

Review Article

Comprehensive Studies of Chitosan and Starch Blend Films

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Abstract

On the basis of Fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetric measurements, it is concluded that blends of chitosan/starch are compatible. The miscibility in chitosan/starch blend system is due to the formation of strong hydrogen bonding between chitosan and starch.

Keyword: Chitosan, infrared spectroscopy, Thermogravimetric analysis, starch.

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Introduction

Chitosan, the most important derivative of chitin, can be obtained by deacetylation of chitin under alkali conditions (Figure 1). When the degree of acetylation of chitin reaches about 50%, it becomes soluble in aqueous acidic media. The solubilization occurs by protonation of the NH₂ functional group on the C-2 position of the D-glucosamine repeating unit, whereby the polysaccharide is converted to a polyelectrolyte in acidic media. The presence

of NH₂ groups in chitosan is the reason why it exhibits much greater potential compared with chitin for use in different applications [1, 2]. It is a special biopolymer having good properties including biodegradability, biocompatibility, and antibacterial activity so it is interesting as a novel type of functional material. Chitosan is the only pseudo-natural cationic polymer and thus has many applications in different fields [3, 4].

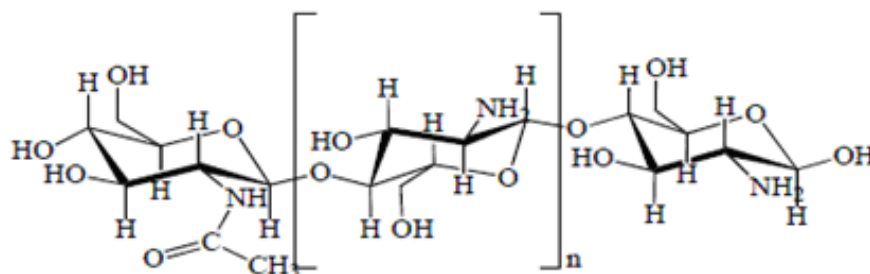


Fig. 1: Chemical Structure of Chitosan.

Starch is a substance of definite chemical composition which occurs widely as the reserve food in most land plants (Figure 2). Since these plants store starch in a number of different forms, the starch from different plant sources will vary somewhat in physical properties. Hence, various native starches exist, each designated by its plant source (e.g., potato-starch, cornstarch, rice starch, tapioca starch). Starch belongs to the class of organic compounds called carbohydrates and is composed of carbon, hydrogen, and

oxygen in the ratio $C_6H_{10}O_5$. These atoms are organized into a simple sugar molecule, D-glucose, or dextrose as it is known commercially.

The glucose molecules are, in turn united to form large starch molecules. Thus starch is a polymer made up of a large number of glucose units [5]. Hence, the miscibility studies of chitosan/starch blend might be important to enhance some of their performance properties.

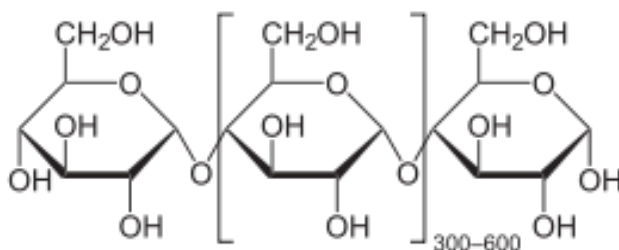


Fig. 2: Chemical Structure of Starch.

The application needs for chitosan and various other suitable water soluble polymer blends makes accurate product characterization very important. In this paper, water soluble polymer namely starch is added to chitosan and its effect on miscibility, thermal and morphological properties was investigated by various methods.

MATERIALS AND METHODS

Polymers employed in the present study are commercial grade Chitosan (kindly provided as a gift sample by India Sea Foods, Cochin, India, $M_v = 2.0424 \times 10^5$ Dalton, degree of deacetylation = 80.3%) and Potato Starch (AR Grade from S.D. Fine-Chem Ltd., Mumbai, India). For SEM, FTIR and TGA studies, thin film of Chitosan, Potato Starch and their different blend compositions were prepared by solution casting method.

The total polymer concentration was kept at 1% w/v. stock solutions of Chitosan, Potato Starch and their different blend compositions were stirred for 45 min at room temperature to ensure complete mixing, then casted onto a Teflon coated clean glass plate and dried using IR lamp in a dust free atmosphere. The dried thin films were peeled off from the glass plate. Scanning Electron Microscopic (SEM) analysis were recorded using a JOEL (JSM 6380LA) analyzer. FTIR spectra were measured using NICOLET AVATAR 530 spectrophotometer.

Thermogravimetric analysis of the blend films were performed over temperature range of 20–600 °C, using Thermogravimetric analyzer (TGA Q50

V20.2 Build 27) under nitrogen environment at a scan rate of 20 oC/min.

RESULTS AND DISCUSSION

Spectroscopy Study-Chitosan-Starch Blend System

To enhance the formation of single-phase in miscible polymer blend, it is necessary to ensure that favorable specific intermolecular interactions exist between the two base components of the blend [6–8]. FT-IR Spectra of chitosan and potato starch homopolymer film and their blends 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80 and 10/90 were recorded. Figure 3a and 3b

shows the FT-IR Spectra of pure and blend films in the wave length range of 2000–500 cm^{-1} . The strong adsorption of 1653.58 cm^{-1} indicates the presence of amide group and the other strong adsorption at 1538.76 cm^{-1} indicates, the chitosan have the N–H bending from amino and amide groups. The strong adsorption at 1381.39 cm^{-1} and 1306.24 cm^{-1} indicates the CH_2 bending and CH_3 symmetrical deformation, respectively. Adsorption at 1226.96 is due to the anti-symmetric stretch C–O–C and C–N. Spectra in 1016.64 cm^{-1} proved the skeletal vibration of C–O stretching.

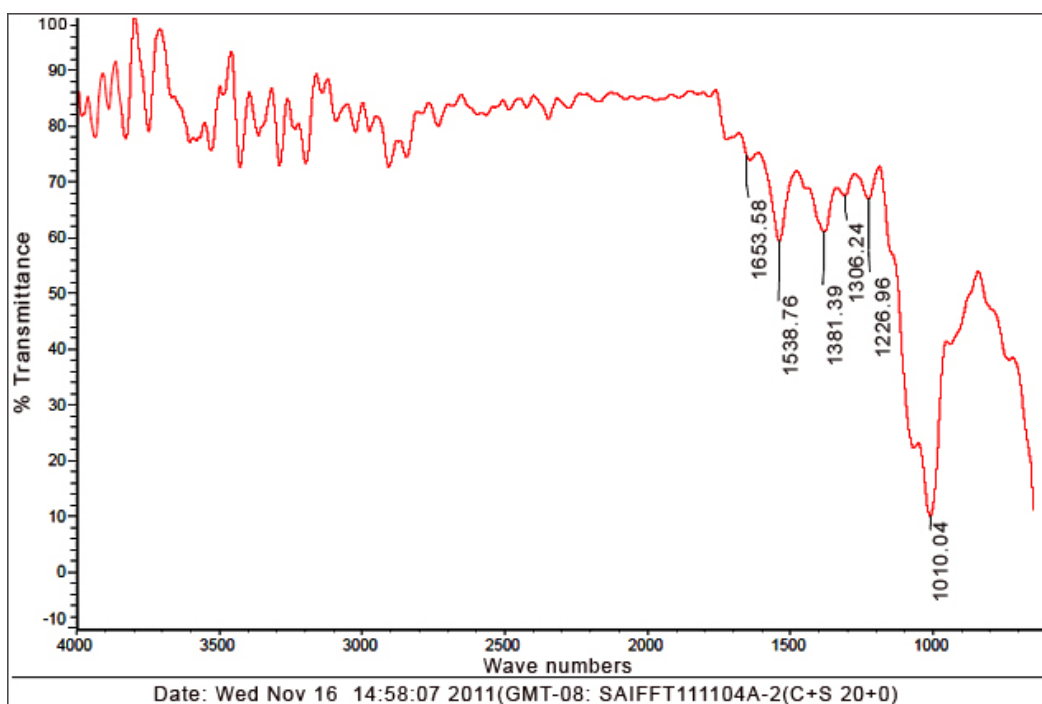


Fig. 3a: FT-IR Spectra of Pure Chitosan.

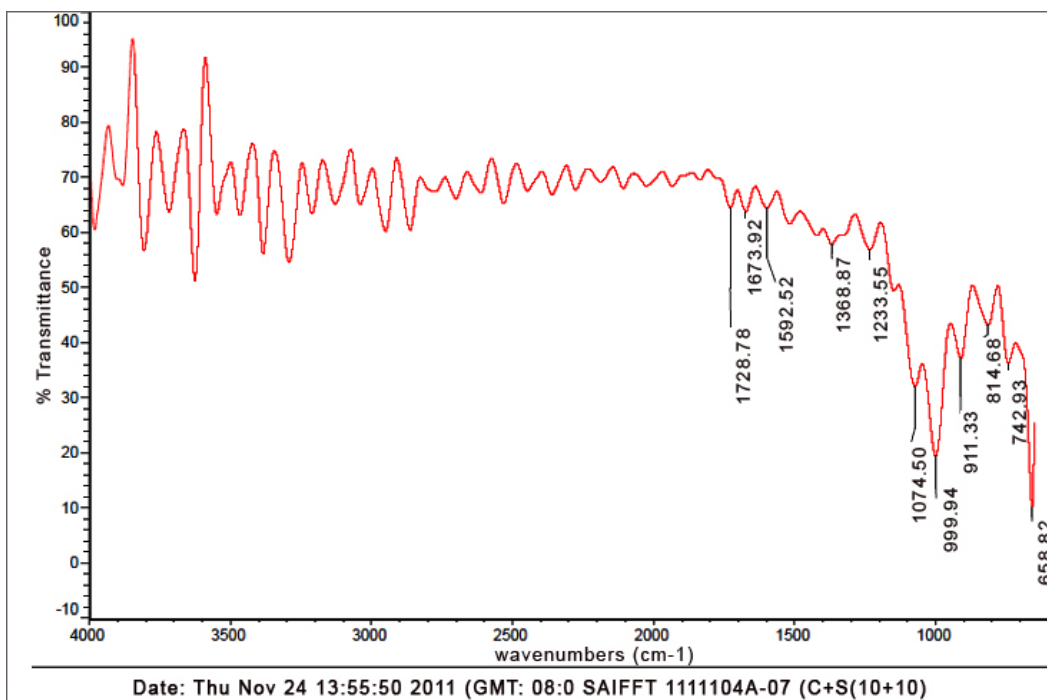


Fig. 3b: FT-IR Spectra of Chitosan and Starch.

On the other hand of starch, the spectra at 1536.63 cm^{-1} is due to the N–H bending, and adsorption at 1407.99 cm^{-1} indicates the C–H stretching. The peak at 1333.26 indicates the presence of amide II & III. The adsorption at 1148.01 cm^{-1} is proved the C–O–H bond. The peaks at 995.06 cm^{-1} , 854.03 cm^{-1} and 680.52 cm^{-1} are indicated the C–O bond stretching. The spectrum of chitosan/starch blend film was characterized by the presence of the adsorption bands typical of the pure components, with the intensity roughly proportional to the blending ratio. It's noticed that the CH_3 symmetrical deformation and CH stretching are absent in chitosan/starch blended films. This is indicating the interaction between them. Due to the secondary force of attraction some extra peaks are noticed in the blended films. This is confirmed that a good interaction between chitosan and starch. This confirms that chitosan and starch blends are miscible in nature.

Morphology Study

The uniformity of the dispersion was examined through SEM of the solution caste films of chitosan, starch and their blends films 10/90, 20/80, 50/50, 70/30 & 80/20 are shown Figure 4 (a, b, c, d and e). It was observed a single phase at 10/90, 20/80, 50/50, 70/30 & 80/20 blend compositions. Chitosan/starch blend did not show any aggregated particles and it can be observed that the starch was well distributed in the chitosan. As shown in Figure 4, measured by high magnification (X 5000), it was observed that all blends are homogeneous which suggest that these blends were miscible.

Thermogravimetric Analysis (TGA)

TGA is used primarily for determining thermal stability of polymers and their blend films [9, 10]. The most widely used TGA method is based on continuous measurement of weight on a sensitive balance (called a thermobalance) as sample temperature is increased in an inert atmosphere. The TGA

curves of homopolymers and blends of chitosan/starch are given in Figures 5, 6 & 7. In order to determine thermal stability trend, the temperature characteristics such as T_0 (Temperature of onset of decomposition), T_{20} (Temperature for 20% mass loss), T_{30} (Temperature for 30% mass loss), T_{50} (Temperature for 50% mass loss), T_{max} (Temperature for maximum mass

loss), ash content and oxidative index(OI) were calculated and presented in Table 1. T_0 , T_{20} , T_{40} , T_{50} , T_{60} and T_{max} are the main criteria of the thermal stability of blends and signal features of the TGA curves. The oxygen index (OI) was calculated based upon the weight of carbonaceous char (CR) as in the empirical equation:

$$OI \times 100 = 17.4 \times 0.4 \text{ CR}$$

Table 1: Thermal Data Obtained from Thermogravimetric Analysis (TGA) of Chitosan/Starch Blend Films.

Compositions	Temp. at different weight						Ash content		Oxygen Index (OI)
	T_0	T_{10}	T_{20}	T_{30}	T_{50}	T_{max}	%	mg	
100/0	53	235	272	294	415	710	37.38	1.8876	0.0615
90/10	40	130	242	280	330	710	28.05	1.3075	0.0910
80/20	41	150	258	279	340	702	31.92	2.2448	0.1562
70/30	44	150	255	277	322	702	28.25	1.9478	0.1355
60/40	50	224	262	280	290	710	32.34	3.0171	0.2099
50/50	43	180	267	292	332	702	27.13	0.9784	0.0681
40/60	50	238	280	300	342	709	27.39	0.9109	0.0634
30/70	51	210	250	290	335	710	25.39	1.7093	0.0475
20/80	52	250	282	300	330	710	24.68	0.9568	0.0665
10/90	51	200	294	310	328	711	14.87	1.5008	0.1044
0/100	52	185	258	287	248	710	31.91	1.8509	0.1288

The blend samples were made in different compositions such as (100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90, 0/100) of chitosan and starch and thermogravimetric analysis were performed using thermogravimetric analyzer under nitrogen environment.

Increase in thermal stability of these blend compositions were observed this may be due to strong specific interaction of hydrogen bonding type between hydroxyl groups in starch and carbonyl group in chitosan.

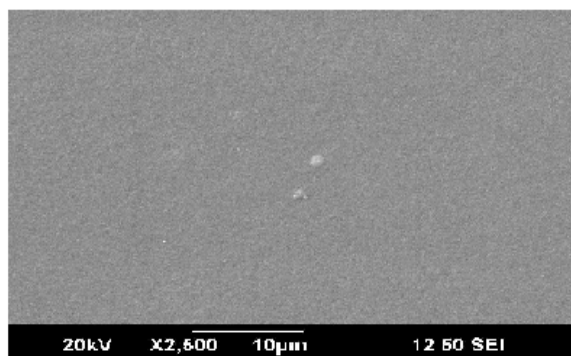


Fig. 4 (a): 10/90 Chitosan/Starch Blend Composition.

Table 2: Temperature Range of Thermal Degradation of Chitosan/Starch Blends from Derivative Curve of TGA Blends from Derivative Curve of TGA.

Chitosan/ Starch Compositions	Transition range (°C)		
	T _i	T _p	T _c
100/0	198	278	368
90/10	229	280	330
80/20	222	279	372
70/30	198	280	405
60/40	209	279	403
50/50	235	294	369
40/60	231	304	381
30/70	240	310	380
20/80	248	316	365
10/90	269	326	369
0/100	209	285	380

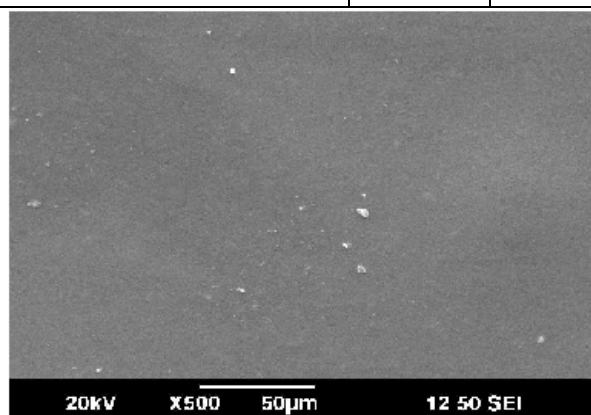


Fig. 4 (b): 50/50 Chitosan/Starch Blend Composition.

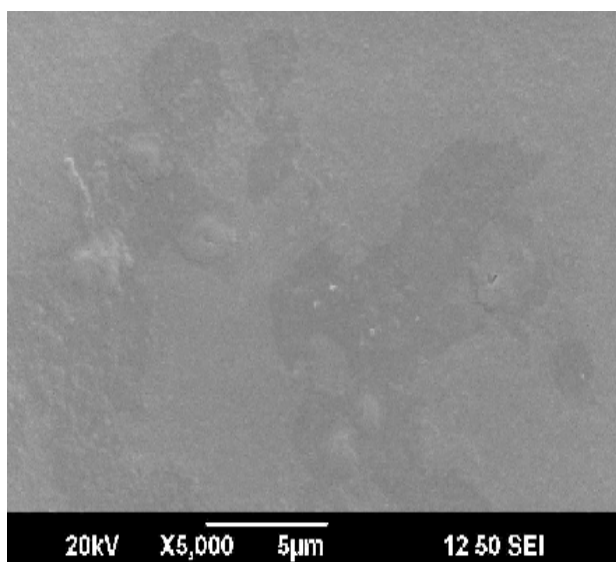


Fig. 4 (c): 20/80 Chitosan/Starch Blend Composition.

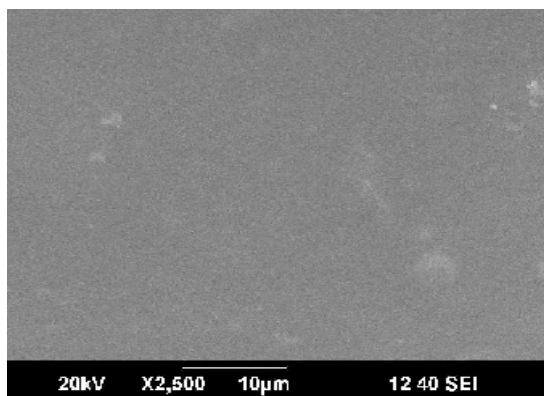


Fig. 4 (d): 70/30 Chitosan/Starch Blend Composition.

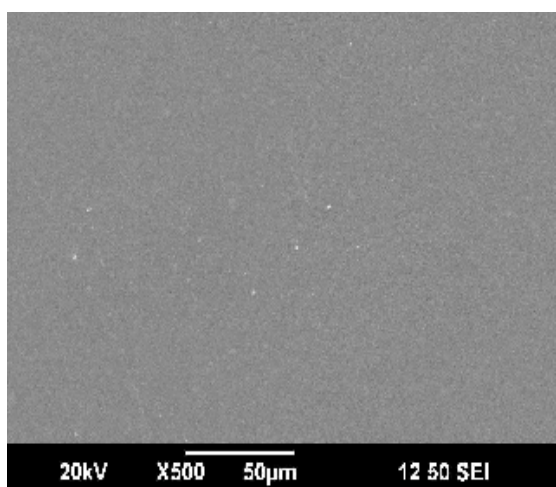


Fig. 4 (e): 80/20 Chitosan/Starch Blend Composition.

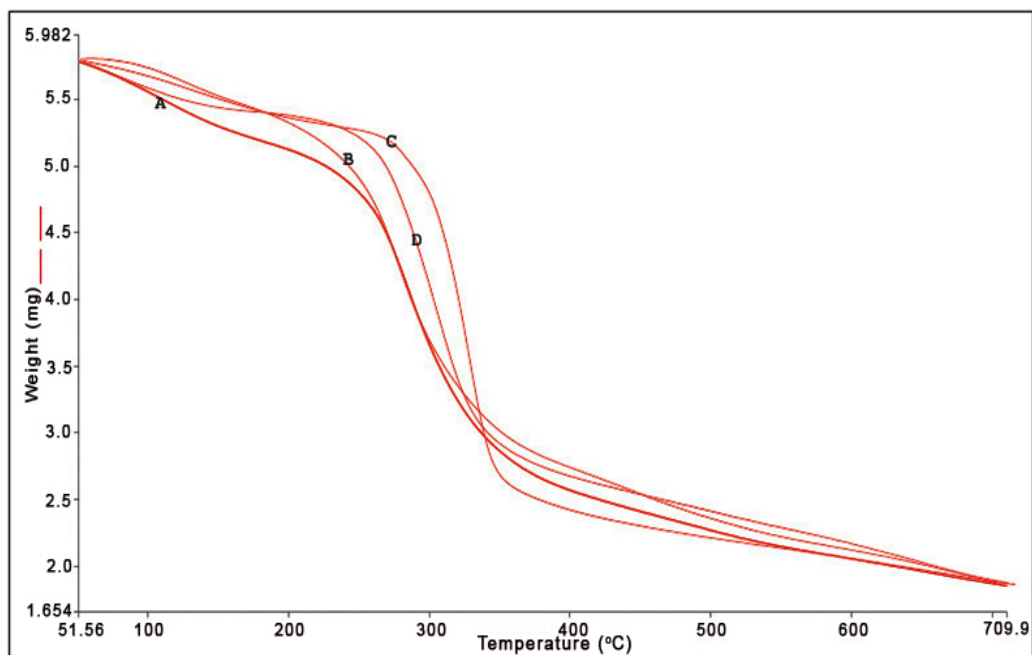


Fig. 5: TGA Curves of (A) Potato Starch, (B) Pure Chitosan, (C) 10/90 Chitosan/Starch Blend and (D) 20/80 Chitosan/Starch Blend.

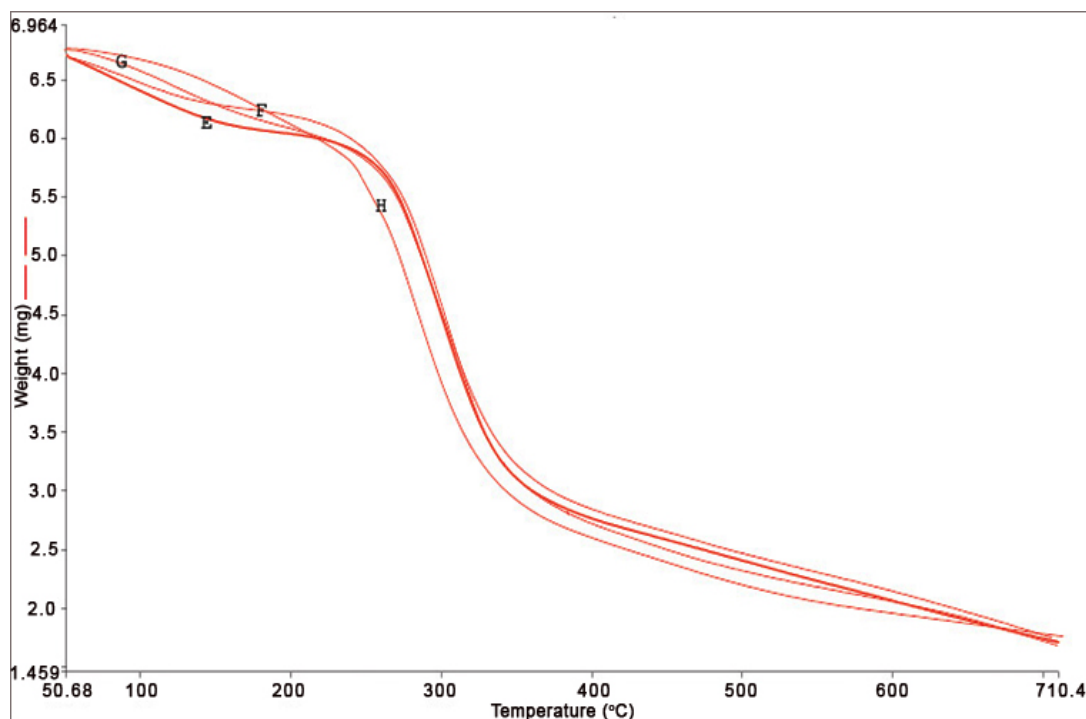


Fig. 6: TGA Curves of (E) 30/70 Chitosan/Starch Blend, (F) 40/60 Chitosan/Starch Blend, (G) 50/50 Chitosan/Starch Blends and (H) 60/40 Chitosan/Starch Blend.

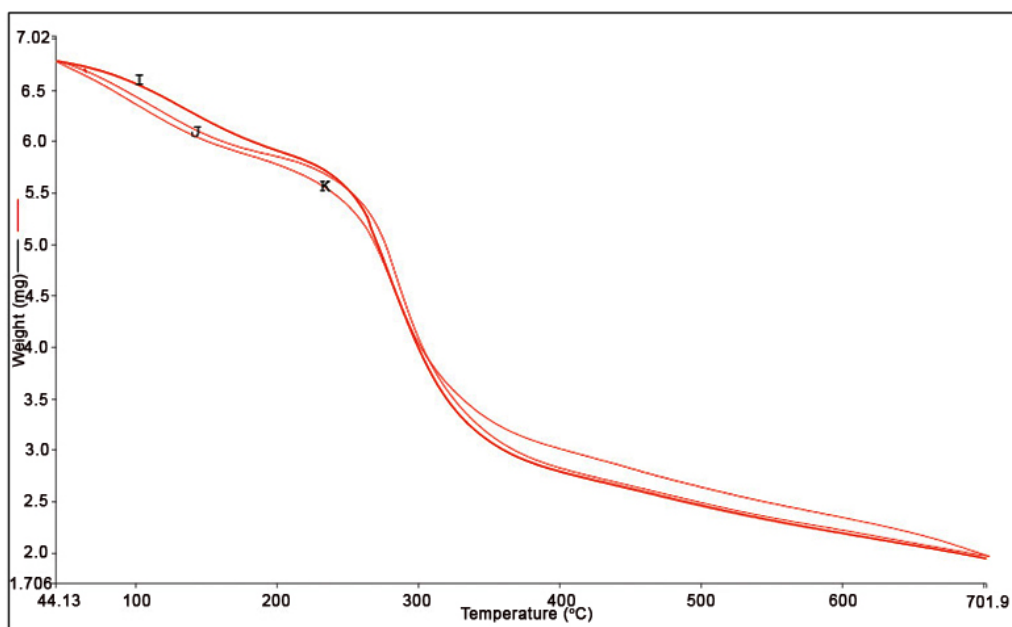


Fig. 7: TGA Curves of (I) 70/30 Chitosan/Starch Blends, (J) 80/20 Chitosan/Starch Blend and (K) 90/10 Chitosan/Starch Blends.

CONCLUSION

On the basis of Fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetric measurements, it is concluded that blends of chitosan/starch are compatible. The miscibility in chitosan/starch blend system is due to the formation of strong hydrogen bonding between chitosan and starch.

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