinyl alcohol) (PVA) a biodegradable, synthetic polymer, innocuous, non-carcinogenic and have good biocompatible properties. Poly (vinyl alcohol) has excellent film forming properties. Because of its good film forming and highly hydrophilic water-soluble with outstanding chemical stability it was blended different synthetic and natural polymers. It is used as a water-soluble film useful for packaging. Poly (vinyl alcohol) is completely water soluble synthetic polymer and non-toxic. It is useful in many applications such as controlled drug delivery systems, recycling of polymers, film formation

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, Januray 2016

and packaging. Because of the good biological activities of chitosan and PVA, a combination of chitosan and PVA may have beneficial effects on the biological characteristics of blend films.

To improve of CS-PVA blend properties and further diversify its applications, various strategies have been adopted. This includes: (1) crosslinking (2) graft copolymerization (3) complexation, (4) chemical modifications and (5) blending [16, 17, 18,19,20,21, and 22]. In particular, the modification of chitosan by means of blending is an attractive method that has been extensively used for providing new desirable characters to chitosan [23, 24]. This is mainly due to its simplicity, availability of wide range of synthetic and natural polymers for blending and effectiveness for practical utilization.

The objective of this study was to develop chitosan based film by blending and crosslinking with polyvinyl alcohol and calcium chloride in order enhance the thermal stability of chitosan biopolymer .This modified chitosan film may be a promising material in packaging applications, and particularly for food preservation 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 [25] 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.

1: 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 5 g 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 $\text{pH}\sim 6$ 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 film with a thickness of about $14\pm 2 \mu\text{m}$. The films thicknesses were obtained at various positions of the samples using a digital thickness gauge and the reported data is the average of 3 readings.

The blended films were ionically crosslinked using the method described by Huang *et al.* [26]. The dried of CS-PVA (50-50) films were immersed in a different weight percentages of calcium chloride 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.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, Januray 2016

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

Sl.no	Films designation	Calcium chloride (grams)	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

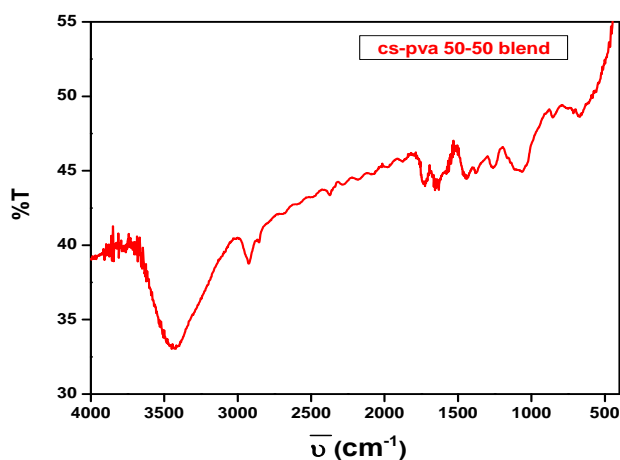
III: EXPERIMENTAL RESULTS

1: FTIR STUDIES:

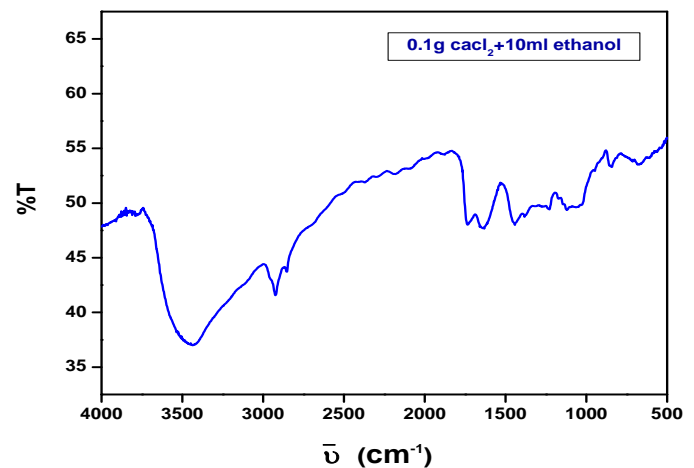
The ftir spectra of CS-PVA (50-50) blend and its ionic crosslinking with different amounts of calcium chloride is as shown in figure 1. As can be seen in figure 1.a) spectra of CS-PVA (50-50) blend, the absorption peak at 3425cm^{-1} is associated with O-H stretching group(i.e. H-bonding which is present in alcohols and phenols) while the absorption peak observed at 1626cm^{-1} represents the amide peak $-\text{NH}_2$ which is present in chitosan. The C-O stretch and CH stretch is also obtained at 1084cm^{-1} and 2931cm^{-1} .this confirms the blending of CS-PVA (50-50) .

Fig 1 of b, c and d represent the ionic crosslinking of CS-PVA (50-50) blend with varying ratios of crosslinker CaCl_2 .In figure c and d we observed that the peak representing $-\text{NH}_2$ group was found to increase when the film was crosslinked by calcium chloride, this was coupled with a similar increase in the size of $-\text{OH}$ representing peak and in fig 1 of b, the peaks representing amide group and hydroxyl group was found to decrease, suggesting a possible involvement of Ca^{+2} with $-\text{NH}_2$ and $-\text{OH}$ groups in formation of polyanionic-cationic complexes. Similar complex formation behavior was observed for Cs when crosslinked by glycerol phosphate disodium by Chenite *et al.* [27].

Based on these results, it is confirmed that of CS-PVA blended film with various compositional proportions of crosslinking has occurred, this is caused by the Cs to induce the formation of polyanionic-polycationic complexes, which stabilizes the medium. Similar behavior was suggested for the addition of chitosan to the gelation medium containing calcium chloride and alginate [28].



(a)



(b)

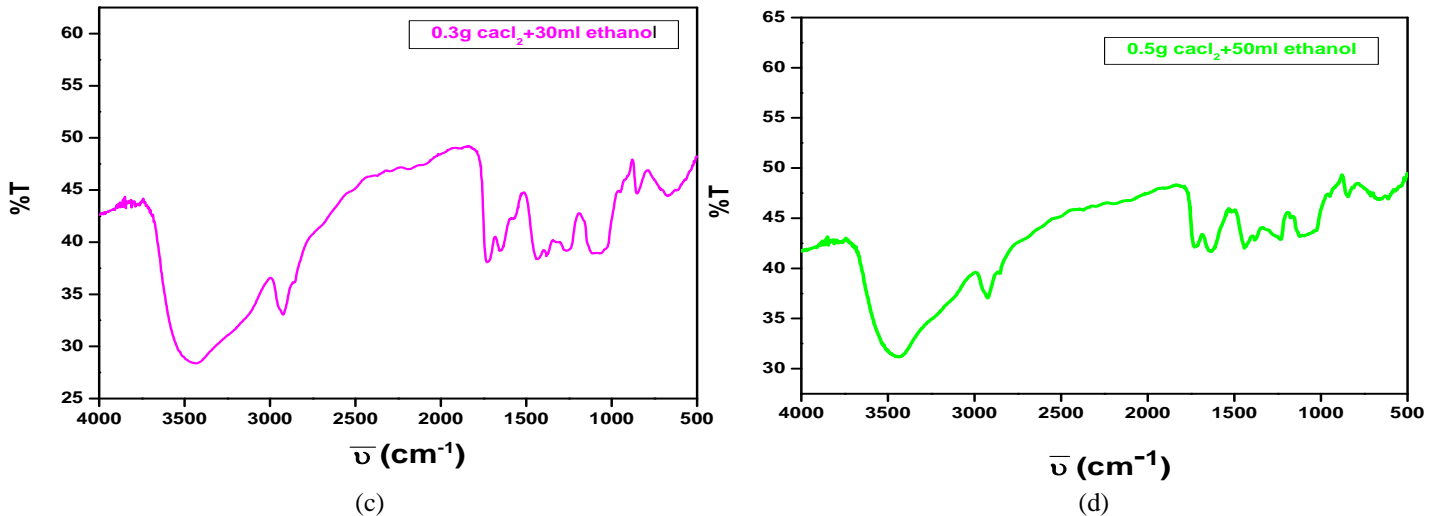
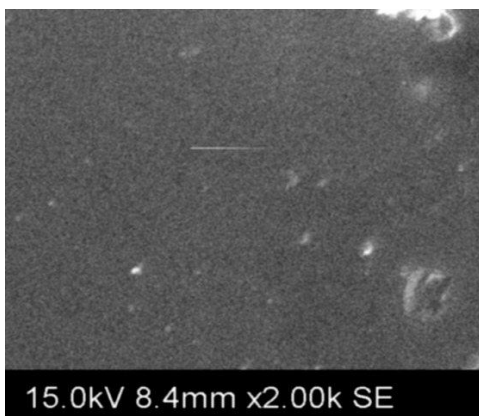


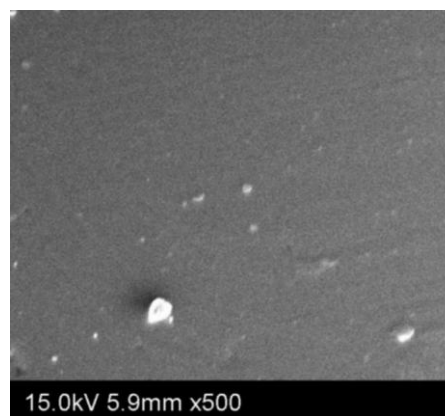
Fig 1. a) FTIR of CS-PVA blend 50-50 b) crosslinking of 50-50 blend with 0.1g CaCl₂ c) crosslinking of blend 50-50 with 0.3g CaCl₂ d) crosslinking of blend 50-50 blend with 0.5g CaCl₂.

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

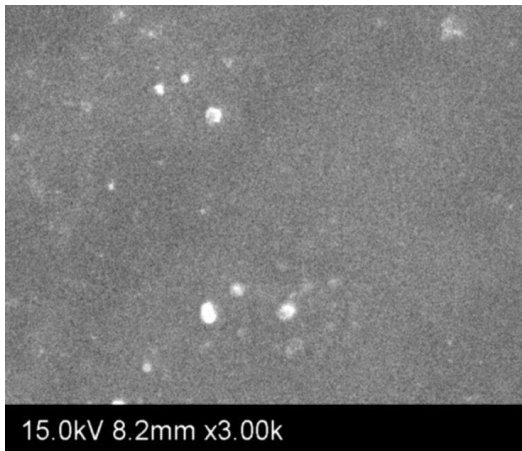
Fig 2 shows the SEM images of surfaces of CS/PVA blended film and its corresponding crosslinked films with calcium chloride as ionic crosslinker. In fig 2 of b and c shows smooth and homogenous surface with some straps or lumps unlike that of (a) and (d) where no straps are seen. The surfaces of the blended film of CS/PVA are homogenous with no pores[29], 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 -NH₂ groups in chitosan and -OH groups in PVA).further, the images b ,c and d shows that the crosslinking is achieved successfully as this completely modified the surface morphology of crosslinked of CS-PVA (50-50) blend.



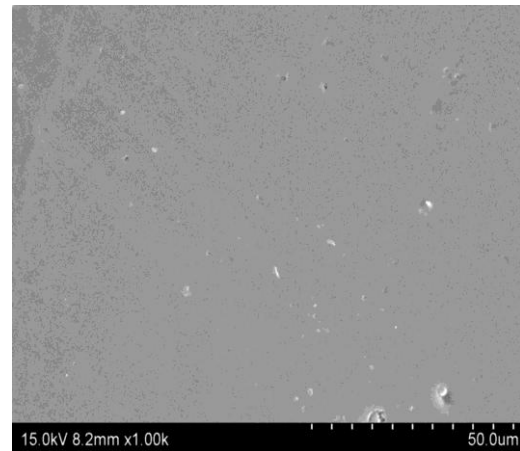
(a)



(b)



(c)



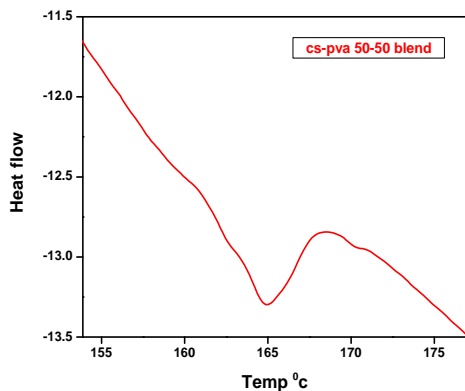
(d)

Fig 2: a) blend of CS-PVA 50-50 b) crosslinked of CS-PVA blend with 0.1g CaCl₂ c) crosslinked of CS-PVA blend with 0.3g CaCl₂ d) crosslinked of CS-PVA blend with 0.5g CaCl₂ .

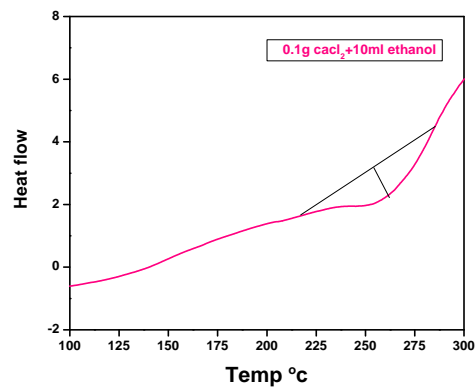
3: THERMAL PROPERTIES:

The Fig 3 of (a) shows DSC curve of Chitosan-PVA blend(50-50), as we can see in figure the melting temperature for blend ratio 50-50 is observed at 165.01°C, when this blend film is ionically crosslinked with 0.1gm of calcium chloride(fig 3 of b) then the melting temperature was observed at 261.84°C. similarly fig 3 of (c) and (d) shows the of CS-PVA blend film crosslinked with 0.3gm and 0.5gm of calcium chloride solution then the melting temperatures again went to higher values and was observed at 266.70°C and 278.21°C [30].

Above results shows that as crosslinking of cacl₂ increases the melting temperature of the blend is increases. This confirms that crosslinked chitosan–polyvinyl alcohol copolymer blend is having more thermal stability when compared to of CS-PVA blend alone.



(a)



(b)

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, Januray 2016

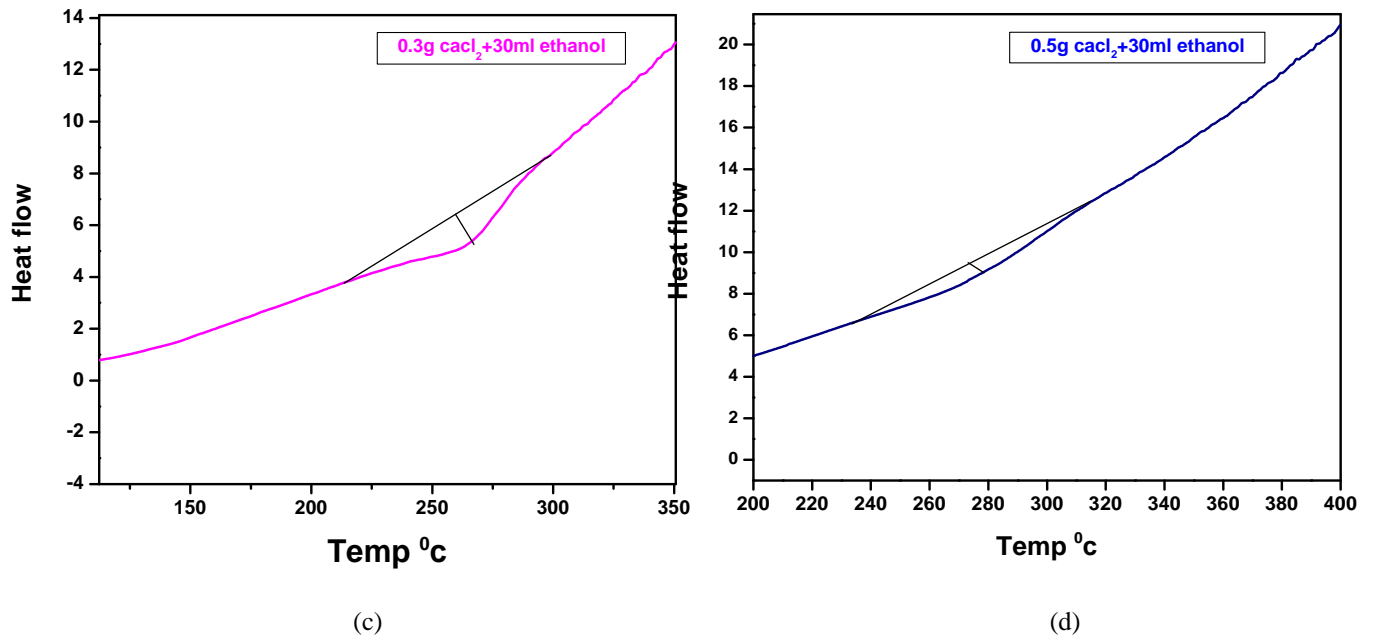


FIG 3: a) DSC curve of CS-PVA 50-50 blend b) DSC of CS-PVA blend with 0.1g CaCl₂ c) DSC of CS-PVA blend with 0.3g CaCl₂ d) DSC of CS-PVA blend with 0.5g CaCl₂

VI. CONCLUSION

Modified CS-PVA blends were prepared using Calcium chloride as ionic crosslinker. Fourier transform infrared spectroscopy of unmodified CS-PVA blend and modified crosslinked blends confirmed the formation of covalent and ionic crosslinking between CS-PVA and calcium chloride. Thus chemically modified Chitosan blends were characterized by FTIR studies, and DSC analysis. The FTIR results pointed out that there is a good molecular miscibility between PVA and chitosan. The thermal analysis of these blends showed improved thermal stability when compared with CS –PVA blend alone. These blends have good adsorption capacity. Since chitosan is recognized as a safe biopolymer suitable for oral administration and its antifungal, antibacterial and antiviral properties; it is very interesting for food industry and the modified chitosan film may be used in packaging applications, and particularly for food preservation applications.

REFERENCES

- [1] L.M. Robeson, Olabisi and M.T. Shaw, Polymer-polymer Miscibility, Academic press, New York, 1979.
- [2] D.R. Paul and L.H. Sperling, Polymer blends, Academic press, New York, 1978.
- [3] L.A. Utracki, Fayt, Jerome, and Ph. Teyssie, Multiphase polymers: blends and ionomers, R.A. Weiss, eds, ACS, Washington D.C., 1989.
- [4] M. J. Folkes, and P. S. Hope, Polymer Blends and Alloys, Blackie Academic & Professionals, London, 1993.
- [5] F. M. Sweeney, Polymer Blends and Alloys-Guidebook for Commercial Products, Technomic, Lancaster, 1988.
- [6] J.L. Angulo-Sanchez and R.D. Short, Polymer, 1995, 3(98), 1559-1567.
- [7] J. Singh, P.K. Dutta, J. Polym. Res. 16 (2009) 231–238.
- [8] R. Jayakumar, R.L. Reis, J.F. Mano, E-Polymers 035 (2006).
- [9] R. Jayakumar, N. Nwe, S. Tokura, H. Tamura, Int. J. Biol. Macromol. 42 (2007) 175–181.
- [10] R. Jayakumar, M. Prabaharan, R.L. Reis, J.F. Mano, Carbohydr. Polym. 62 (2005) 142–158.
- [11] R. Jayakumar, H. Tamura, Asian Chitin J. 2 (2006) 61–68.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, Januray 2016

- [12] R. Jayakumar, H. Tamura, Asian Chitin J. 2 (2006) 91–96.
- [13] C. Caner, J. Sci. Food Agric. 85 (2005) 1897–1902.
- [14] V. Coma, Bioactive Chitosan-based Substances and Films, in: R. Jayakumar, M.Prabaharan (Eds.), Current Research and Development on Chitin and Chitosan in Biomaterials Science, Vol. 1, Research Signpost, Trivandrum, Kerala, India,2008, pp. p.21–51.
- [15] S. Tripathi, G.K. Mehrotra, P.K. Dutta, Asian Chitin J. 4 (2008) 29–361253-1258.
- [16] K Yamada , Chen T, Kumar G, Vesnovsky O, Timmie L D and Payne G F,Biomacromol., 2000, 1, 253-258.
- [17] G R. Mahdavinia , Pourjavadi A, Hosseinzadeh H and Zohuriaan M J, Eur Polym J.,2004, 40, 1399.
- [18] G. Huacai , Wan P and Dengke L, Carbohydr Polym., 2006, 66, 372.
- [19] T. Sun , Xu P X, Liu Q, Xue J A and Xie W M, Eur Polym J., 2003, 39, 189.
- [20] M. Yalpani and Hall L D, Macromol., 1984, 17, 272.
- [21] M K . Cheung ,Wan K P Y and Yu P H, J Appl Polym Sci., 2002, 86,
- [22] N E Suyatma, Copinet A, Tighzert L and Coma V, J Polym Env., 2004, 12(1), 1-6.
- [23] B. Smitha , Dhanuja G and Sridhar S, Carbohydr Polym., 2006, 66, 463-472.
- [24] L. Ma, Gao C Y, Mao Z W, Zhou J, Shen J C, Hu X Q and Han C M. Biomat., 2003,
- [25] R A A. Muzzarelli, and Rochetti R, Carbohydr Polym., 1985, 5, 461-472.
- [26] Y. Huang., Yu H and Xiao C, Carbohydr Polym., 2007, 69, 774.
- [27] A. Chenite , Chaput C, Wang D, Combes C, Busch-mann M D, Hoemann C D, Leroux J,
- [28] A. Polk , Amsden B, De Yao D, Peng T and Goosen M F, J Pharm Sci., 1994, 83, 1
- [29] F. Peng , Pan F, sun, H, Lu L and jiang Z, j Membr Sci., 2007, 300, 13-19
- [30]. S.Raghunadh Acharyulu, T. Gomathi and P. N. Sudha.