Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2016, 8(7):241-248

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Preparation and Evaluation of Surface Morphology and Swelling Behavior of Ternary Blend Films

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ABSTRACT

The present study aims to prepare ternary blend films composed of chitosan/guar gum/vanillin (CH/GG/Vn) by solvent casting method. The surface morphology and interaction among the components of blend films were determined by Atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FTIR). The blend films were subjected to swelling study under water and different pH media. The roughness of the blend films increased with increase in guar gum and vanillin (wt%). By the addition of equal weight percent of GG/Vn into chitosan film, the swelling behavior enhanced than pure chitosan and swelling behavior at different pH medium than water. Based on the results, we conclude that the prepared blend films can find potential application in pharmaceutical industry for drug delivery.

Key words: Chitosan, surface morphology, swelling behavior, FTIR and AFM.

INTRODUCTION

Chitosan is a natural polysaccharide derived from the naturally occurring chitin in crab and shrimp shells [1-2]. Chitosan is biocompatible, biodegradable and non toxic in nature. The most promising feature of chitosan, its excellent property to form porous structures [3] that has been widely used in diverse fields like food processing, medical field in cell transplantation, tissue regeneration and biotechnology [4-10]. Chitosan has ability to form clear and flexible film with good mechanical properties. In addition, the absence of pores [11] makes chitosan degrades before its melting. Many medical applications of chitosan depend on adsorption processes which in turn related the surface of material. The surfaces of chitosan films widely discussed [12-16] and microstructures, including roughness can be effectively examined by using atomic force microscopy (AFM). Swelling and chemical resistivity of blend films plays an important role in control and development of mechanism for filtration and separation and also in drug delivery. The objective of the study is to prepare ternary blend films of CH/GG/Vn and to investigate the surface morphology of blend films, swelling and chemical resistivity of blend films.

EXPERIMENTAL SECTION

Chitosan (200-500 mPa's 0.5% in 0.5% acetic acid at 20^{o}C) procured from Tokyo Chemical Industry Co. Ltd (Tokyo, Japan). Gaur gum was supplied by Central Drug House (CDH), New Delhi. Vanillin with assay of 99% was purchased from Merck Specialties Private Ltd (Mumbai). Commercial acetic acid (from Spectrochem, Mumbai) and double distilled water used as a solvent throughout the experiment.

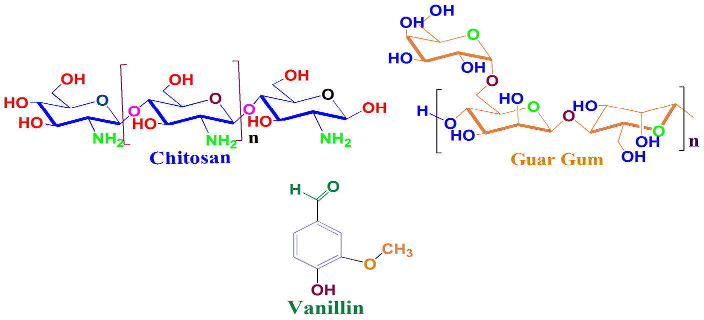

Fig. 1. Chemical Structures of Raw Materials

Preparation of blend films

Ternary blend films of chitosan/guar gum/vanillin (CH/GG/Vn) were prepared by solvent casting technique. Different weight percent of individual chitosan dissolved in 2% acetic acid. Guar gum and vanillin was dissolved in water separately. The individual solutions were mixed with each other and stirred overnight on magnetic stirrer to get clear and homogeneous ternary blend solution (100/00/00, 95/2.5/2.5, 90/5/5, 85/7.5/7.5, 80/10/10). After ensuring viscosity and clear homogeneity, blend solution poured onto Petri dishes and allowed to evaporate at room temperature. Then films were peeled off from the Petri dishes and kept in desiccators until use.

Table 1. Composition of Chitosan/Guar gum/Vanillin Blend Films

Sample Code	Blend Ratio		
	Chitosan (%)	Guar Gum (%)	Vanillin (%)
A	100	0	0
B	95	2.5	2.5
C	90	5	5
D	85	7.5	7.5
E	80	10	10

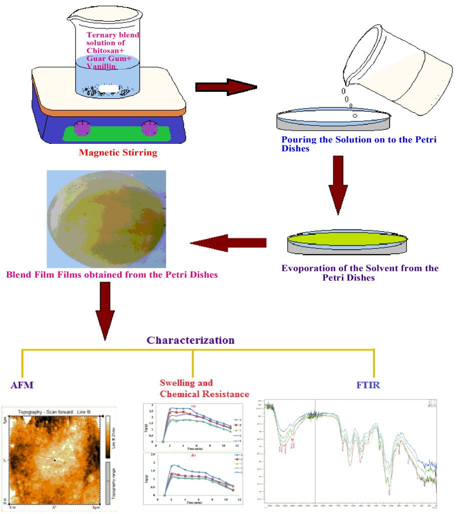

Fig. 2 . Pictorial Representation of Research Work Carried out in the Present Study

Atomic force microscopy (AFM)

The surface morphology of the all blend films were studied by employing Atomic force microscopy (AFM) (Digital instruments AFM, Dimension 3000 Santa Barbara, CA). AFM studies were carried out using the tapping mode under air atmosphere at ambient temperature. The scan size, set point and scan rate are shown in the images. The tapping set-point was adjusted to minimize probe-sample interactions.

Equilibrium Swelling in Different Solvents

The prepared blend films were subjected to the swelling study in different solvents (water, n-butyl alcohol, carbon tetrachloride, alcohol and DMF). Blend samples of size 1x1 cm taken and weighed to the nearest digital balance. Blend samples dried before the swelling study in an oven for two hrs at 45°C temperature and cooled to room temperature. A known weight (W_i) of the film samples immersed in 50 ml of each solvent at room temperature for 15 days. The excess solvent removed by blotting with tissue paper and final weight (W_f) of the blend films noted. The percent of swelling of blend film calculated by using following equation.

$$\text{Percent swelling (\% Ps)} = \frac{\mathrm{Wf} - \mathrm{Wi}}{\mathrm{Wi}} \mathrm{X100}$$

Dynamic Swelling in Water and Different pH Medium

The swelling of the blend films also studied in different pH disciplines by swelling measurements in water and pH-1.2 and 9.0 using standard buffer solutions at room temperature. All the weight measurements carried out taken in digital electronic balance (Shimadza AUX120, Japan, accuracy of ±0.1mg). Previously weighed dry films were immersed in excess of the buffer solution and in water. After certain intervals of time, the films were taken out from the solution and wiped with blotting paper to remove adhered liquid drops. The increase in weight of the film measured. The swelling ratio (S) and total water holding capacity of the films at equilibrium (percent equilibrium water content, %EWC) calculated by using following equations.

$$\mathrm{S} = \frac{\text{Weight of the swollen gel} - \text{Weight of the dry gell}}{\text{Weight of the dry gel}} \qquad (1)$$

$$\%\mathrm{EWC} = \frac{\text{Weight of the swollen gel} - \text{Weight of the dry gel}}{\text{Weight of the swollen gel}} \mathrm{X100} \qquad (2)$$

Chemical Resistance

The influence of acidic and basic condition (chemical resistance) on films were investigated by immersing known weight (T_i) of films (size 1x1 cm) in 100 ml of 1 N NaOH and 1 N HCl solution. At different time intervals (24–120 hours) samples removed from the solution then dried and weighed (W_{aci}) accurately. The percent of chemical resistance (Pcr) calculated (in term of weight loss) from the following equation.

$$\text{Percent chemical resistance} = \frac{\mathrm{Ti} - \mathrm{Waci}}{\mathrm{Ti}} \mathrm{X100}$$

Where T_i = initial weight and W_{aci} = weight after certain interval.

Fourier transform infrared spectroscopy (FT-IR)

The FTIR spectroscopy was used in order to determine the possible interactions among the components of CH/GG/Vn blend films. The FTIR spectra of films were recorded by using an attenuated total reflection (ATR) method in IR spectrometer (FT-IR-ATR, Prestage 21, Shimadzu, Japan). Samples were analyzed between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

Atomic force microscopy (AFM)

Atomic force microscopy utilized to probe surface morphology of CH/GG/Vn blend films. Fig. 3 shows the topographic images of pure chitosan and CH/GG/Vn blend films. The topographic images of pure chitosan exhibits smooth and homogeneous surface morphology. In contrasts, the surface morphology of CH/GG/Vn films considerably rougher than pure chitsoan and composed of non-continuous globular bulbous structure. This could be due to the consequence of its amorphous nature. As the percent of GG/Vn increased roughness began to alter and also slightly increased.

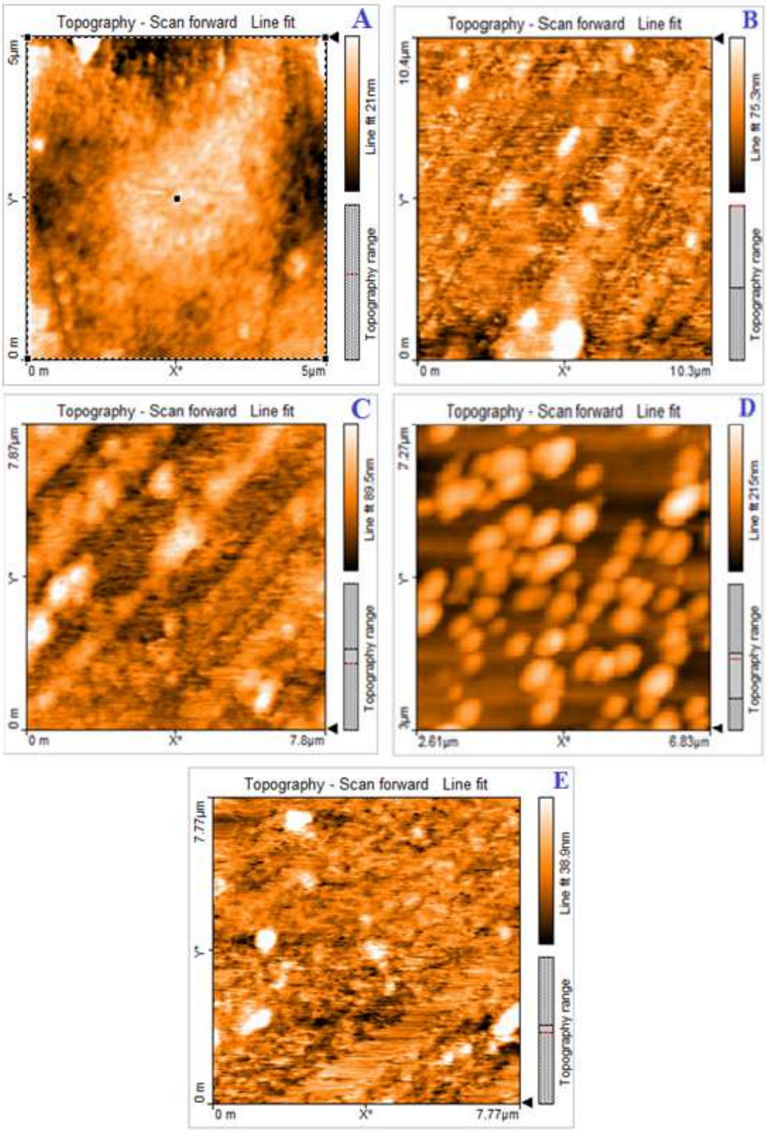

Fig. 3. Tapping mode AFM images: A) Chitosan, B) 95/2.5/2.5, D) 85/7.5/7.5 and E) 80/10/10 blend films

Equilibrium Swelling Study in Different Solvents

Table 2 shows the results obtained from equilibrium swelling in different solvents. The order of swelling observed in different solvents as follows H_2O>C_2H_5OH> DMF>CCl_4>n-butyl alcohol. Greater swelling observed in water compared to other solvents which could be due to the hydrophilic nature of the blend films. In ethanol, DMF, CCl_4 and n-butyl alcohol swelling decreases it could be due to the non availability free hydroxyl groups.

Table 2. % Swelling Behavior of Blend Films Different Solvents

	% of Swelling Behavior				
Sample	Water (%)	DMF (%)	Alcohol (%)	CCl_4 (%)	n-Butyl alcohol (%)
A	69.81	30.37	66.21	1.56	0.99
B	99.81	36.00	83.14	2.39	0.25
C	80.81	47.72	77.41	1.39	0.62
D	99.11	47.47	82.16	2.09	4.73
E	90.90	48.14	76.53	2.22	26.17

Dynamic swelling in water and different pH conditions

Fig. 4 reports the dynamic swelling of blend films in water. The results of swelling in water showed slightly increased value compare to pure chitosan films. The blend films of B and D presented higher swelling in water. But dynamic swelling in water presented lower value than equilibrium swelling, which could be due to the short time exposure of the material shows less swelling.

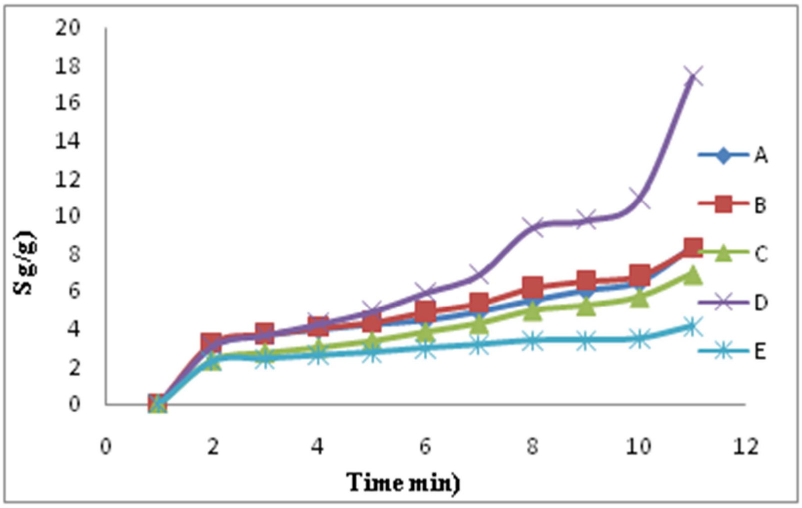

Fig. 4. Swelling isotherms of CH/GG/Vn in H_20

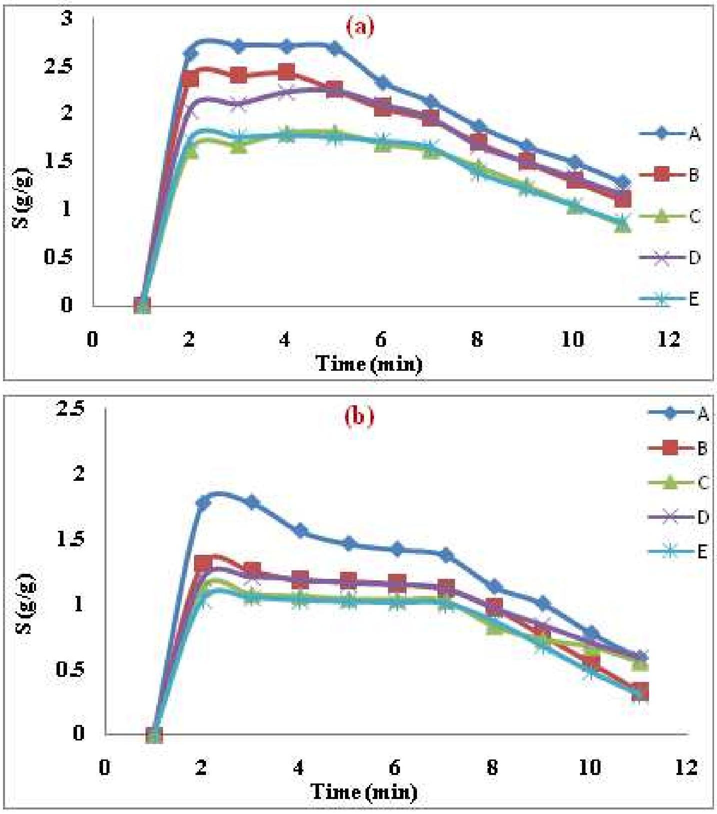

Fig. 5 a, b. Swelling Isotherms of CH/GG/Vn Blend in (a) pH-1.2 and (b) pH-9.0

Fig. 5 a, b shows the diagram of dynamic swelling in different pH medium. In assessing the swelling in different pH medium, it was noted that different pH medium (pH- 1.2 and 9.0) influences much on blend films compare to pure chitosan. Under both acidic and basic conditions blend films not stable and showed swelling up to 60 minutes thereafter due to instability, films started to degrade. Weight of the blend films initially increased due to swelling but as the exposure time increased decomposition of blend films noticed. All blend films have good response towards pH and the order of the swelling observed as water >pH 1.2> 9.0. The results confirm that, at higher pH the cross link between the three components can breakdown easily and degradation of films can be observed.

Table 3. Equilibrium Water Content in Water and pH 1.2 and 9.0

Sample	Water	pH-1.2	pH-9.0
A	89.24	56.36147	37.05357
B	89.19	52.50432	24.82394
C	86.57	46.04878	35.80729
D	94.57	53.75354	37.04293
E	80.38	46.50206	23.49727

The results of equilibrium water content (Table. 3) showed that blend films has presented highest water holding capacity. But in different pH medium the blend films where completely unstable exhibiting lower water content.

Chemical Resistivity

In this study, results of chemical resistance showed that (Table 4, 5) resistance of the films in acidic and basic medium (1N NaOH and 1N HCl) decreases with the increase in exposure of time. Also significant increase in percent of degradability of blend films under such chemicals was noticed. The results of chemical study were similar to the above discussion. This could be due to the effect of acidic and basic medium on blend films causing breaking of bonds.

Table 4. Chemical Resistances (In terms of % wt. loss) of Blend Films of CH/GG/Vn at Different Time Intervals against (A) 1 N NaOH

Sample	24 Hour(%)	48 Hour (%)	72 Hour (%)	96 Hour (%)	120 Hour (%)
A	5.3	11.1	12.7	15.4	17.0
B	11.2	13.1	14.4	16.0	17.0
C	10.4	10.4	12.0	13.8	15.4
D	9.7	10.8	12.8	15.3	16.3
E	5.8	8.6	11.6	12.72	13.6

Table 5. Chemical Resistances (In terms of % wt. loss) of Blend Films of CH/GG/Vn at Different Time ntervals against (B) 1N HCl

Sample	24 Hour(%)	48 Hour (%)	72 Hour (%)	96 Hour (%)	120 Hour (%)
A	3.9	7.5	8.5	11.6	17.1
B	1.5	3.7	6.5	10.4	15.2
C	2.6	6.7	16.0	21.2	25.6
D	9.4	12.7	26.2	30.6	37.2
E	11.2	15.3	24.2	31.6	35.5

Fourier transform infrared spectroscopy (FT-IR)

FTIR spectra of pure chitosan and CH/GG/Vn are shown in Fig. 6. Pure chitosan shows a broad absorption peak at 3395 cm^{-1} due to –OH and N-H stretching [17-19]. The absorption band at 3427cm^{-1} attributed to -OH stretching vibrations, while the peak at 2922 and 2810 cm^{-1} indicates the presence of C−H aliphatic stretching vibrations. Chitosan is characterized by its saccharide structure for which the peaks appear at 899 cm^{-1}and 1154 cm^{-1}. Absorption peak at 1076 cm^{-1} attributed to the C-O stretching band.

In different weight ratio of CH/GG/Vn blend films (Fig. 6 B, C, D &E), the characteristic peak of both CH and GG are observed in addition to a new peak appeared at 1635, 1641, 1639, 1638 cm^{-1} respectively. This is due to C−N stretching vibration of the imine group of Schiff base formed due to reaction of aldehydic functional group of vanillin and amino group of chitosan. Presence of C=O group in vanillin disappeared in blend films indicating that strong intermolecular interaction between CH, GG and Vn. Peak appeared at 1021,1024,1022,1020 cm^{-1}, confirms the presence of an acetal group formed due to the reaction between hydroxyl groups of vanillin and hydroxyl groups of GG by elimination of water. Thus, FTIR data confirms the successful cross-linking of Vn with CH, GG to form compatible films. Broad transmission peak at 3600-3100cm^{-1} produced by stretching of hydroxyl group in the spectrum of GG can be remarkably distinguished. By observing figure 6 (B, C, D, E,), it proposes hydroxyl stretching vibrations shifted slightly to a lower wave number with increasing amount of chitosan 95/2.5/2.5, 90/5/5, 85/7.5/7.5, 80/10/10 respectively. This could be attributed to the formation of strong hydrogen bonding between -OH groups of GG and CH. Thus FTIR study confirms complete miscibility and compatibility of the films.

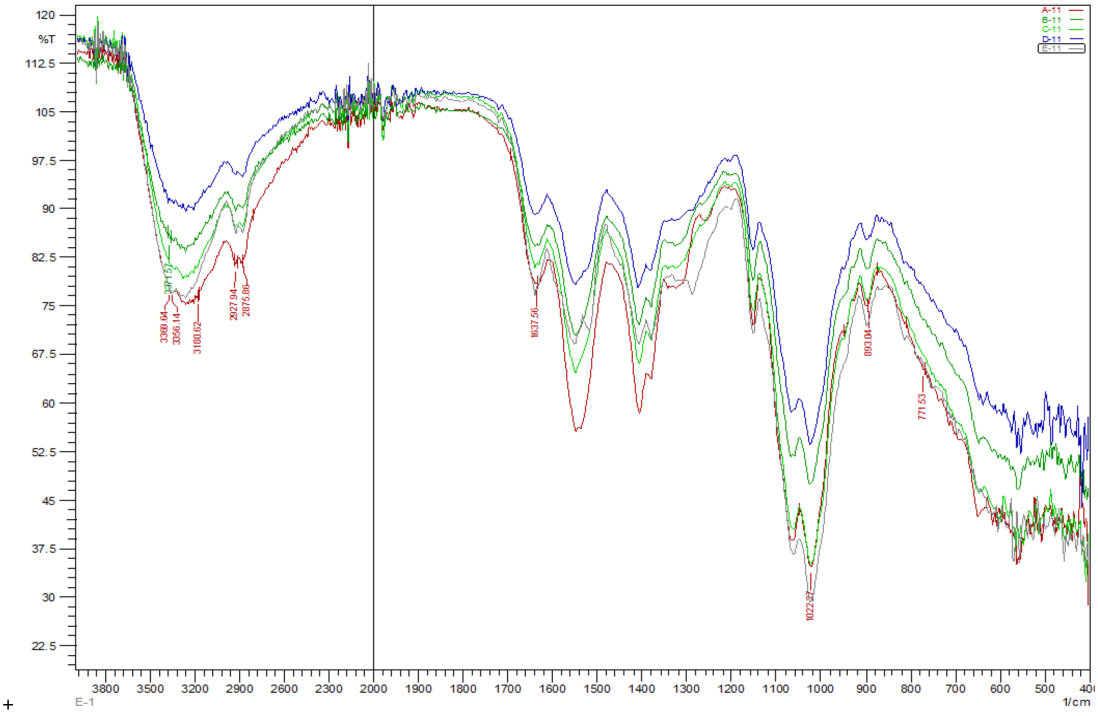

Fig. 6. FTIR Spectra of Pure Chitosan & Chitosan/Guar gum/Vanillin Blend films

CONCLUSION

In the present study, the surface morphology, swelling and chemical resistance of CH/GG/Vn blend films were studied. The results of AFM study attests that blend films showed different surface morphology with increasing concentration of GG/Vn. The results of swelling behavior confirms that blend films were hydrophilic in nature, showed more swelling in water and more active in different pH solutions (pH 1.2 and pH 9.0). Meanwhile, the reduced chemical resistance was noticed, which suggests that blend films not stable at acidic and basic medium. Based on the results we can conclude that blend films can be suitable alternative to synthetic material which can find application in pharmaceutical as well as in food packaging industry.

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