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SYNTHESIS AND CHARACTERISATION OF BIOCOMPOSITE FILMS OF CHITOSAN AND LIGNIN

S. L. Pandharipande *, Nisha Pujari, Kaustubh Deshmukh
* Chemical Engineering Department, Laxminarayan Institute of Technology, Nagpur, India

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ABSTRACT

Chitin is one of the most widespread biopolymer found in nature. Shells of crustaceans such as prawns, crabs and lobsters are the main commercial sources of chitin. Chitin can be processed into chitosan, another, having varied industrial and biomedical significance. Lignin is another biomaterial, usually generated from agricultural waste and paper industry. The present work aims at synthesising chitosan from prawn shell and extracting lignin from wheat straw. It is further extended to form biocomposite films using these biomaterials by solution-casting technique. Appropriate analytical tests have been conducted like FTIR, SEM and tensile strength to study functional groups present, surface morphology and mechanical strength of the biomaterials synthesised and biocomposite films formed. The present work has successfully synthesised chitosan from crustacean shells and lignin from wheat straw. The results of analysis are encouraging & indicative of potential of lignin-chitosan biocomposite films specially in packaging of food material and in wound dressings. Use of lignin will reduce chitosan quantity and there by cost. It also utilises waste materials like crustaceans shell & wheat straw successfully in developing value added products chitosan and lignin.

KEYWORDS: Chitosan, Lignin, Prawn shells, Wheat straw, Chitosan-Lignin Biocomposite.

INTRODUCTION

The shell and head portions of prawns, shrimps and lobsters are generated as wastes, during the processing [1]. Although these wastes are biodegradable, it is comparatively slow. Extraction of commercially viable substances and conversion into value added seems to be the immediate solution to this problem [2].

Chitin and Chitosan

Chitin is the second most abundant natural, stable and biodegradable biopolymer after cellulose [3]. It is a long-chain polymer of N-acetyl D-glucosamine and derivative of glucose. Chitin is poly-β-(1-4)-N-acetyl-D-glucosamine as shown in Fig.1.

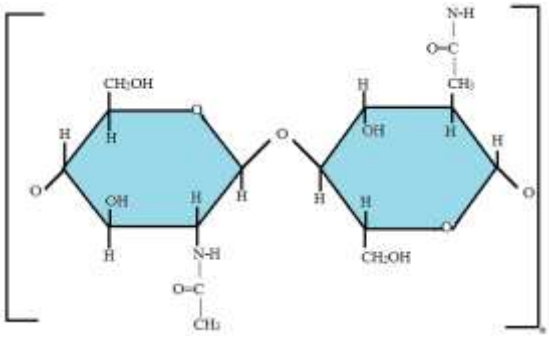

Fig.1: Molecular structure of Chitin

Although Chitin itself being insoluble in water, a valuable chemical substance, on deacetylation yields chitosan, having a wide range of viable uses, which is soluble under acidic conditions [4].

Chitosan is obtained by removing enough acetyl groups (CH3-CO) from chitin. The acetyl content of the polymer is the actual difference between chitin and chitosan. Chitosan is a co-polymer of glucosamine and N-

acetylglucosamine units with 1–4 glucosidic bonds. It is a natural carbohydrate biopolymer derived by N-deacetylation of chitin. Chitosan is poly-β-(1-4)-D-glucosamine as shown in Fig.2 [5].

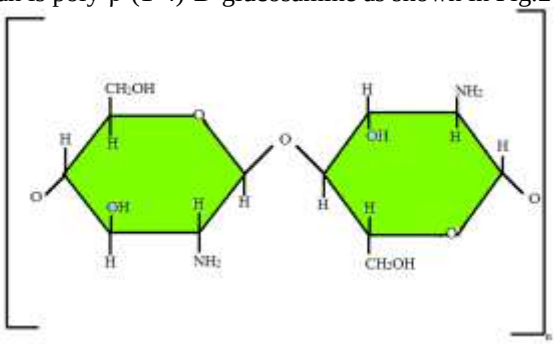

Fig.2: Molecular structure of Chitosan

LIGNIN

Lignin is an amorphous, cross-linked and an aromatic polymer which is a waste by product of paper and pulp industries [6]. According to sources, about 40 to 50millon tons per annum of lignin are generated worldwide as mostly non commercialized waste product [7]. It acts as a *glue* that connects cellulose and hemicellulose and is insoluble in water. Wide sources of lignin are available such as wood pulp, jute, hemp and can also be extracted from non –wood cellulosic biomass such as kenaf, alfalfa etc. Due to its physical and chemical properties, lignin is used widely to alter properties of product [8]. The areas where lignin is applicable include dyes, additives, batteries, cement, food additives and thermosets.

The present work is based on synthesis and characterisation of chitosan and is presented in sections. The first section gives introduction to chitin and chitosan synthesised from crustacean shells followed by a brief literature review of the related papers published. The next section gives the objective of the present work and methodology that includes experimental setup, procedure & observations. The quality of chitosan synthesised in present work is evaluated using analytical methods FTIR and SEM. The detailed interpretation of the functional groups of chitosan and structural morphology have been discussed in result and discussion. The paper also focusses on the extraction of lignin from wheat straw by organosolv technique and formation of a biocomposite film by blending chitosan with lignin. The functional group and mechanical properties of film have been determined by FTIR and tensile strength. The paper concludes highlighting the findings of the present work and indicating the possible areas of further work that need to be explored.

LITERATURE REVIEW

Abhrajyoti Tarafdar & Gargi Biswas [1] performed the extraction of chitosan from prawn shells. This study highlighted the antimicrobial properties of chitosan, having properties against gram negative bacteria as compared to gram positive bacteria. The outcome of the work was in finding that antimicrobial property is dependent on degree of deacetylation. Musarrat H. Mohammed, Peter A. Williams et.al. [4] performed the extraction of chitin and chitosan from prawn shells. Effects of various parameters such as NaOH concentration, temperature and reaction times on the deacetylation process were investigated. F. Nessa, Shah Md. Masum et.al. [5] reported the effect on physiochemical and functional properties by the deacetylation process of chitosan production. V. Mohanasrinivasan, Mudit Mishra et.al. [9] studied the adsorption properties and degree of deacetylation of the prepared chitosan. Divya K, Sharrel Rebello and Jisha M S [10] synthesised chitosan with degree of deacetylation upto 85%. Anshar Patria [11] produced chitosan with a yield which ranged from 50.39 to 88.25 % with average of 67.42 %, while the chitin yield was 40 %. Sumathi, S., Hamsa, D. et. al. [12] focused on the isolation of chitin from the prawn shell and its conversion to chitosan. Chitosan thus synthesised was characterized using FTIR and was also proved to possess antimicrobial activity.

Dereca Watkins, Md. Nuruddin et. al. [8] extracted lignin from non-wood cellulosic biomass by formic acid treatment followed by peroxyfomic acid treatment. The isolated lignin were characterized by FTIR, TGA, and DSC to compare thermal properties and chemical composition .It was found that lignin extracted from wheatstraw had the greatest thermal stability. J. Zhang, Haibo Deng et. al. [13] extracted lignin from dewaxed wheatstraw using H_2SO_4 as catalyst and formic acid as a solvent at different residence time and reaction temperature .The obtained lignin was characterized and the results indicated that oxidative cleavage of bonds in lignin macromolecule has occurred during formic acid treatment. Feng XU, Jin-Xia Sun et. al. [14] treated wheat straw (dewaxed)with acetic acid –water taking different compositions, formic acid-acetic acid –water, methanol-water

and ethanol-water using 0.1%HCl as a catalyst for extraction of lignin. The lignin obtained were characterized by their content of hemicellulose, composition of phenolic acid and aldehydes. The results showed that aqueous organic acid was more effective than aqueous organic alcohol. Also, addition of formic acid gave a significant effect on dissolution of lignin.

Long Chen, Chang-Yu Tang et. al. [6] prepared biodegradable composite films based on chitosan and lignin by varying their compositions by solution casting technique. It was seen that mechanical and thermal properties of chitosan films were enhanced largely by addition of lignin. Vaishakh Nair, Ajitesh Panigrahy et. al. [15] prepared and characterised chitosan-alkali lignin composite films which proved to be effective in treating wastewater.

MATERIALS AND METHODS

Objective

The objective is to prepare biocomposite films of chitosan and lignin. It aims at synthesis of chitosan & lignin from prawn shell & wheat straw respectively followed by formation of chitosan-lignin films. The characterisation is done to validate the claim of synthesis & possible area of application.

Methodology

The schematic representation for lignin extraction and chitosan synthesis have been shown in Fig. 3.

Materials

Prawns were obtained from Mumbai local market. Laboratory grade hydrochloric acid, sodium hydroxide, formic acid, acetic acid and hydrogen peroxide were used. Wheat straw was procured from local market.

Experimental Procedure

Synthesis of Chitosan

Prawn shells were removed manually, washed with water and solar dried for 48 hrs followed by oven drying at approximately 60^{o}C for 1 hr. 10 grams was crushed in mortar and pestle to about 2-4 mm average particle size. Demineralisation of prawn shell flakes was carried out using dil. HCl acid. Demineralised shell powder was washed with water and further processed with dil NaOH. This step is called as deproteinisation, wherein chitin is produced. Deacetylation of chitin synthesised was carried out using conc. NaOH, leading to formation of chitosan. The details of process parameter & yield obtained are given in Table 1.

Extraction of Lignin

Wheatstraw was oven dried for 3 hours at 45 ºC. The dried biomass was first cut into aprrox.1 cm length pieces & then using mixer it was crushed into small size using grinder. A mixture of 85% organic acid (ratio of formic acid to acetic acid as 70:30 by volume) was added to biomass in the ratio1:8. The entire mixture was subjected to heat treatment for a time period of 2 hours at 80 ºC. The mixture was cooled at ambient conditions followed by filtration of fibres and washing with water. The entire process is known as pulping. The treated pulp was further delignified

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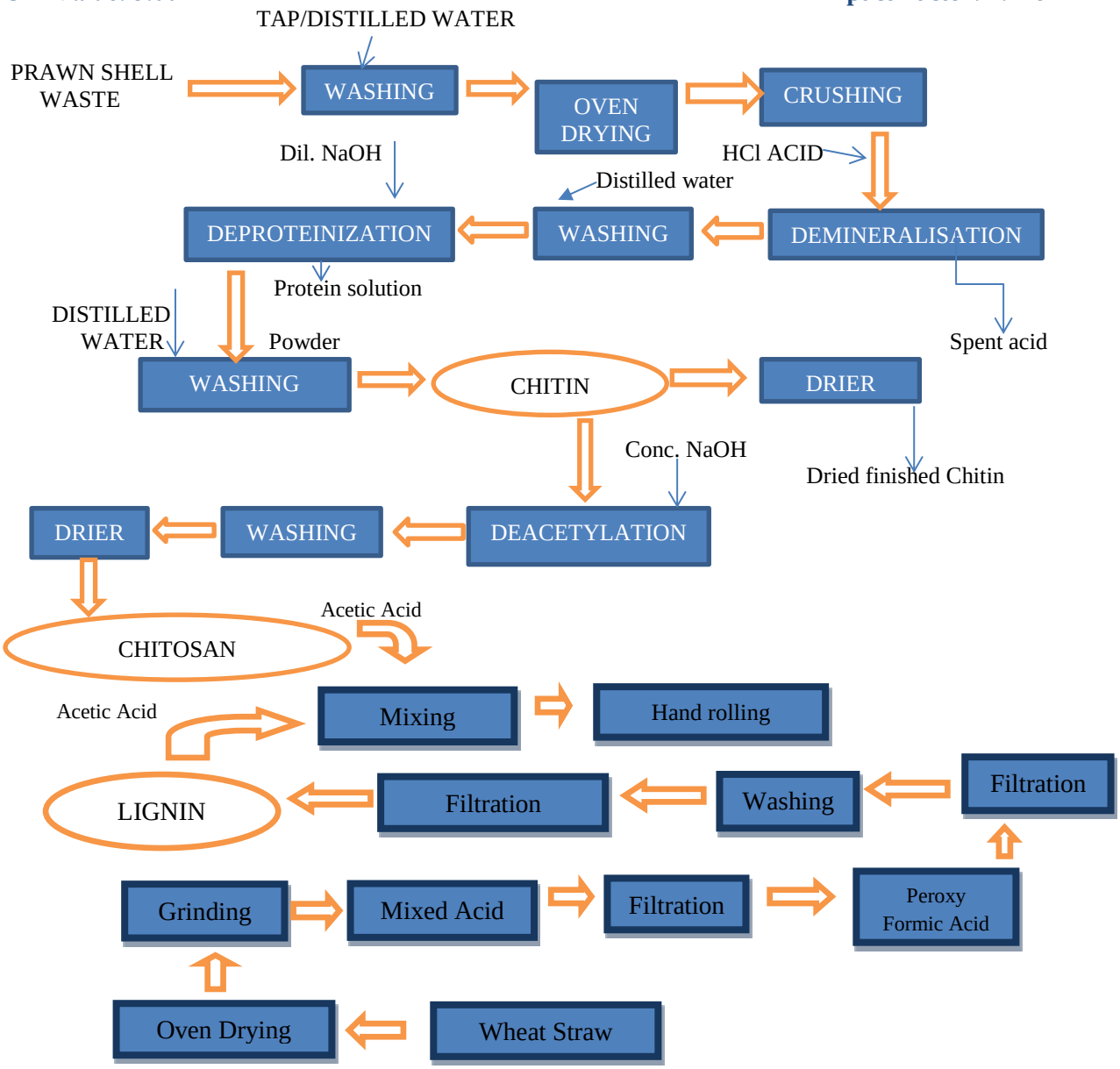

Fig. 3: Schematic representation for lignin extraction & chitosan synthesis

by using a mixture of peroxyformic acid/ peroxyacetic acid solution (PFA/PAA) at 45°C for 2 hours. PFA/PAA solution mixture was prepared by adding 10 ml 15% hydrogen peroxide with 85% formic acid /acetic acid mixture. The lignin dissolved in formic acid was precipitated by adding water to a volume ratio of 1:5 water. The lignin was then allowed to settle for a time span of 48 hours followed by filtration using Whatman filter paper.

Preparation of Biocomposite films

Known quantity of chitosan gel was prepared by dissolving synthesised chitosan flakes in 3% acetic acid. Known quantity of lignin which was extracted from wheatstraw was mixed with known quantity of acetic acid solution to form a mixture. These two mixtures were stirred for about 30 minutes. The composite mixture was hand rolled on plastic sheet & kept at ambient conditions for 12-13 hours. The picture of biofilm sample CL2 has been given in Fig. 4. Details of parameters in formation of biocomposite films CL1 & CL2 are given in Table 2.

Fig. 4: Picture of biofilm sample CL2

Observations

Observations for synthesis of chitosan

The details of the observations and process parameters are given in Table 1. Four samples of chitosan have been synthesized.

Table 1. Details of process parameter and yield obtained

SN	WS	S	Demineralisation				Deproteinisation				CN	Deacetylation				CS
			T	C	t	R	T	C	t	R		T	C	t	R	
NS1	10	Whole	R.T	5.6	2	1:10	60-90	4	1	1:15	4	120	50	1	1:15	1
NS2	10	Whole	R.T	5.6	2	1:10	60-90	4	1	1:15	4	120 + 70-75	50	0.5 + 1	1:22.5	1.49
NS3	10	2-4	R.T	4.5	2	1:10	R.T	4.5	24	1:10	3	R.T	60	48	1:24	2
NS4	10	2-4	50	4.5	1	1:10	90-100	4.5	1	1:10	3	80	45	1	1:26	1.87

SN: Sample Name, WS: Weight of shell in grams, S: Size of crushed shells in mm, T: Temperature in °C, C: Concentration in %, t: Time in hours, R: Ratio in w/v, R.T. : Room temperature, CN: Chitin produced in grams, CS: Chitosan produced in grams.

Observations of Chitosan-Lignin film preparation

The details of the observations and process parameters are given in Table 2.

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Table 2. Details of process parameter of biocomposite films

Sr. No.	Film Code	Chitosan	Lignin	Concentration of acetic acid (v/v %)
1	CL1	0.8 grams	0.2 grams	50%
2	CL2	0.5grams	0.347grams	40.54%

RESULTS AND DISCUSSION

Based on the visual obsevations one sample has been identified for further analysis using FTIR and SEM. Similarly raw prawn shell powder and commercial chitosan have also been analysed. The details of yield obtained and gel formation property of chitosan synthesised is given in table 3.

Yield and Gel formation

The experimental yield of samples and the gel formation characteristics of chitosan are given in Table 2. 0.25g chitosan was taken with 12.5 ml acetic acid (3% w/v) for gel solution.

Table 3. Yield and gel formation of chitosan

Sr. No.	Sample Name	Yield on basis of chitin (%)	Overall yield (%)	Gel formation
1	NS1	25	10	Yes
2	NS2	37.25	14.9	Yes
3	NS3	66.67	20	Yes
4	NS4	62.33	18.7	Yes

The details of analytical methods are given in the following sections.

FTIR analysis

Fig.5 to Fig. 8 show the graphs plotted between % transmittance and wave number for samples NS1, commercial chitosan sample NSC1, raw prawn shell sample NSR1 and chitosan-lignin biofilm sample CL2 respetively.

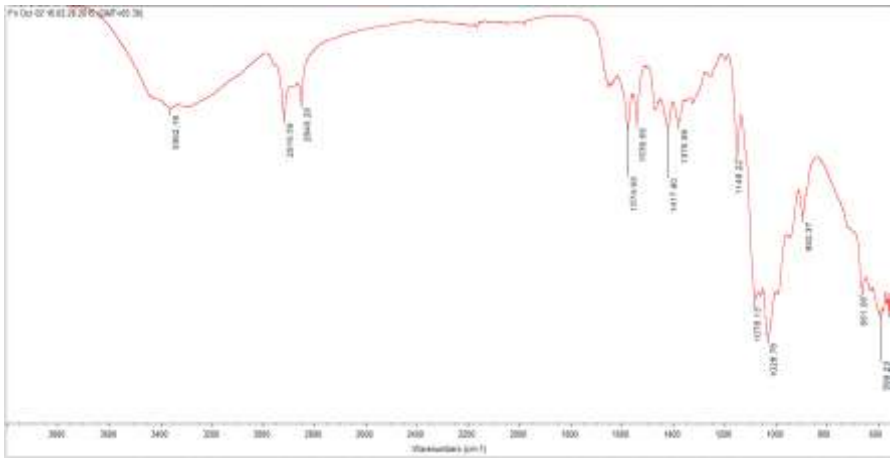

Fig. 5: FTIR spectrogram of sample NS1

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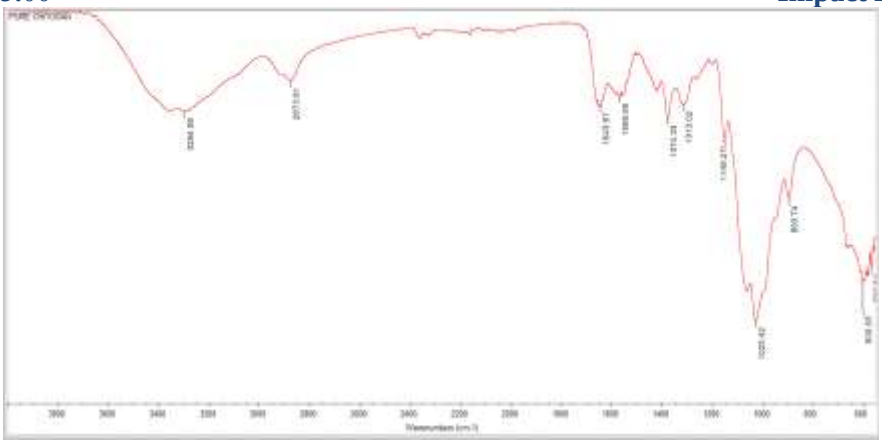

Fig. 6: FTIR spectrogram of sample NSC1

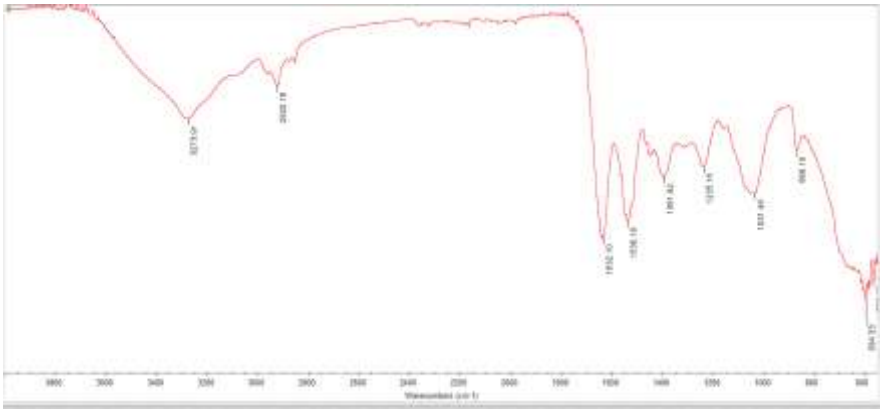

Fig. 7: FTIR spectrogram of sample NSR1

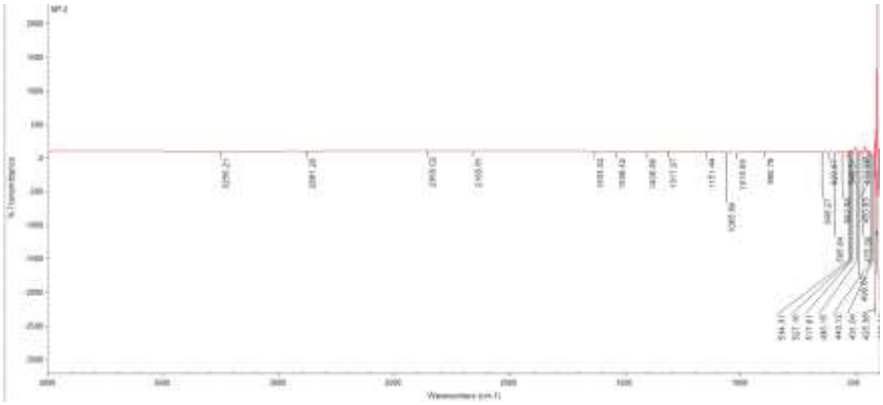

Fig. 8: FTIR spectrogram of sample CL2

The FTIR analysis shows the presence of certain functional groups. The FTIR interpretation of the samples NS1, NSC1, NSR1 and CL2 are shown in Table 4.

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Table 4. FTIR interpretation of the samples.

Sr. No.	Functional groups	Wave number (cm^{-1})				Wave no. identified from literature (cm^{-1})	Ref. No.
		NS1	NSC1	NSR1	CL2		
1.	OH and NH stretching	3362.18	3294.28	3359.37	3256.21	3450.65	5
	C-H stretching	-	-	-	2881.29	-	17
2.	CH3	2916.56	-	2920.18		2924.09	5
3.	CH2	2849.26	2873.81	-	-	2835-2890	5
	Si-H stretching	-	-	-	2160.81	2100-2250	17
4.	Vibration of amide I band	1574.93	1643.87	-	-	1629.85	5
5.	NH deformation	1539.69	1566.65	1536.19		1552	16
	C=C stretching vibrations	-	-	-	1635.52	1580-1660	17
	C=O stretching vibrations	-	-	-		1620-1640	17
6.	Amide I stretching of C=O	-	-	1632.10		1654	16
	CN stretching vibrations	-	-	-	1538.42	1530-1600	17
7.	CH deformation vibration	1376.99	1374.33	1391.92	1406.86	1375	16
	O-H deformation vibration	-	-	-	1317.07	1310-1410	17
8.	C-O-C	1148.22	1149.21	1265.16	1151.44	1150-1040	17
9.	C-O stretching vibration	1078.13	1025.42	1031.49	1015.69	1020-1060	17
10.	C-C	589.23	600.93	594.33	440.12	445-570	17
11.	CH_3-metal group	892.37	893.74	868.10	896.78	800-900	17

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SEM Analysis

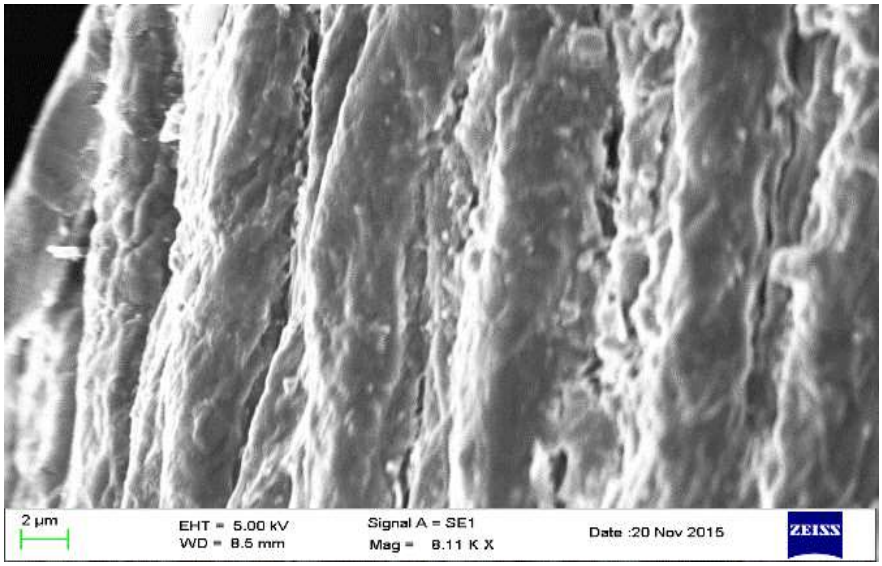

Fig. 9: SEM image of sample NS1

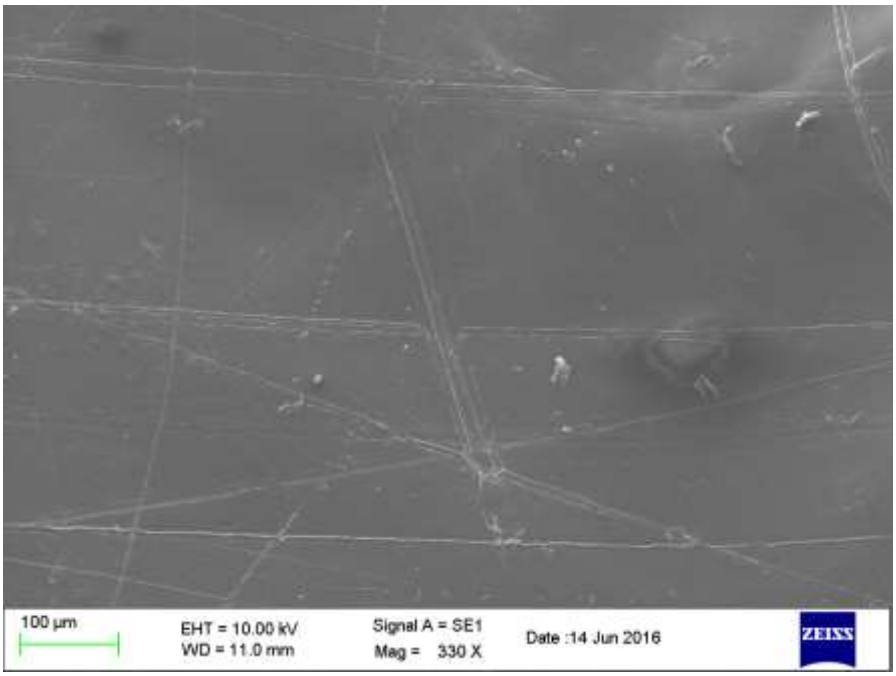

Fig. 10: SEM of sample CL1

Fig. 9 and 10 give images of SEM analysis of samples NS1 & CL1 respectively. The SEM analysis is to study the surface smoothness and homogeneity of the sample. The interpretation for the samples NS1 & CL1 synthesis in present work have been shown in Table 5.

Table 5. SEM interpretation of the samples.

Sr. No.	Sample Name	Interpretation
1	NS1	Long thin fibrous structure, Non-homogeneous and non-smooth surface structure
2	CL1	Long thin fibrous structure, non –smooth surface with ripples. a very good interfacial adhesion is evidenced between lignin and chitosan

Tensile Strength

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Table 6 shows the ultimate tensile strength of film sample CL1.

Table 6. Ultimate Tensile Strength of chitosan-lignin biofilm sample CL1

Sr. No	Sample	W (mm)	T (mm)	CSA (mm^2)	P (KN)	U.T.S (N/mm^2)	U.T.S from literature review (N/mm^2)	Ref. no.
1.	CL1	16.0	0.07	1.12	0.016	14.375	23.3	6

The sample CL1 is comparatively lower value of tensile strength than the reported values in previous papers. The difference may be due to ratio of the two composite materials.

CONCLUSION

Chitosan is a biodegradable, stable and commercially valuable product. The quality and physicochemical properties of chitosan vary widely with crustacean species and methods of preparation. The present study indicates that chitosan have been successfully prepared from prawn shells. The interpretation of analytical methods FTIR and SEM along with gel formation property of the prepared chitosan validates the claim. Biofilms formed of chitosan-lignin i.e. CL1 and CL2 are have found to possess nearly similar tensile strengths as that reported in previous papers. These biofilms have possible applications in packaging field of sensitive materials. Chitosan being of higher cost, its biocomposite with lignin, which is a low cost natural product, would lower down the cost of biocomposite films formed. To this is an added advantage that the waste products like crustacean's shells and blending it with another waste product lignin, is proper utilisation of such materials into useful applications. These biofilms have been analysed for functional group presence, surface morphology and mechanical property using FTIR, SEM and tensile strength respectively.

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