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Synthesis, characterization and study on the water absorption capacity of binary blends of chitosan

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ABSTRACT

In the present work, the binary polymer blends were prepared by mixing starch and chitosan in the 1:1 ratio with and without the cross linking agent like glutaraldehyde. The characterization of prepared polymeric blends was carried out by advanced analytical tools such as Fourier transform resonance spectroscopy (FT-IR), X-ray diffraction (XRD) and Thermo gravimetric analysis (TGA). The obtained results of FT-IR studies reveal the presence of cross linking between the polymers and cross linking agents. The results of TGA and DSC studies confirms that the blend prepared with glutaraldehyde as a cross linking agent was found to be highly thermally stable. In addition to this the results of water absorption studies carried out as a function of time for the polymer blend samples prepared with and without the cross linking agent at room temperature and high temperature was also investigated.

Key words: Polymer blends, starch, chitosan, cross linking agents, thermal stability.

INTRODUCTION

In the recent decades there has been a considerable interest in polymer blends owing to their potential applications [1,2]. In terms of scientific research the field of the synthetic polymer blends had experienced an enormous growth in recent years. Blending and alloying of polymers with other polymeric components had a significant development [3-5]. One of the main advantages of blending the polymer at the various compositions was the achievement of the change in properties of the final product. Polymer blends can be obtained with a range of properties depending on their chemical nature of the polymer mixed and more precisely on the polymer-A-polymer-B interactions [6].

Mixing of two or more polymers to produce binary and ternary blend is a well established route to achieve a certain amount of improved properties in the polymeric systems [7]. Negligible probability of formation of hydrogen bonds of chitosan with other polymer molecules results from the blending phenomenon. Previous studies reported that the blends of chitosan with other polymers showed significant mechanical properties. Starch is a polysaccharide derived from plants which has fully biodegradable and easily renewable nature [8, 9]. Recently, many researchers have extensively explored the development of starch composite films with other polymers such as collagen [10] poly(vinyl alcohol) [11], carrageenan [12] and gelatin [13].

Chitosan is is a linear, crystalline polysaccharide which composed of β-(1→4) linked N-acetyl-D-glucosamine(Poly-(1-4)-2-Amino-2-deoxy-ß-D-Glucan).Due to its nontoxic, biodegradable, biocompatible nature

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[14, 15] chitosan can be easily combined with other materials [10, 16, 17]. In the present work, effort has been made in synthesizing binary blends by mixing starch and chitosan with cross linking agent to produce the manmade polymer blends that confer unique thermal properties.

MATERIALS AND METHODS

Materials

Chitosan was kind gift from India Sea Foods, Cochin, Kerala which is 92% deacetylated. Starch and glacial acetic acid was purchased from SISCO Research Laboratories PVT, LTD, India. The cross linking agent glutaraldehyde was obtained from SDFINE-CHEM LTD, India.

Blend preparation

Binary blend preparation

A known weight of the solutions of starch (1g) and chitosan(1g) were prepared by dissolving in water and glacial acetic acid separately. These solutions was then mixed in the presence and absence of glutaraldehyde (10ml) as a cross linking agent at room temperature with moderate agitation for one hour. Then the above prepared mixture were poured into a petri dish and dried in vacuum for 10 hrs to remove the solvent completely.

Water Absorption Studies

Water uptake capacity of binary blend was done by immersing approximately 0.1g of the sample in a beaker containing 25ml of water kept in a thermostatic water bath set at room temperature(32˚C) and high temperature(42 ˚C).These samples were then periodically removed from the water bath after a definite time intervals. Then these samples were weighed after blotting with filter paper.

The percentage weight gain at any time‘t’ as a result of solution absorption was determined using the equation which was given below [18].

$$W_t\ (\%) = (W_t - W_o) / W_o \times 100$$

where, W_t = Weight of the sample at different time intervals (after soaked in water).
W_o = Initial weight of the dry sample respectively.

CHARACTERIZATION

FT-IR Spectroscopy

FTIR measurements of the prepared polymeric blend samples was recorded by Fourier transform infra-red spectrophotometer (FT-IR) using the Perkin Elmer 200 FTIR spectrophotometer, in the range of 400-4000cm^{-1} at 25°C with a resolution of 4 cm^{-1}.

TGA analysis

The thermo gravimetric analysis of the starch / chitosan(1:1) blend prepared with and without the crossing linking agent glutaraldehyde was carried out on a Perkin Elmer thermal analysis instrument.

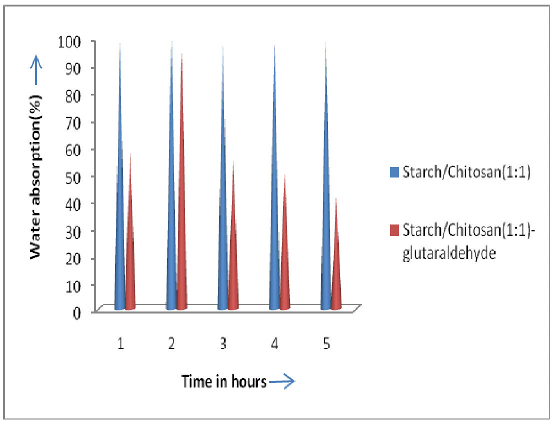
DSC analysis

DSC analysis of the polymeric blend samples was carried out with the Perkin Elmer thermal analysis instrument, with pierced lid in the nitrogen atmosphere at a heating rate of 10° K/min.

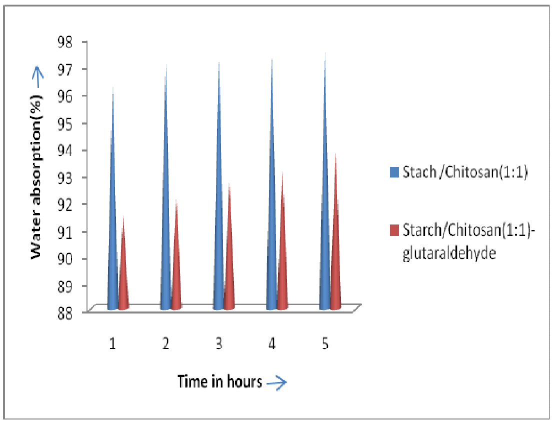
RESULTS AND DISCUSSION

Water absorption studies

Water absorption studies of the binary polymeric blend samples were performed as per the method reported earlier. The results of water absorption percentage values of binary blend prepared with and without cross linking agent glutaraldehyde carried out at room temperature and higher temperature was represented in figures (1) and (2).



Figure(1)



Figure(2)

On comparing the results of water absorption percentage values of binary blend (1:1) prepared with and without cross linking agent, it was observed that the water absorption capacity of blend decreases drastically in the presence of cross linking agent glutaraldehyde. This may be due to the fact that, the addition of glutaraldehyde decreased the average size of the polymer particle and then decreased the free volume and voids by increasing the affinity between the starch, chitosan with the cross linking agent [19]. Due to the decrease in free voids, water absorption capacity of the blend prepared in the presence of the cross linking agent glutaraldehyde decreases.

FTIR analysis:

Figure-3 shows the FTIR spectra of starch-chitosan (1:1) blend. The prominent peaks observed at 3431.84 cm^{-1} corresponds to the intermolecular hydrogen bonding. A peak obtained at 2925.53cm^{-1}, 2855.66cm^{-1} indicates the asymmetric and symmetric C-H stretching in CH_2 respectively. A peak observed at 1718.20cm^{-1}, 1623.22cm^{-1} indicates the presence of C=O stretching in secondary amide and N-H bending respectively. These peaks confirm the blending of starch and chitosan.

Figure: 4 shows the FTIR spectra of starch-chitosan prepared with the cross linking agent glutaraldehyde. On comparing the FT-IR spectra of starch-chitosan blend prepared with (Figure-4) and without the cross linking agent (Figure-3), it was observed that the figure-4 shows an additional peak at 1592.48 cm-1 indicating the presence of C=N stretching. This observed peak confirms strong blending of starch, chitosan with cross linking agent glutaraldehyde.

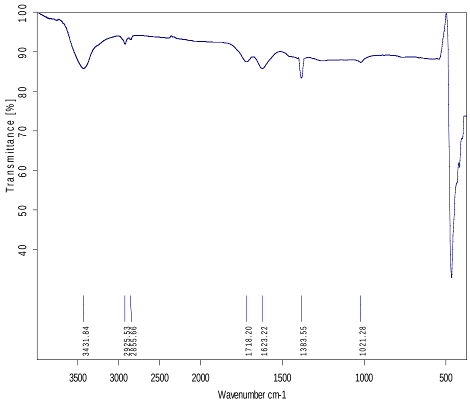


Figure:3 starch/chitosan (1:1) blend

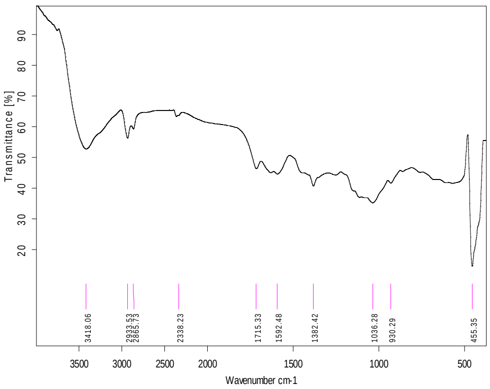


Figure:4 starch/chitosan (1:1) blend- glu

Thermal analysis

Thermo gravimetric analysis

The TGA thermogram of starch and chitosan blend (1:1) (Figure: 5) shows that 80% of the blend is disintegrated within 750ºC. At the end of the experiment i.e., at 850 ºC only 18.003% of the blend remained as a residue. Residual weight was found to be 0.24408 mg which is only 18.003% mg of the sample taken. From 450ºC there is only linear shallow decrease in weight with increase in temperature.

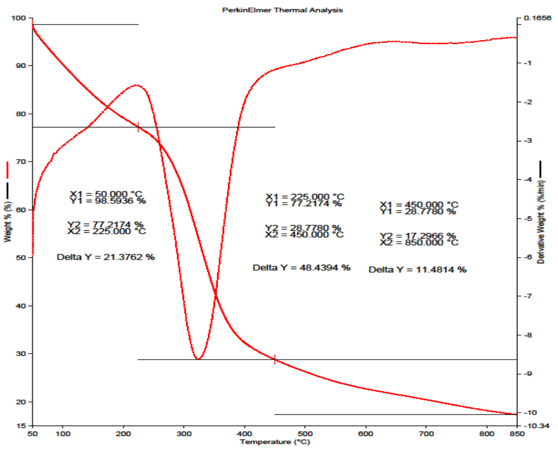


Figure-5 starch/chitosan (1:1) blend

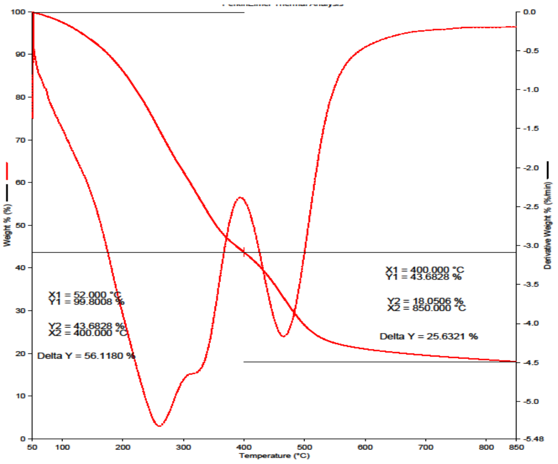


Figure:6 starch/chitosan(1:1) blend- glu

Table:2 and Figure: 6, represents the TGA thermogram details of starch, chitosan(1:1) blend prepared in the presence of cross linking agent glutaraldehyde. Around 80% of the sample is disintegrated within 800 ºC .At the end of the experiment i.e., at 850 ºc only 18.2499% of the blend remained as residue. The residual weight is found to be 0.7315 mg which is 18.2499% of the sample taken. On comparing fig (5) & (6) it was found that the binary starch / chitosan blend prepared with cross linking agent glutaraldehyde was found to be highly thermally stable. This was confirmed from the amount of blend remained as residue at the end of the experiment, and the various decomposition temperatures.

Differential Scanning Calorimetry:

Figures (7) and (8) represents the DSC curve of starch and chitosan (1:1) blend prepared in the absence and presence of glutaraldehyde as the cross linking agent respectively. The glass transition temperature of starch / chitosan (1:1) blend was observed at 155ºC whereas for the starch /chitosan (2:1) blend prepared with the cross linking agent glutaraldehyde, the glass transition temperature was observed at 165°C. On comparing the DSC curves of starch and chitosan (1:1) prepared with and without the cross linking agent, it was found that the endothermic peaks and the glass transition temperatures are shifted to higher values. It confirms that the starch-chitosan polymer blend prepared in the presence of the cross linking agent has higher thermal stability with the formation of different crystalline forms. In addition to this the occurrence of a single, broad glass transition in the Starch/chitosan(1:1)-glutaraldehyde indicate the attractive molecular interactions and a high degree of compatibility of both materials.

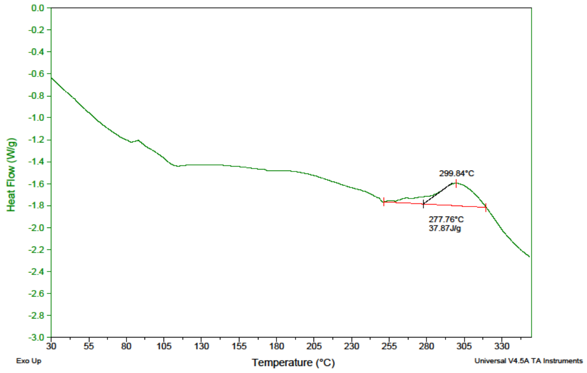


Figure:7 starch/chitosan (1:1) blend

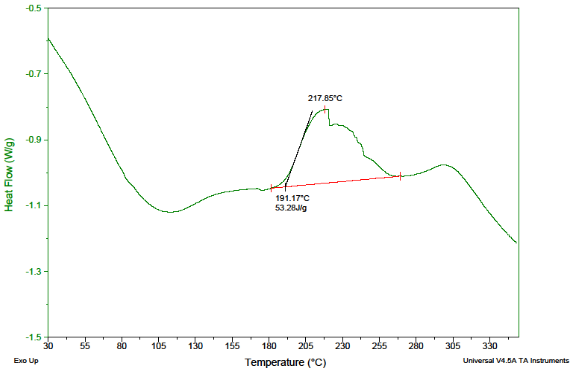


Figure:8 starch/chitosan (1:1) blend- glu

X-RAY diffraction studies

Figures -9,10 show the X Ray diffraction patterns of starch / chitosan (1:1) blend prepared in the absence and presence of cross linking agent glutaraldehyde. X-Ray diffractogram of starch / chitosan (1:1) blend shows peaks at 2θ=11.30▫, 14.90▫, 18.00▫, 22.80▫, 40.60 whereas XRD of starch / chitosan (1:1) prepared in the presence of cross linking agent shows only 2 broad peaks at around 18^0 and $41^{0.}$ From the number of peaks observed, it was concluded that, the sample starch / chitosan (1:1) blend has higher crystalline nature whereas the starch / chitosan (1:1) blend with glutaraldehyde as cross linking agent has semi-crystalline nature. On comparing the XRD patterns of starch and chitosan (1:1) prepared with and without the cross linking agent, it was found that the degree of crystallinity was found to be increased. The above resultsconfirms that, the blend prepared in the presence of cross linking agent has higher thermal stability. with the formation of different crystalline forms.

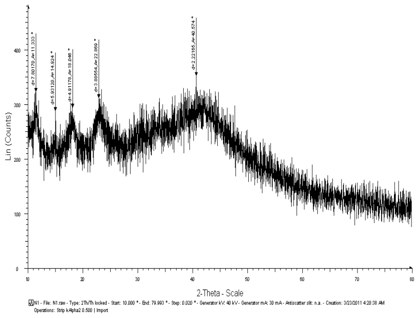


Figure:9 starch/chitosan (1:1) blend

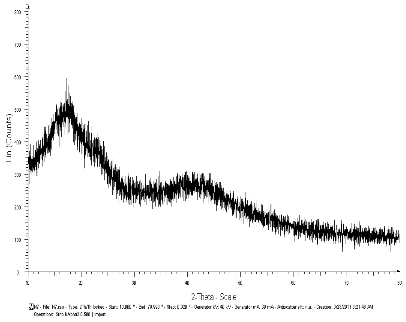


Figure:10 starch/chitosan (1:1) blend- glu

CONCLUSION

The results suggest that there is strong interaction between the molecular chains of chitosan and starch, which may lead to the miscibility at specific ratios of the two components blended. From the FTIR results, it was found that the C=N type of linkage was obtained. This observed peak confirms the strong blending of the starch and chitosan with the cross linking agent glutaraldehyde. From the results of DSC and TGA it was concluded that the cross linking agents enhanced the thermal stability of the polymer blend. The results of x-ray diffraction studies conclude the change in the crystalline nature of the polymer blends prepared with and without the cross linking agent glutaraldehyde.

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