



Investigation of Morphological and Mechanical Behavior of Poly (vinyl alcohol) /Chitosan/Papain Ternary Blend Films

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Abstract

Ternary polymer blended films were prepared by mixing different weight percent of papain in equal weight percent solutions of poly (vinyl alcohol) (PVA) and chitosan (CS) by solvent evaporating technique. The phase morphology and mechanical properties of various polymeric blended films were carried out using scanning electron microscopy (SEM) and universal testing machine (UTM) at room temperature. SEM micrographs for the blend system showed good miscibility among the blend components. The tensile strength increases with increase in wt% of papain (dried papaya latex in power form) and then decreases.

Keywords: Poly (vinyl alcohol), chitosan, papain, mechanical behavior.

Introduction

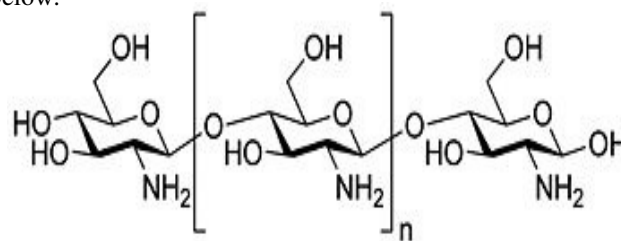
Polymer blending has received much attention in the recent years. This is mainly due to the fact that new materials with better physicochemical properties can be observed when the original polymers are compatible^{1,2}. Blending of synthetic with natural biopolymers is considered as a new class of materials that is of particular significance³.

Poly (vinyl alcohol) (PVA) is a non-toxic, water soluble synthetic polymer that has been commercially produced on a large scale. It has a large number of hydroxyl groups which allows it to react with many types of functional groups. This advantage makes it suitable as biocompatible materials. PVA has been widely utilized in diverse fields, ranging from thickening agent to controlled release systems⁴.

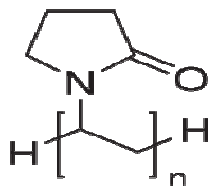
Chitosan, a natural polysaccharide, has attracted much attention of researcher in various parts of the globe. It is produced by excessive alkaline deacetylation of the second most abundant naturally occurring chitin of crab and shrimp shells⁵. Due to the presence of amino groups in its chain, chitosan can be dissolved in dilute aqueous acid solutions, such as acetic acid and propionic acid, formic acid and lactic acid. Since it is inexpensive, non-toxic and possesses potentially reactive amino functional groups, chitosan has been widely used in the fields of medicine, food, cosmetics, agriculture, wastewater treatment and so on⁶⁻¹⁰.

Synthetic polymers offers a broad range of properties that can be reasonably modified using plant products which are attractive and alternative to synthetic products because of biocompatibility, low toxicity, environmental friendliness and low price compared synthetic products¹¹. Papain (papaya latex,

PL) is a natural proteolytic enzyme that is extracted from the latex in the leaf, the stem and unripe fruits of papaya tree¹². Papain is present in all parts of the papaya plant but maximum amount can be found in their plants leaves and in the skin of the full grown but unripe fruits. Papain (papaya latex, PL) is a milky white sticky substances or latex that flows from fully grown and unripe papaya when it is cut. This milky white substance or latex is collected in a container and dried as papain. Papain (papaya latex, PL) is characterized by its ability to hydrolyze large proteins into smaller peptides and amino acids¹³. Papain (papaya latex, PL) has wide range of applications in different industries, especially in personal care products such as soap, shower gel and good industry¹⁴. It is also being used to tenderize meat and meat products, in the manufacture of protein hydrolysis, in confectionary industry to prepare chewing gums, in brewing industry to remove cloudiness in beer and in dairy industry for cheese¹⁵. Similarly, papain is also used in pharmaceutical industry, textile industry and tanning industry¹⁴. In addition to tenderizing effect on meats, papain may also be used to make beer chill proof. The main objective of this study was to prepare poly (vinyl alcohol)/chitosan/papain (papaya latex, PL) blend films and to investigate their morphology and mechanical properties. The chemical structures of the polymer used in the study are given below.



Chitosan



Poly (vinyl pyrrolidone)

Figure-1
 Chemical structure of the polymers

Material and Methods

Poly (vinyl alcohol) having molecular weight 1,40,000 and Chitosan were obtained from HIMEDIA Mumbai. Papain was received from Sisco Research Laboratory, Mumbai and acetic acid was procured from, Spectrochem, Mumbai, and was used as received. Doubly distilled water was used throughout the experiment.

Preparation of Blend Films: Ternary polymer blends films of poly (vinyl alcohol)/chitosan/papain of different compositions were prepared by solution casting method. For the preparation of blend films, exactly weighed amount of polymers and papain were dissolved separately. Chitosan solution was prepared in 2% acetic acid and poly (vinyl alcohol) and papain solution was made in universal solvent water. After allowing them to dissolve completely, papaya latex was not dissolved completely, then polymer solutions were mixed with continuous stirring four hours and subsequently definite volume of all blend solutions poured onto previously cleaned and dried glass petri dishes and solvent is evaporated at room temperature to form blend films. Finally the petri dishes containing films was dried in hot air oven at 45°C for a week to ensure complete removal of trace amount of solvent present in the blend films. After evaporation of complete solvent all films peeled off from petri and kept under evacuated desiccator over fresh silica gel until use. All obtained films were semitransparent, uniform thickness and bubble free.

Mechanical Properties: A LLOYD LRX plus universal testing machine, UTM, (LLOYDS – 5 KN, London, UK) was used to measure tensile strength, young’s modulus and percent elongation (%). The tests were carried out according to ASTM D-882 standard test (ASTM, 1992). Rectangular shaped sample of films (25 × 100 mm) were taken for the determination of tensile properties. Two metallic grips were attached for gripping both ends of the test specimen of the film. The lower grip was stationary and the upper grip moved upward with constant rate of extension 50 mm/min keeping constant initial grip separation 50 mm for all samples. An automatic speed controller was attached to keep the speed of the upper grip. The machine was electrically driven. All measurements were carried out at room temperature in air. Tensile Strength was calculated by dividing the maximum load for breaking the film by cross-sectional area. Elongation at Break by dividing the

film elongation at rupture to initial gauge length (% elongation is the ratio of the extension to the length of the sample). The modulus of elasticity (young’s modulus) is the ratio of stress to strain at the linear portion of the curve or slope of the linear portion of the curve of stress strain.

Scanning Electron Microscopy: It should be noted that the viscosity difference among the polymers or component of blend films has a significant impact on the phase morphology of the blends. If the minor component has lower viscosity compared to the major one, it will be finely and uniformly dispersed in the major continuous phase owing to the diffusion restrictions imposed by the matrix¹⁶ and otherwise coarsely dispersed. Films surface morphology was examined using scanning electron microscopy (SEM). Prior to the examination, blend films were dried overnight in a hot air oven at 45°C and mounted on a metal stub with double side sticky tape. Then the blend films were coated with a thin layer of platinum in order to improve conductivity and prevent electron charging on the surface. The morphological structures of the films were studied by a JSM- 6360 scanning electron microscope (SEM) of JEOL, Germany, and the images were taken at accelerating voltage 5 kV and a magnification 500 times of origin specimen size.

Results and Discussion

Mechanical properties: The phase morphology and the interfacial adhesion among the components of polymer blend, influence the mechanical properties of polymer blend films. The stress-strain behavior of blend films is demonstrated in figure 2. From the stress-strain curves, we estimated maximum tensile strength, elongation at break and young’s modulus, data was analyzed using NEXOGEN Plus software, and these tensile properties are summarized in table 1. The tensile strength, young’s modulus (modulus of elasticity) and percent elongation could be used to describe how the mechanical properties are related to their chemical structure. The tensile strength indicates the maximum tensile stress that the film can sustain.

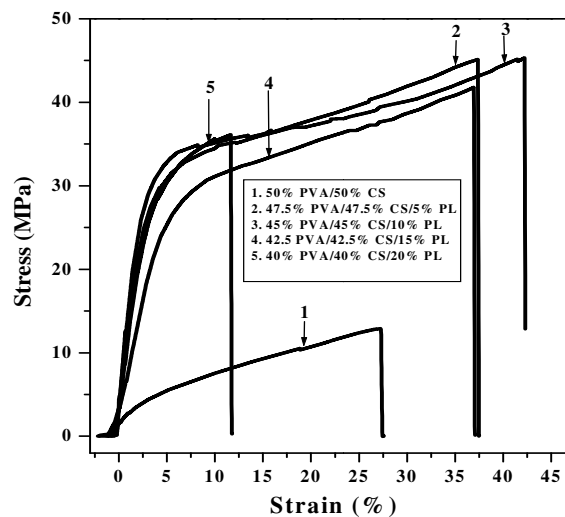


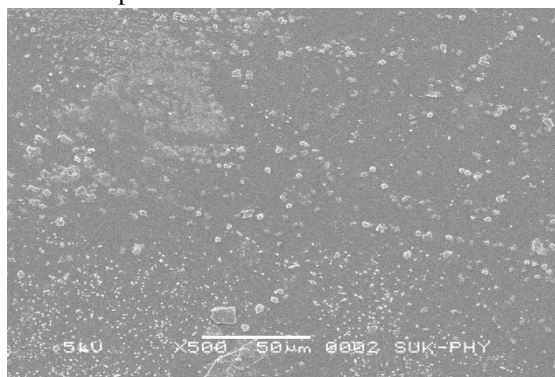
Figure-2
 Stress-Strain curves of PVA/CS/PL blend films

Table-1
Tensile properties of PVA/CS/PL blend films

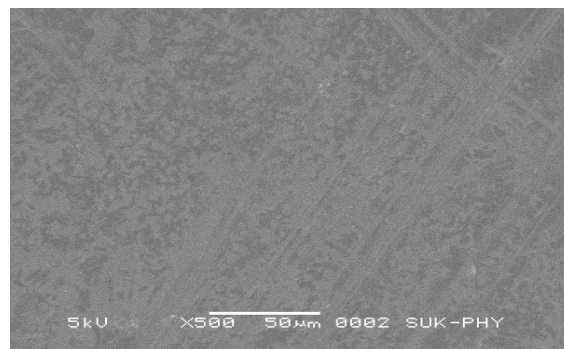
Blend ratios (wt%)	Tensile Strength (MPa)	Young's modulus (MPa)	Elongation at Break (%)
50% PVA/50% CS	12.881	136.639	27.489
47.5% PVA/47.5% CS/5% PL	45.128	1452.918	37.413
45% PVA/45% CS/10% PL	45.338	1291.455	42.300
42.5% PVA/42.5% CS/15% PL	41.719	607.270	37.090
40% PVA/40% CS/20% PL	36.119	1183.68	11.784

Young's modulus is a measure of the stiffness of the blend film material. Elongation at break is the maximum change in length of a test film before breaking. The results indicate that the addition of the papaya latex increases the tensile strength and then decreases. Blend film exhibits maximum tensile strength with 10% papaya latex and above this wt% tensile strength decreases which may be due to decrease in interfacial adhesion among the blend components.

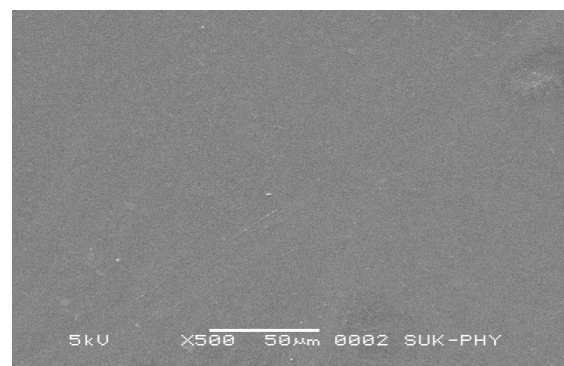
Scanning electron microscopy (SEM): Figure 2 shows SEM photographs of the top surface of the pure poly (vinyl alcohol)/chitosan blend film and poly (vinyl alcohol)/chitosan/papaya latex blended films. The result of SEM indicates that on surface of poly (vinyl alcohol)/chitosan film there are many non spherical granules with varying sizes and these kinds of granules are not seen in the films prepared from papaya latex. Blend films prepared from 10 wt%, 15 wt% and 20 wt% papain displayed clear and homogenous surfaces with no interface layers. The formation of homogeneous blends of poly (vinyl alcohol)/chitosan/papain was mostly due to the interactions of hydrogen bonds among the functional groups of the blend component. However, the ratio 47.5%PVA/47.5%CS/5%PL blend film showed a little rougher surface indicating more hydrophilic top surface than the other blend films. According to Chen *et al*¹⁷ such a rough surface could be due to the reorientation of polar functional groups toward to the top surface of the blend film. Based on these observations it can be concluded that all papaya latex blended films were compatible at all ratios.



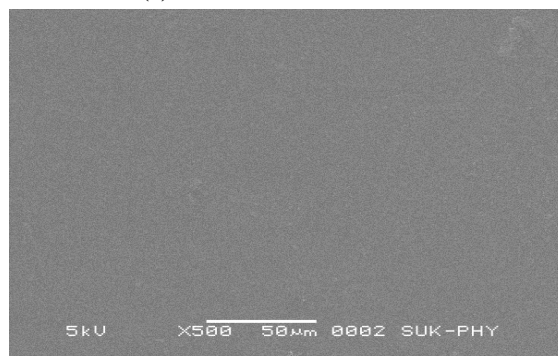
(a) 50%PVA/50%CS



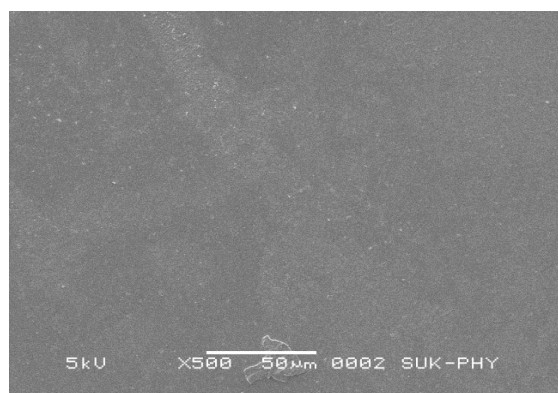
(b) 47.5%PVA/47.5%CS/5%PL



(c) 45%PVA/45%CS/10%PL



(d) 45%PVA/42.5%CS/15%PL



(e) 40%PVA/40%CS/20%PL

Figure-2
SEM micrographs of pure PVA/CS and PVA/CS/PL blended films

Conclusion

Ternary blended films of poly (vinyl alcohol)/chitosan/papain were prepared at various proportions of papaya latex. SEM Investigation of the obtained blend films displayed good miscibility among poly (vinyl alcohol), chitosan and papain due to the interaction existing among the components of blend films.

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