



Short Communication

Thermal Behavior of Poly (vinyl alcohol)/ Poly (vinyl pyrrolidone)/ Chitosan Ternary Polymer Blend Films

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Abstract

In this study, equal weight percent of poly(vinyl alcohol) (PVA)/poly(vinyl pyrrolidone) (PVP) blend solutions filled with different weight percent of chitosan (CS) up to 12 wt% were prepared by solution blending followed by solvent evaporation technique in the form of film. The prepared poly(vinyl alcohol) (PVA)/poly(vinyl pyrrolidone) (PVP)/chitosan (CS) ternary blend films of different weight percentage compositions were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results obtained show an increase in glass transition temperature of the blend films with increasing chitosan content.

Keywords: Chitosan, poly (vinyl alcohol), poly (vinyl pyrrolidone), ternary blend films.

Introduction

Polymer blends are physical mixtures of two or more structurally different homopolymer or copolymers and they interact through secondary forces with no covalent bonding. Polymer blends are prepared by various methods and among them solution blending is very simple and rapid because it requires simple equipment such as glass plates only and not involved any complicated process. Blending of three or more polymers has become an increasingly important technique for preparing materials with tailormade properties different from those of the constituent polymers. Blending of polymers may result in reducing their basic cost, improving their processing and maximizing their important properties. The increase in properties of the blend depends on the degree of compatibility or miscibility of polymers at the molecular level. Depending upon the degree of molecular mixing, blends may be classified as compatible blends or completely miscible, semicompatible or semi-miscible, incompatible or immiscible blends. The extent of compatibility or miscibility results in altogether different morphologies of the blends, ranging from single phase to multiphase systems. Compatibility of polymer blends can also be predicted using differential scanning calorimetric method. Miscible blend films exhibits one phase and single glass transition temperature (T_g). Immiscible blends are phase separated and exhibit glass transition temperature (T_g) of each component.

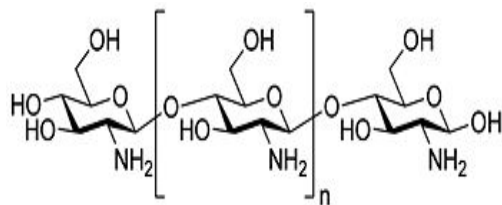
Poly (vinyl alcohol) (PVA) is semicrystalline, water soluble, non toxic, better film and fiber forming, biocompatible, excellent chemical resistance, good mechanical properties and biodegradable synthetic polymer which is widely used in the biomedical field^{1,2}. Poly (vinyl pyrrolidone) (PVP) is an amorphous vinyl polymer which has wide applications in

biomedical field because of its properties including adhesion, excellent physiological compatibility, low toxicity and reasonable solubility in water and most organic solvents³. When these two polymers are mixed, the interaction between poly (vinyl alcohol) and poly (vinyl pyrrolidone) are expected to take place through intermolecular hydrogen bonding between the hydroxyl group of PVA and carbonyl group of PVP.

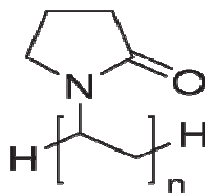
Chitosan is second most abundant natural polysaccharides next to cellulose and is well known for its biocompatibility and biodegradable properties⁴. Chitosan has high modulus of elasticity owing to high glass transition temperature and crystallinity^{5, 6}. Chitosan is, a deacetylated derivate of chitin, renewable, nontoxic and biodegradable carbohydrate polymer. It has been widely applied as functional biopolymer in food and pharmaceuticals. Chitosan is known to have various biological activities including immunoenhancing effects, antitumoral, antifungal and antimicrobial activities⁷⁻⁹. Since chitosan contains hydroxyl and amine groups, it is potentially miscible with PVA/PVP blend matrix due to the formation of hydrogen bonds¹⁰. Therefore chitosan was blended with PVA/PVP blend matrix to study thermal behavior of PVA/PVP blend matrix in presence of chitosan at various proportions by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG). The chemical structures of the polymer used in the study are given below.

Materials and Methods

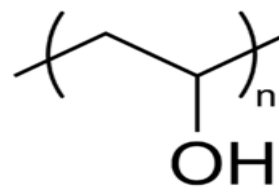
Poly (vinyl alcohol) (PVA), molecular weight, 1, 40,000 and poly (vinyl pyrrolidone) (PVP) average weight, 40,000 and chitosan (CS) were procured from, Himedia, Mumbai, and were used as received. Acetic acid was procured from, spectrochem, Mumbai, and was used as received. Doubly distilled water was used throughout the experiment.



Chitosan



Poly (vinyl pyrrolidone)



Polyvinyl alcohol

Preparation of blend films: Poly (vinyl alcohol) (PVA) and Poly (vinyl pyrrolidone) (PVP) solutions were prepared separately by dissolving the required amount of PVA and PVP in doubly distilled water and chitosan (CS) solutions were prepared by dissolving the definite and exact quantity of chitosan in 2% acetic acid solution at ambient temperature with constant stirring overnight. Then the two same concentration (wt%) of Poly (vinyl alcohol) (PVA) and Poly (vinyl pyrrolidone) (PVP) solutions were mixed and stirred till the solution become homogenous. Then, the required quantity of chitosan solutions in different concentrations (0.0, 0.4%, 1.2%, 2%, 6% and 12 wt %) was added to the equal quantity binary polymer blend solution. The mixture was stirred till the solution becomes homogenous and subsequently highly viscous bubble free solution poured onto cleaned and dried petri dishes to form blend films. The thickness of the blend film was controlled by pouring a definite quantity of blend solution at every time and solvent was evaporated at room temperature and to ensure complete removal of trace amount of solvent present in the blend films petri dishes were kept in hot air oven at 45°C for 72 hours. After drying, all films were peeled from petri dishes and kept in vacuum desiccators before use.

Differential scanning calorimetry: The glass transition temperature, T_g , and other thermal transitions of ternary blend samples was measured on a differential scanning calorimeter (DSC) (Universal TA Instruments, USA), in an inert atmosphere, to minimize oxidative degradation, from room temperature to 600°C at a scanning rate of 10°C/min. The mass of each sample was about 10 mg. The results were recorded and analyzed. The glass transition temperatures (T_g) were obtained from the midpoint of the transitions and melting temperatures (T_m) and decomposition temperature (T_d) from the maximum of the melting peaks.

Thermogravimetric analysis: A thermogravimetric analyzer (TGA) (TA Instruments, USA) was employed to measure thermal weight loss of the PVA/PVP/CS ternary blend films in the temperature range from room temperature to 600°C with the heating rate of 10°C min. under a nitrogen stream. The TG and DTG curves are plotted for each sample. The weight losses at different stages were analyzed. The temperature at which an abrupt decrease in sample weight occurred was designated as the decomposition temperature, T_d .

Results and Discussion

Differential scanning calorimetry: The thermal behavior of PVA/PVP blend doped with different wt% of chitosan were

investigated by differential scanning calorimetry to estimate how thermal transition of the prepared blend films were affected by adding the various wt% of chitosan as shown in figure 1. The exothermic peak is observed at about 47°C for all the samples could be due to the small amount of moisture present in the blend films. The glass transition temperature, T_g , of the blend increases with increase in concentration (wt%) of chitosan and then decreases as shown in the figure 1 and 2 and table 1. This is resulted from intermolecular interaction (hydrogen bonding) formed among PVA, PVP and chitosan. The blend shows maximum T_g up to 6 wt% of chitosan. Above this wt% of chitosan T_g decreases may be due to chitosan was immiscible with PVA/PVP blend matrix. Up to 6 wt % chitosan was miscible with PVA/PVP blend matrix and for 12 wt% chitosan was immiscible. From DSC studies, single glass transition temperature was observed for each blend sample as shown in figure 2 which clearly indicates that PVA/PVP blends doped with different wt% of chitosan were completely miscible in the range of composition investigated in our study. An endothermic crystalline peak, T_m , is observed at about 328°C and another endothermic peak is observed, T_d , at about 425°C

Table-1
 The values of T_g , T_m and T_d of PVA/PVP blend filled with different weight % of chitosan

CS (wt%)	T_g (°C)	T_m (°C)	T_d (°C)
0.4	86.90	328.02	438.40
1.2	90.43	331.51	438.50
2	104.05	325.20	441.05
6	112.29	328.02	438.40
12	98.52	334.85	441.59

Thermogravimetric analysis: Figure 3 shows thermograms of weight loss as a function of temperature for PVA/PVP blend filled with different wt (%) of chitosan with heating rate of 10°C/min. in the temperature range from room temperature to 600°C. It is evident from the figure 3 that the initial weight loss for all the samples starts around 62°C and shows about 10.13% loss of weight. This may corresponds to the loss of bound water and acetic acid from the blend. The second weight loss starts around 250°C and continues up to 360°C which attributed to melting temperature, T_m , during which there was 35% weight loss. The third weight loss was observed in the range from 370-450°C which may be correspondent to the structural decomposition of the blend during which there was 48.38% weight loss.

Conclusion

The thermal behavior PVA/PVP blends filled with different weight % of chitosan films were studied. Results indicate that the glass transition temperature and melting temperature of the PVA/PVP/CS ternary blend film increased when the amount of chitosan in the ternary blend film is increased. This is because hydrogen bonding interaction among the poly (vinyl alcohol) (PVA), poly (vinyl pyrrolidone) (PVP) and chitosan (CS). Therefore it can be concluded from the present study that chitosan can be used as a modifier to improve the thermal properties of PVA/PVP blend. The optimum ratio of chitosan was found to be 6 wt%. These blends films are very suitable as natural materials for food packaging and also for controlled release of various pharmaceutical antimicrobial drugs.

Acknowledgment

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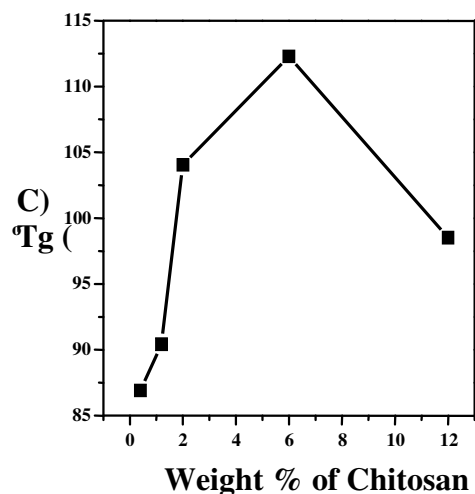


Figure-1

Variation of T_g with different weight % of chitosan

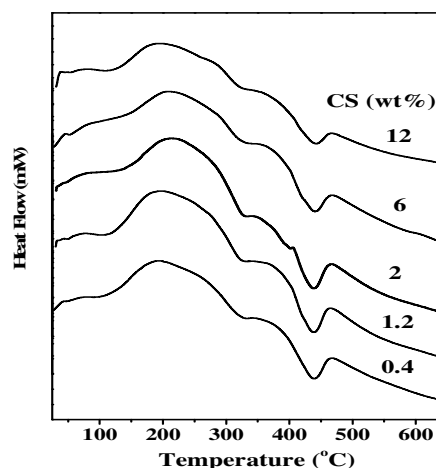


Figure-2

DSC thermograms of PVA/PVP/CS blend

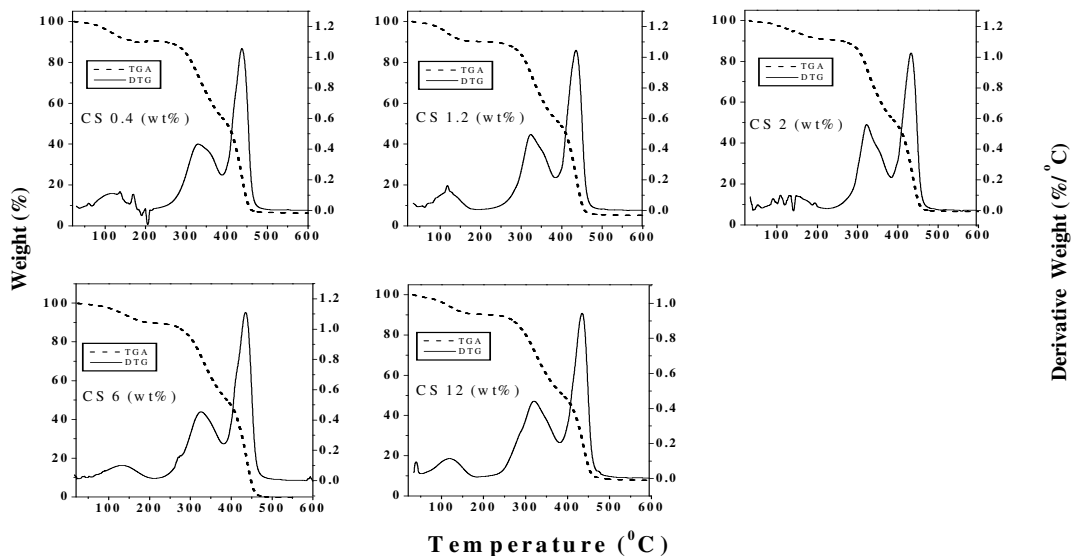
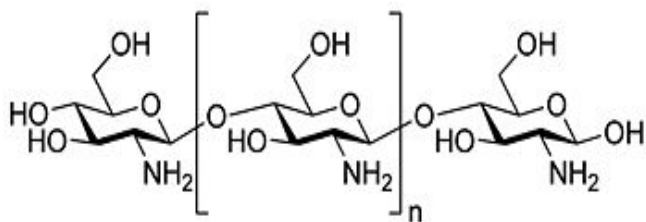
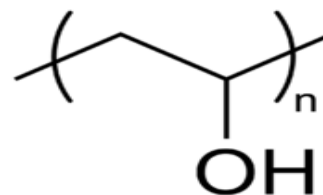


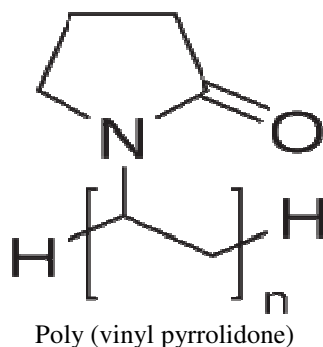
Figure-3
 TG/DTG thermograms of blend



Chitosan



Poly (vinyl alcohol)



Poly (vinyl pyrrolidone)

Figure-4