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Novel layer-by-layer casting of Chitosan-Alginate edible films

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ABSTRACT
In recent years, there has been remarkable development in edible films and coatings using biopolymers. Edible packaging is usually prepared with natural polymers that are non-toxic, biodegradable & readily available. The advantages such as biodegradability, non-toxicity and improved shelf life have caused edible packaging used widely in food industry. Edible films are synthesized either by direct casting or layer by layer assembly using polysaccharides such as chitosan, sodium alginate, carboxymethyl cellulose, starch, pectin etc. Chitosan based film have tendency to form gel solution when comes in contact with moisture whereas alginate-based films have zero water resistance. The novel feature of the present work is that, it addresses to the experimental studies on layer by layer casting of chitosan and alginate, using glycerol as a plasticizer. Film samples are analyzed for the GSM, functional group presence & water resistance. Based on the observations, result and discussion it can be concluded that, the novel method of the present work involving layer by layer casting of chitosan and alginate have successfully resulted in films with better moisture resistance.
Keywords – Chitosan-Alginate composite film, Edible film, layer by layer, moisture resistance

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I. INTRODUCTION

The growing environmental concerns regarding non-biodegradable plastic packaging materials have increased interest in the use of biodegradable alternatives from renewable sources. In recent years, there has been remarkable development in an edible film and coatings using bio-polymers.[1] An edible packaging film is a continuous layer of edible material formed on, placed on or between the food components. Edible packaging is usually prepared with natural polymers that are non-toxic, biodegradable & readily available. The film forming matrix, solvent, plasticizer and other additives are food grade component. The advantages such as biodegradability, non-toxicity and improved shelf life have caused edible packaging used widely in the food industry. Edible films are synthesized either by direct casting or layer by layer assembly using polysaccharides such as chitosan, sodium alginate, carboxymethyl cellulose, starch, pectin etc.,

Chitosan is a cationic polysaccharide isolated from chitin. It consists of β -1,4-linked polymer of glucosamine (2-amino-2-deoxy- β -D-glucose). It imparts antibacterial property to the packaging film. Alginate is sodium salt of alginic acid, with block copolymer of β- d -mannuronic acid (M) and α- l -guluronic acid (G), and is isolated from brown seaweed.[2] It forms strong, translucent, glossy films. The mechanical strength of the edible film can be improved by using plasticizers as an additive. The present work addresses to the experimental study on alternate layer by layer casting of chitosan and alginate films using glycerol as a plasticizer.

II. LITERATURE REVIEW

The outline of literature survey conducted is given below;

P.K.Dutta et.al, highlighted various preparative methods and antimicrobial activity including the mechanism of antimicrobial action of chitosan-based films by incorporating garlic oil. Chitosan films are prepared by solution cast method. Garlic oil enhances antimicrobial activity of chitosan film and had little effect on mechanical and physical properties of chitosan films.[3]

F. Karimnezhad, V. Razavilar et.al conducted experimental studies on the antimicrobial effects of chitosan-based edible film containing T. ammi essential oil on shelf-life of chicken meat. Chitosan solution was prepared by dissolving chitosan powder in an aqueous acetic acid. T. ammi essential oil was added to homogeneous solution. Tween 80 was used as plasticizer. The pH was maintained at 5.8 using NaOH solution. After drying the films at room temperature for at least 36 h, they were peeled from the plates. All meat samples were surrounded and packaged using the prepared

chitosan based edible films containing the T. ammi essential oil. The films have good potential to enhance the safety and also shelf-life of chicken fillet up to 12 days.[4]

Shekhar L. Pandharipande, Saroj Katekhaye prepared bio composite films by using chitosan, CMC, starch & essential oil. They have prepared ten bio-composite films with varying compositions. Chitosan films were prepared using sol-gel method while chitosan and CMC films were prepared by gel-gel method. The GSM of films synthesized was in the range of 66-72. Anti-microbial test report validates the anti-bacterial property of the film. The tensile strength of film was observed to be 2.853 MPa which can be further increased by addition of other bio-materials like gelatin, lignin, etc. [5]

E Poverenov, S. Danino, B.Horev & Rina Granit, Yakov Vinokur & Victor Rodov reported a study on a layer by layer electrostatic deposition of oppositely charged natural polysaccharides such as alginate and chitosan for coating fruits. Freshly cut melons were dipped into alginate solution followed by $CaCl_2$ wash for crosslinking. Thereafter melons were dipped in chitosan solution and drying is carried out. The firmness of melons was examined and LbL-coated melons were much firmer than uncoated.[6]

Jiawei Yana, Zisheng Luoa reported layer by layer (LbL) electrostatic deposition, based on chitosan and carboxymethyl cellulose. Postharvest strawberries were washed with water. Strawberries were then dipped in 1% chitosan solution and dried. Chitosan layered strawberries were dipped in 1.5% CMC solution and dried for 2 min followed by chitosan solution. Not only did the LbL coating decrease the resistance to environmental stress stimuli from exogenous coating, it also slowed down the primary and secondary metabolism as well as delayed the strawberry senescence during storage.[7]
J. Kim, W. Hong, S. Wook Oh studied the effect of layer by layer electrostatic deposition coating of alginate and chitosan with grapefruit seed extract that was also investigated on the shelf life of shrimp stored for 15 days under refrigeration. Shrimps were dipped in 2w/v% of sodium alginate solution followed by 3% $CaCl_2$ wash for crosslinking and dried for 5 min. In 1.5% chitosan solution 0.25% of grape fruit seed extract is added with tween 80 as plasticizer. Shrimps were dipped in chitosan solution and then air dried at room temperature.[8]

Cristina Bilbao-Sainz, Bor-Sen Chiou studied layer by layer edible coating made by alginate and fungal chitosan that was applied to fruit bars. 1.5 % sodium alginate solution was brushed on grape fruit bars and then immersed in $CaCl_2$ solution followed by 1.5% chitosan solution. Microbiological analyses also showed a delay in yeasts and fungal growth from 28 days for noncoated fruit bars to 31 days for alginate chitosan coating.[9]

III. METHODOLOGY

3.1 Objective

The main objective of the present work is to prepare edible and eco-friendly packaging films. The present work puts emphasis on the use of natural polysaccharides such as chitosan, alginate that make them biodegradable.[10]

3.2 Methodology

The present work is divided into two parts:
I)Preparation of edible films: The films were prepared using biodegradable materials such as chitosan, alginate by direct casting and layer by layer methods. The general methodology is depicted in flow chart as shown in Fig.1.

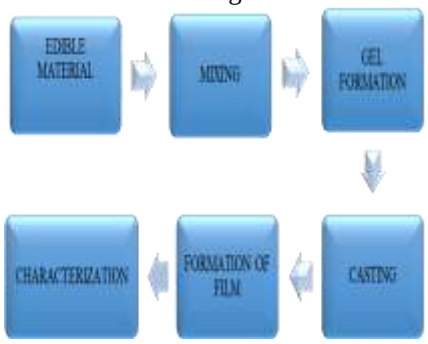

Fig.1 Methodology of present work

II)Analysis of prepared films: Several experimental runs have been conducted and some of film samples were analyzed using Fourier-transform infrared spectroscopy (FTIR) and Gram per meter square (GSM).

3.3 Materials

Following materials and chemicals have been used in present work:

Commercial grade chitosan from HiMedia Laboratories Pvt. Ltd, Sodium alginate from S.d. Fine-chem Ltd., Glycerol, laboratory grade glacial acetic acid, Calcium chloride from Thermo Fisher scientific India Pvt. Ltd., and distilled water.

3.4. Experimental Procedure

Various films have been synthesized using different combinations and proportions of chitosan and alginate with glycerol as plasticizer.

3.4.1 Chitosan edible film preparation:

Commercial grade chitosan (90% deacetylate) was dissolved in 2v/v% acetic acid and heated up to 50-60°C.Glycerol was added to the solution with continuous stirring. The homogeneous solution was allowed to cool down and cast in petri

dish. The film was dried at ambient condition and analyzed using FTIR & GSM.

3.4.2 Alginate film preparation: Sodium alginate solution was prepared by adding sodium alginate to water with gentle heating. Direct casting is carried at ambient conditions. This was followed by 5% $CaCl_2$ wash to the film that leads to gelation by cross-linking alginate COO^- group with Ca^{+2}.

3.4.3 Layer by Layer (LBL) films: LBL films were synthesized by alternately casting solutions of chitosan and alginate as mentioned in the previous section.

The block representation of a formation of LBL edible film is shown in Fig.2

Fig.3 gives the actual photograph of process steps in preparation of the A1 sample.

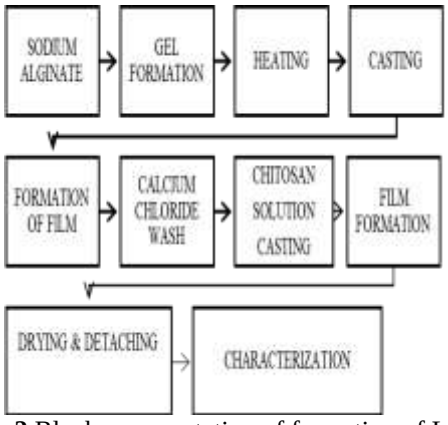

Fig.2 Block representation of formation of LBL films

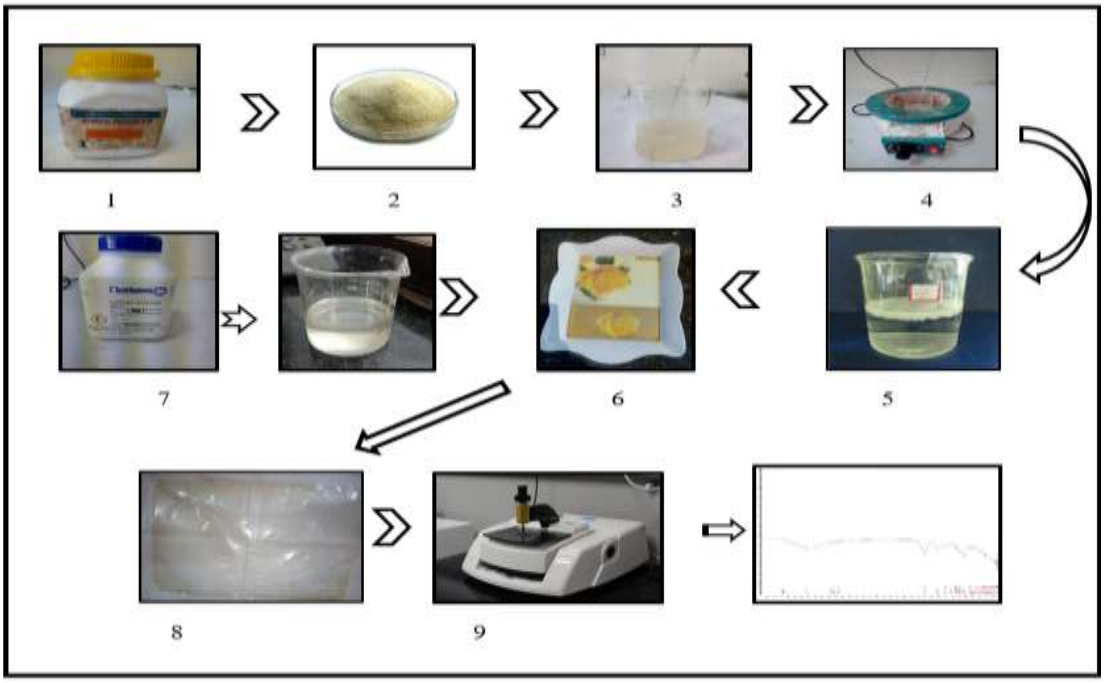

Fig. 3 photographs of process steps for A1 sample

The details of process parameters for various experimental runs are given in Table 1 and photographs of film samples prepared are shown in Fig.4.

3.5 Observation Table

Table 1: Details of the process parameters

Sr. no	Sample code name	Qty of chitosan (g)	Qty of acetic acid (ml)	Qty of Alginate (g)	Qty of water (ml)	Qty of glycerol (ml)	Drying Period (Day)	Remark
1	CH4	1	0.6	---	60	0.3	3	Thin opaque film
2	CH6	0.5	1	---	100	2	3	Transparent film with good texture.
3	A1	---	---	1	40	0.3	10	Transparent film with good strength

4	A2	---	---	5	150	3	4	Partly opaque film with good texture.
5	L2	1.5	2	1.5	250	2	4	Transparent film
6	L3	---	---	1	100	0.5	5	Transparent film with good strength.
7	L4	0.5	2	1	300	4	5	Partially transparent film
8	L5	4	2	4	200	4	2	Opaque film but low foldability
9	L6	1	1	1	100	2	2	Transparent film
10	L7	1	1	0.5	100	1.5	3	Transparent triple layered film
11	L8	0.5	0.5	1	75	1	2	Transparent film with good strength.

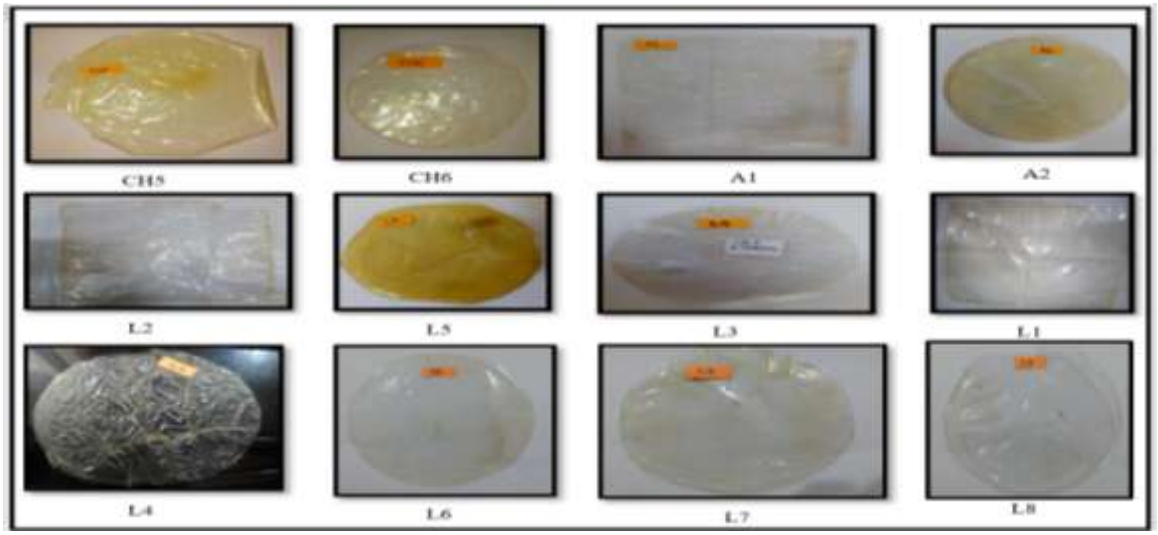

Fig.4: Photographs of film samples.

IV. RESULTS & DISCUSSION

4.1.GSM (g/m^2):

Thickness of the films is calculated using Micrometer having least count of 0.01µm. The details of GSM of various samples are given in Table 2.

Table 2: Details of GSM of films

Sr. No.	Sample name	Thickness in micron	Weight (g)	Area in m^2	GSM= Weight/Area	GSM of Paper	Common use of paper
1	CH6	252	0.516	0.00528	97.72	89-104	Book pages, Note pad
2	A1	360	1.26	0.02100	60	40-60	Tracing paper
3	A2	1080	5.28	0.01583	333.54	325	Book cover, greeting card
4	L3	540	1.16	0.01266	91.62	90	Newspaper
5	L4	360	1.68	0.01431	117.4	118	Poster, Brochures
6	L5	1440	7.51	0.01474	509.49	460-590	Postcards or business card

4.2 Functional group analysis using FTIR:

In order to know the molecular interaction in the film synthesized in the present work, FTIR was carried out for three samples:CH2, A1& L2 and spectra are shown in Fig 5A, Fig 5B, Fig 5C respectively. Comparative study of FTIR spectra of sample CH2, A1 & L2 is given in Table 3 with literature spectra.[11][12]

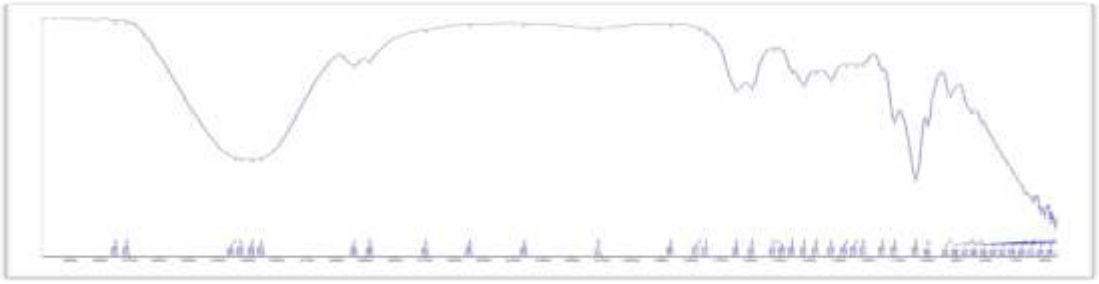

Fig 5A: FTIR spectra of CH2 film

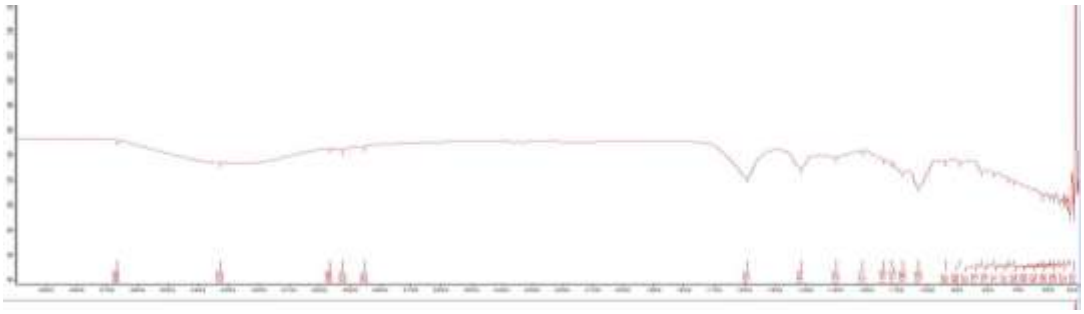

Fig 5B: FTIR spectra of A1 film

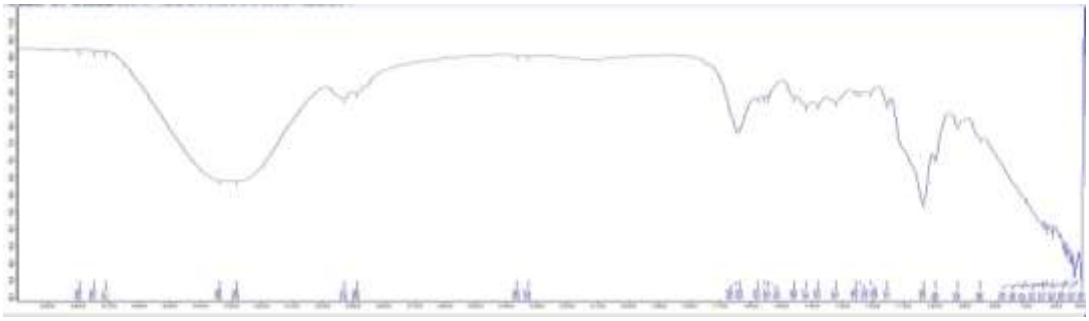

Fig.5C: FTIR spectra of L2 film.

Table 3: Comparative study of FTIR spectra of sample CH2, A1 & L2 with literature references in below table:

Sr. No.	Functional groups		Wavenumber (cm^{-1})				
		CH*	CH2	A*	A1	L2*	L2
1	OH stretching			3500-3100	3325	3338	3423
2	OH/NH Stretching	3361-3291	3341-3253	---	---	---	3338-3284
3	C-H Stretching	2877	2886	2965-2913	2921	2939	2889
4	C=O Stretching	1645	1644	1592	1591	1629	1645
5	N-H Bending	1589	1591	---	---	---	1575
6	CH_2	1423	1456	1416	---	---	1417
7	CH_3 Bending	1373	1374	---	---	---	1379
8	C-N Stretching	1325	1323	---	---	---	1321
10	C-O-C Stretching	1153	1150	965	937	1166	1151
11	C-O Stretching	1066 &1028	1036	1119	1119	1033	1035
9	C-C Stretching	---	---	1018	1026	1033	1035
12	$CaCl_2$	---	---	1294	1297	---	1258

V. CONCLUSION

In the present work several experimental runs are conducted & edible films are synthesized using bio- materials such as chitosan, sodium alginate with varying composition. Some of the films, that are synthesized have been chosen for the GSM & FTIR characterization.

Novel feature of the present work is use of layer by layer casting technique that is planned so as to impart moisture resistance to the films. Based on the result and discussion following inferences can be drawn:

- Chitosan based films are clear, flexible with low strength & with fair moisture resistance
- Alginate based films are labile, opaque with good strength and highly hygroscopic and have tendency to gel formation
- Layer by layer films of Chitosan-Alginate synthesized are labile, have good strength, are transparent & have good moisture resistance.

The present work has demonstrated the potential in layer by layer casting technique in making of Chitosan-Alginate films. However, it is felt necessary to conduct more experimental runs followed by rigorous tests to validate the claims further.

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REFERENCES

[1]. Jeya Jeevahan, M.Chandrasekaran, a brief review on edible food packing materials. Journal of Global Engineering Problems & Solutions, vol. 1, no. 1, pp. 9-19, 2017.

[2]. Subhas C. Shit and Pathik M. Shah, Edible Polymers: Challenges and Opportunities, Journal of Polymers, Volume 2014, Article ID 427259.

[3]. Shipra Tripathi, G. K. Mehrotra, P. K. Dutta, Chitosan based antimicrobial films for food packaging applications, e-Polymers 2008, no. 093.

[4]. F.Karimnezhad, V.Razavilar S. Eskandari, Study the AM effect of chitosan based edible film with trachyspermum ammi EO on shelf life of chicken meat, Microbiology Research 2017; volume 8:722.

[5]. Shekhar L. Pandharipande, Saroj Katekhaye, Synthesis and Characterization of Biocomposite Films using Chitosan, CMC, Starch & Essential oils, International Journal of Innovative Research in Science, Engineering and Technology, Vol. 6, Issue 7, July 2017.

[6]. E. Poverenov, S. Danino, B. Horev, R Granit, Y.Vinokur, V. Rodov, Layer-by-Layer Electrostatic Deposition of Edible Coating on Fresh Cut Melon Model: Anticipated and Unexpected Effects of Alginate–Chitosan Combination, Food Bioprocess Technol, May 2013.

[7]. J. Yana, Z. Luoa, The eff ect of the layer-by-layer edible coating on strawberry quality and metabolites during storage, Postharvest Biology and Technology, Volume 147, January 2019, Pages 29-38.

[8]. J. Kim, W. Hong, S. Wook Oh, Effect of layer-by-layer antimicrobial edible coating of alginate and chitosan with grapefruit seed extract for shelf-life extension of shrimp stored at 4 °C, International Journal of Biological Macromolecules Volume 120, Part B, December 2018, Pages 1468-1473.

[9]. Cristina Bilbao-Sainz, Bor-Sen Chiou, Layer-by-Layer Alginate and Fungal Chitosan based Edible Coatings Applied to Fruit Bars, Journal of Food Science Vol.0,2018.

[10]. Rajashri. D. Turak, Edible films for packaging, Project report stage-I, Department of chemical engineering Laxminarayan institute of Technology, RTMNU Nagpur, India.

[11]. S Gokila, T. Gomathi., et al. "Removal of the heavy metal ion chromiuim(VI) using Chitosan and Alginate nanocomposites" 2017.

[12]. A.Sadiq et.al. Biosorption of chromium ions by calcium alginate nanoparticles. J. Chil. Chem. Soc., 63, 2018.