

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 7, July 2017

Synthesis and Characterization of Bio-composite Films using Chitosan, CMC , Starch & Essential oils

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ABSTRACT: The increase in number & variety of food products has drawn attention of manufacturers, government regulatory bodies & consumers towards food storage, packaging & safety of these products. Researchers are also channelizing their energy & efforts in development and testing of newer packaging materials such as bio-composite films having antimicrobial properties. Bio-materials like chitosan, carboxymethyl cellulose, starch, etc. are some of the potential materials having necessary properties that include biodegradability, biocompatibility, antimicrobial activity & non-toxicity. The present work aims at synthesis & characterization of thin films of bio-composites made from chitosan and starch or carboxymethyl cellulose as base materials blended with essential oils such as eucalyptus, lemongrass, etc. Besides food product preservation and packaging, there could be other possible applications of these bio-composite films in pharmaceutical industry.

KEYWORDS: Bio-composite films, chitosan, carboxymethyl cellulose, essential oils.

I.INTRODUCTION

Bio-composite is the material synthesized from two or more constituent bio materials having biological origin. These materials are combined to form a new material which often show the similar properties of the materials which are involved in the making process. The bio-materials used in the present work are chitosan, carboxymethyl cellulose, starch, essential oils like eucalyptus oil, lemongrass oil, oleoresin, etc.

Chitosan is a polymeric compound composed of acetylated unit and de-acetylated unit made by treating chitin shells obtained from shrimps and other crustaceans with alkaline substance like sodium hydroxide. Starch is a composition of a large number of glucose units. It is present in large amounts in the food grains like wheat & rice. The other important sources are corn & potatoes. Carboxymethyl cellulose (CMC) is the cellulose derivative containing carboxymethyl groups ($-\text{CH}_2\text{-COOH}$) and some hydroxyl groups. It is formed by alkali-catalyzed reaction of cellulose with chloroacetic acid. Eucalyptus oil is the concentrated hydrophobic liquid obtained from eucalyptus plant. Similarly lemongrass oil and oleoresins are obtained from lemongrass plant and chilies. Essential oils are added to further enhance antimicrobial properties.

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II. LITERATURE REVIEW

The outline of literature survey conducted is given below;

Saranya Sugumar, Amitava Mukherjee, and Natarajan Chandrasekaran [1] prepared films from chitosan and eucalyptus using nano-emulsification method. P.K. Dutta, Shipra Tripathi, G.K. Mehrotra, Joydeep Dutta [3] highlighted various preparative methods and antimicrobial activity including the mechanism of the antimicrobial action of chitosan based films. P.A.S.R. Wickramarachchi, I.N. Samaratunge, C.H.T.C. Kaushalya, W.P.M. Rasangika and P.A. Paranagama [4] reported a paper based on the in vitro antimicrobial activity of *Alpinia malaccensis* rhizome oil incorporated into chitosan films. Ioannis Liakos, Loris Rizzello, David J. Scurr, Pier Paolo Pompa, Ilker S. Bayer, Athanassia Athanassiou [5] presented natural polymeric composite films made of essential oils (EOs) dispersed in sodium alginate (NaAlg) matrix, with remarkable anti-microbial and anti-fungal properties. Osvaldo Vega, Juan J. Araya, Max Chavarria Erick Castello'n [6] prepared a film using cinnamon oil and for the design of antibacterial materials comprising hybrid silica-containing plant oils capable of performing a controlled release of essential oil components. Y. Ruiz-Navajos, M. Viuda-Martos, X. Barber, E. Sendra, J. A. Perez-Alvarez, J. Fernandez-Lopez [7] aimed at developing edible films prepared using chitosan added with essential oils obtained from two *Thymus* species, *Thymus moroderi* (TMEO) and *Thymus piperella* (TPEO) and their applications in increasing shelf life of cooked cured ham (CCH) stored at 4 °C during 21 days by imparting antioxidant and antimicrobial properties in the films. Jahit, I.S., Nazmi, N.N.M., Isa M.I.N. and Sarbon, N.M. [8] examined the variation of drying temperatures on the physical properties of different formulations of gelatin/CMC/chitosan composite films.

III. MATERIALS & METHODS

1. Objective

The main objective of present work is to prepare bio-composite films made from renewable resources with possible areas of applications in pharmaceuticals and food packaging. The present work puts emphasis on the use of bio-materials such as chitosan, starch and carboxymethyl cellulose in preparation of bio-composite films. To further enhance the antimicrobial properties of films essential oils such as eucalyptus oil, lemon grass oil, oleoresins are to be tried.

2. Methodology

The present work is divided into following parts;

2.1 Preparation of bio-composite films

The films were prepared by using sol-gel process. The general methodology is depicted in flow chart in following fig-1. Bio-composite films having varying proportions of combinations of bio-materials mentioned in observation table have been prepared.

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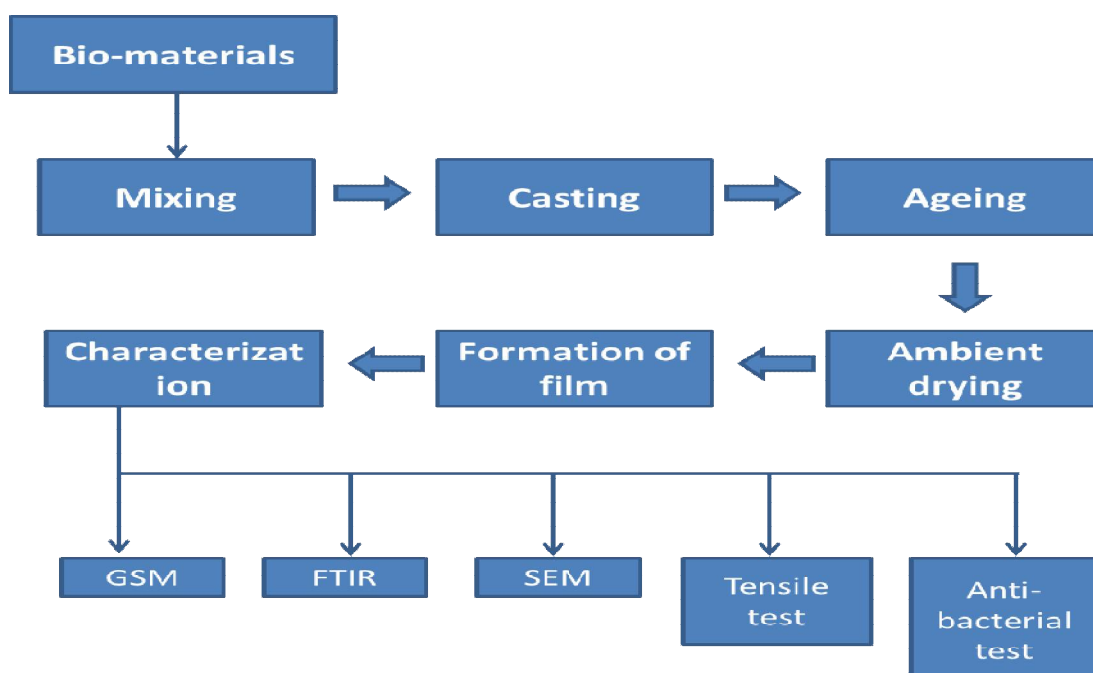


Fig.1 The general methodology of present work

2.2 Analysis of prepared films

Characterization of films were carried out which includes GSM, FTIR (Fourier transform infrared spectroscopy), SEM (Scanning electron microscopy), Tensile test, Anti-microbial test.

3. Materials

Commercial grade chitosan, chili extract [2], eucalyptus oil from Allin Exporters, lemon grass oil from Allin Exporters, laboratory grade starch, laboratory grade carboxymethyl cellulose (CMC), laboratory grade glacial acetic acid, distilled water, commercial grade glycerin.

4. Experimental Procedure

Various bio-composite films have been synthesized using different combinations and various proportions of chitosan, starch or carboxymethyl cellulose with essential oils i.e. eucalyptus oil, lemon grass oil, chili extract. Hence procedure is divided into three parts as follows;

Part-A Chitosan-essential oil film preparation

Part-B Chitosan-starch-essential oil film preparation

Part-C Chitosan-CMC-essential oil film preparation

Part-A -The procedure of part-I is as follows;

- Chitosan gel formation: Chitosan gel was prepared by taking known amount of chitosan and water. Few drops of acetic acid were added and the mixture is stirred continuously at slightly elevated temperature around 50-60 ° C to get the homogeneous gel.
- Nano-emulsion formation: It was prepared by taking known quantity of oil water mixture in air tight bottle. The bottle was shaken vigorously till formation of emulsion.
- Sol-gel formation: The nano-emulsion was added to gel and the sol-gel mixture was stirred. The resulting mixture formed is sprayed on plastic film. The sprayed mixture was dried in ambient conditions to form film.

Part-B: The procedure of part-B is similar to the part-A. Instead of nano-emulsion, starch solution was used.

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Part-C: The procedure of part-C includes gel-gel formation. Chitosan gel and the CMC gel were formed. Chitosan gel is prepared as per given in the procedure of part-A. CMC gel was prepared by taking known amount of CMC and water. The mixture was stirred continuously at slightly elevated temperature around 30-50° C to get the gel mixture. The schematic of procedure followed is shown in fig.2.

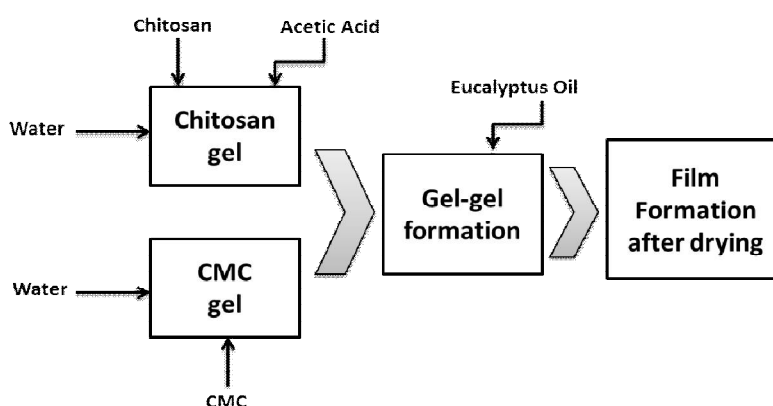


Fig.2 Schematic diagram of chitosan-CMC-essential oil film (CCmE)

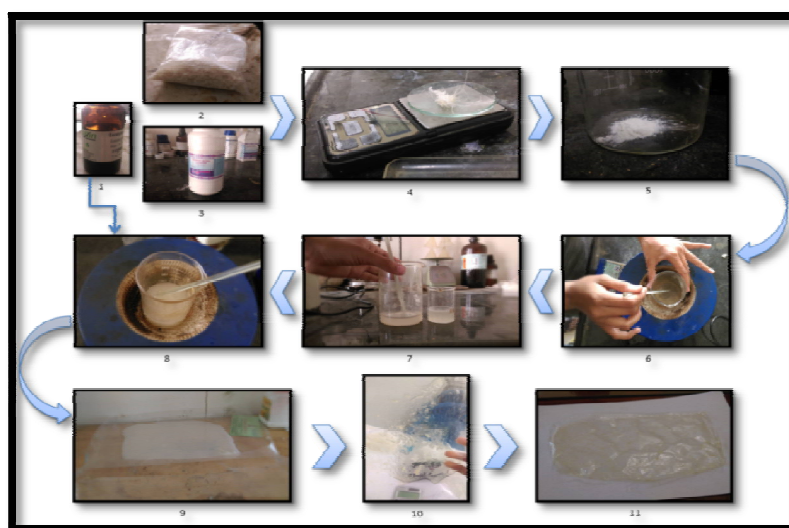


Fig. 3 Photographic representation of chitosan-CMC-essential oil film

The photographic representation of process steps given in fig-3.are-

1. Eucalyptus Oil, 2. Chitosan, 3.CMC, 4.Weighing of bio-materials, 5.Transferring to beaker, 6.Gel formation,
7. Chitosan and CMC gel, 8.Gel-gel formation, 9. Spreading the mixture on plastic film tray, 10.Film formation after drying, 11.Final product.

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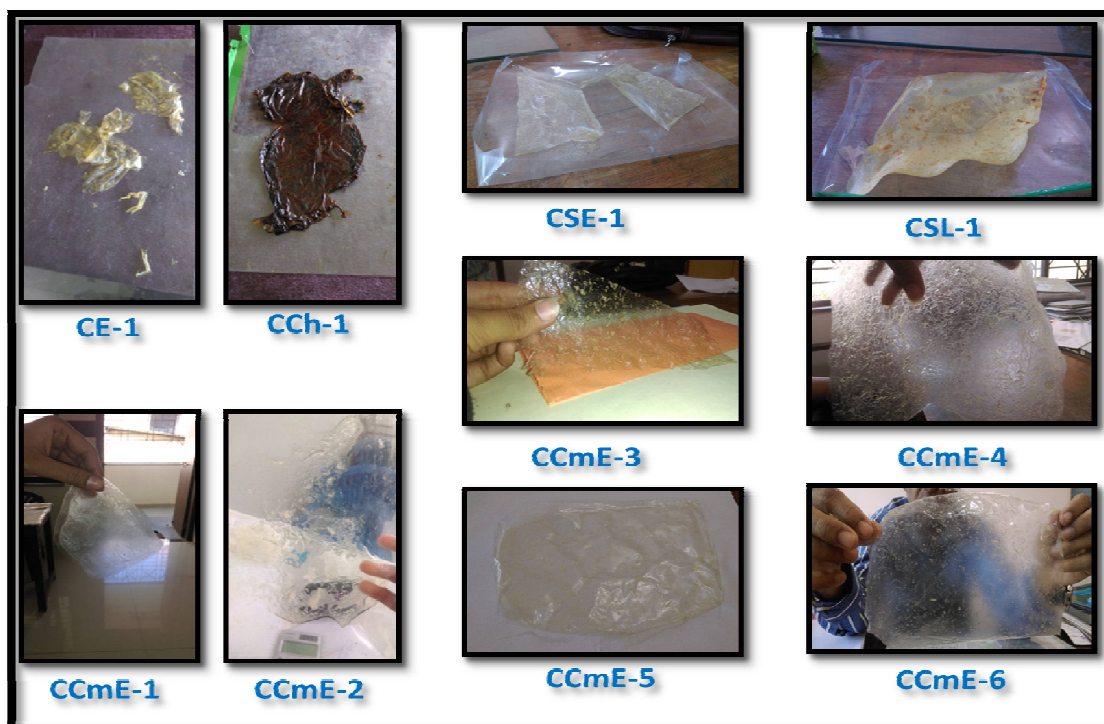


Fig. 4 Samples of Bio-composite films synthesized

5. Observations

The details of process parameters are given in table no.1;

Table no. 1 Details of process parameters

Sr. no.	Sample name	Process part	Quantity of chitosan	Quantity of starch	Quantity of CMC	Quantity of acetic acid	Quantity of essential oil	Quantity of water
1.	CE-1	Gel formation	5g	-	-	2 ml	-	40 ml
		Nano-emulsion	-	-	-	-	10 ml (EO)	5 ml
2.	CCh-1	Gel formation	5g	-	-	2 ml	-	40 ml
		Homogenous solution	-	-	-	-	Approx. 3-5 ml (ChE)	10 ml
3.	CSE-1	Gel formation	1g	-	-	2 ml	-	50 ml
		Starch solution	-	1.75g	-	-	3 ml (EO) to mix	50 ml
4.	CSL-1	Gel formation	1g	-	-	3 ml	-	50 ml
		Starch solution	-	1.75g	-	-	3 ml (LO) to mix	25 ml
5.	CCmE-1	Gel formation-1	0.3g	-	-	0.5 ml	-	20 ml
		Gel formation-2	-	-	1g	-	4 ml (EO)	50 ml

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							to mix	
6.	CCmE-2	Gel formation-1	0.4g	-	-	0.5 ml	-	50 ml
		Gel formation-2	-	-	0.4g	-	2 ml (EO) to mix	25 ml
7.	CCmE-3	Gel formation-1	0.4g	-	-	0.5 ml	-	50 ml
		Gel formation-2	-	-	0.1g	-	2ml (EO) to mix	50 ml
8.	CCmE-4	Gel formation-1	1g	-	-	2 ml	-	25 ml
		Gel formation-2	-	-	0.5g	-	3 ml (EO) to mix	25 ml
9.	CCmE-5	Gel formation-1	0.3g	-	-	0.5 ml	-	25 ml
		Gel formation-2	-	-	1g	-	2ml (EO) to mix	50 ml
10.	CCmE-6	Gel formation-1	0.3g	-	-	0.5 ml	-	30 ml
		Gel formation-2			1.37g		2ml (EO) to mix	70 ml

Note- C is for chitosan, S- starch, Cm- carboxymethyl cellulose, E- Eucalyptus oil, L- lemon grass oil, Ch- chili extract.

IV.RESULTS & DISCUSSION

The discussion of experimental observations and results of characterization methods is done in following section.

1. GSM (g/m^2)

Thickness of films is calculated using Vernier caliper and details are listed below in table no.2;

Table no.2 Details of thickness of films

Sr. no.	Sample name	Thickness in cm	Thickness in micron
1	CSE-1	$0+0.01*2 = 0.02$	200
2	CSL-1	$0+0.01*9 = 0.09$	900
3	CCmE-1	$0+0.01*1 = 0.01$	100
4	CCmE-2	$0+0.01*9 = 0.09$	900
5	CCmE-3	$0+0.01*2 = 0.02$	200
6	CCmE-4	$0+0.01*1 = 0.01$	100
7	CCmE-5	$0+0.01*9 = 0.09$	900
8	CCmE-6	$0+0.01*9 = 0.09$	900

Where 0.01 is the least count of Vernier caliper.

From the above table no.2, it is observed that thickness of samples is in the range of 100 to 900 micron.

GSM of following samples are calculated by calculating the area (in m^2) and weight;

Table no.3 Details of GSM of films

Sr. no	Sample name	Weight in gram	Area in m^2	GSM=Weight/area	Thickness in microns	GSM of PVC film in literature	Ref. no.
1	CCmE-4	1.74	0.026	66.92	100	20-90 (for 200-350 micron)	[9]
2	CCmE-5	4.33	0.06047	71.61	900	20-90 (for 200-350 micron)	[9]

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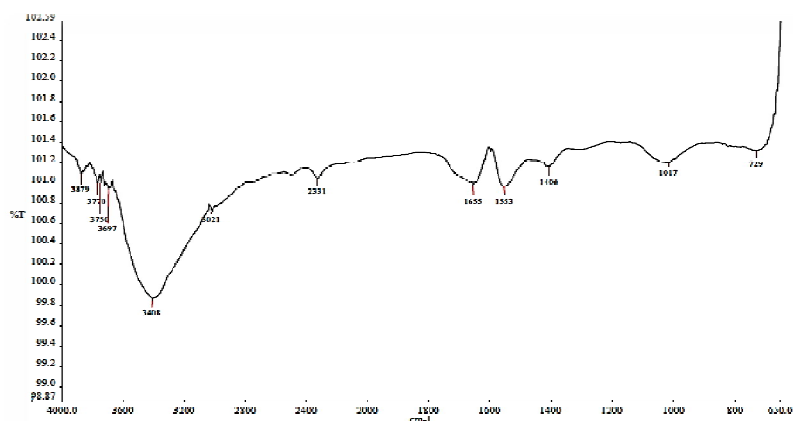
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2. FTIR Analysis

FTIR analysis was conducted to identify various functional groups present in bio-composite film. The wave form diagram of FTIR analysis for sample CCmE-3 is shown in fig.5.



bio composite film.pk

Fig.5 FTIR of sample CCmE-3

The interpretation of the peaks of the waves in fig.3 is given in the following table no.4;

Table no.4 Interpretation of peaks observed in wave form diagram

Sr. no.	Wave number in cm^{-1}	Functional groups	Wave number identified from literature in cm^{-1}	Ref. no.
1	3750	OH group	3756	[12]
2	3697	OH stretch	3500-3700	[11]
3	3408	OH/NH ₂ stretching	3450-3250	[12]
4	3021	(C=C-H)	3040-3010	[12]
5	2331	NH ₂ ⁺ , NH ⁺ , =NH ⁺	2700-2250	[12]
6	1655	Keto-aldehydes as enols o-amino/o-hydroxyarylketones	1670-1645 1655-1635	[12]
7	1553	NH group Conjugated, cyclic (C=N)	1580-1490 1660-1480	[12]
9	1406	Carboxymethyl group	1414-1401	[10]
10	1017	C-O (ether)	1000-1300	[11]
11	729	C-Cl stretch	600-800	[11]

3. SEM

SEM analysis was carried out using ZEISS SEM & the interpretation is given in table no.5. Photographs are shown in fig 6 to 9;

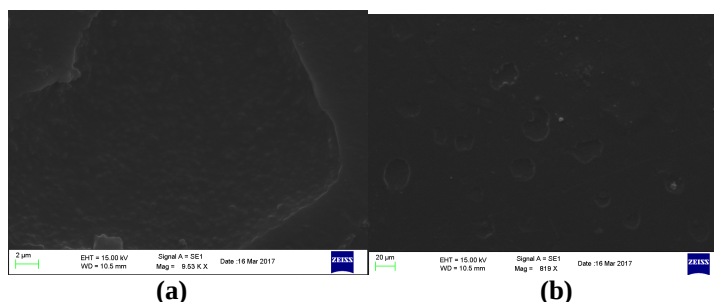


Fig.6 SEM of Sample CSE-1; (a) particles of film on the scale of $2\mu\text{m}$, (b) particles of film on the scale of $20\mu\text{m}$

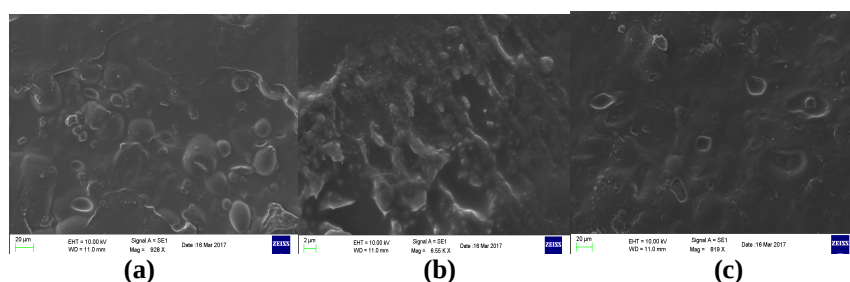


Fig.7 SEM of Sample CSL-1; (a) particles of film on the scale of $20\mu\text{m}$, (b) particles of film on the scale of $2\mu\text{m}$, (c) particles of film on the scale of $20\mu\text{m}$

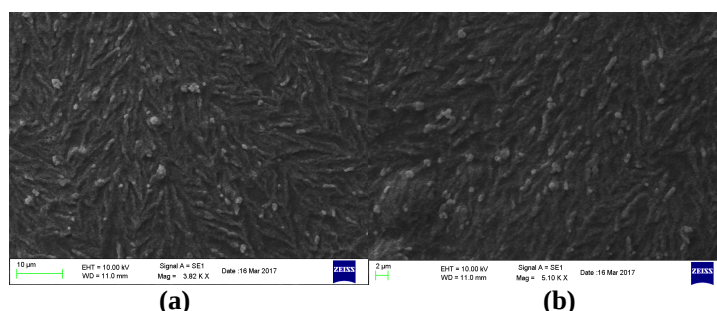


Fig.8 SEM of Sample CCmE-1; (a) microcrystalline particles of film on the scale of $10\mu\text{m}$, (b) microcrystalline particles of film on the scale of $2\mu\text{m}$

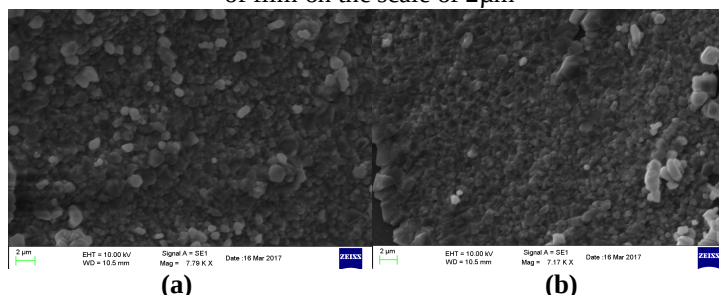


Fig.9 SEM of Sample CCmE-3; (a) microcrystalline particles of film on the scale of $2\mu\text{m}$, (b) microcrystalline particles of film on the scale of $2\mu\text{m}$

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Table no. 5 Table for interpretation of SEM analysis

Sr. no	Sample names	Observations	Inference
1	CSE-1	Homogenized smooth surface structure	It may be due to starch as one of its constituents
2	CSL-1	Fairly homogenized surface structure	It may be due to the quality gel formed
3	CCmE-1	Micro-crystalline surface structure	It may be due to CMC as one of its constituents
4	CCmE-3	Small circular micro-crystalline surface structure	It may be due the presence of CMC

4. Antibacterial test

Anti-bacterial test was conducted to check the anti-bacterial properties of bio-composite film synthesized. It was observed that the sample CCmE-3 showed no growth of micro-organism after 48 hours of incubation.



Fig.10 Anti-bacterial test of Sample CCmE-3; fig (a) & (b) gives the photographs of test conducted

5. Tensile test

To determine the strength of the films synthesized, sample CCmE-6 was selected for tensile strength test. The Ultimate Tensile Test was found to be 2.853 MPa.

V. CONCLUSION

The main objective of the present work is to explore the possibilities of formation of antimicrobial films using various bio-materials. For this purpose, bio-materials such as chitosan, starch, carboxymethyl cellulose, eucalyptus oil, lemon grass oil and oleoresin have been used in various combinations and compositions. Ten bio-composite films have been synthesized. Some of the films have been chosen for the characterization that includes GSM, FTIR, SEM, Tensile test and Anti-microbial test.

The GSM of films synthesized was in the range of 66-72. FTIR analysis has been conducted successfully to identify different organic and inorganic functional groups present in the bio-composite films synthesized. SEM analysis has shown the micro-crystalline surface morphology of the films. 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.

Hence, it can be concluded that the present work has successfully been carried out. Bio-composite films are synthesized using bio-materials having good anti-microbial property & mechanical strength. The present work is demonstrative & it is felt necessary to conduct more experimental runs followed by appropriate characterization methods so as to validate the claim further.

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AKNOWLEDGEMENTS

Authors are thankful to the Director, LIT Nagpur for constant support & encouragement. Authors express thanks to Department of Physics RTMNU, Nagpur for SEM analysis and Department Metallurgy, Materials Engineering VNIT, Nagpur for FTIR Analysis & Tensile Strength Test & Parate Diagnostic Centre, Nagpur for antimicrobial test.

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