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Tensile and Thermal Properties of Poly (vinyl pyrrolidone)/Vanillin Incorporated Poly (vinyl alcohol) Films

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Abstract

This study reports the fabrication of PVA/PVP/vanillin blend films by using solvent casting method. The objective of this study was to investigate the correlation between PVA/PVP/vanillin blend films of different weight ratio, mechanical properties and thermal properties. The PVA/PVP/vanillin blend films were subjected to the mechanical study and thermo gravimetric analysis. Addition of PVP/vanillin has significant effect on PVA films, exhibiting decreased tensile strength and young's modulus. The tensile strength of blend films is lower compare to the pure PVA film. Results obtained from thermal analysis indicate that all the components in the blend films are miscible showing single glass transition temperature and are stable up to 185^{o}C suggesting that, a considerable amount of interactions may exist between components in each blend films.

Keywords: PVA, PVP, vanillin, tensile properties, thermal properties.

Introduction

In recent years blend films have gained much attention as packaging material for food. These blends are assumed a very important status scientifically and technologically. Poly (vinyl alcohol) is a water-soluble synthetic polymer and is an odorless, tasteless, translucent, white or cream colored granular powder[1]. Due to the existence of numerous hydroxyls, PVA is easily soluble in water and soluble in hydroxyl-contained organic compounds. The prominent properties of poly (vinyl alcohol) are its biodegradability[2] in the environment and biocompatibility[3-5]. Poly (vinyl alcohol) has high tensile strength, flexibility, high oxygen and aroma barrier property. It also has excellent film forming, emulsifying and adhesive properties.

Poly (vinylpyrrolidone) (PVP) is a water-soluble polymer made from the monomer *N*-vinylpyrrolidone[6]. Poly (vinyl pyrrolidone) is derived from vinyl polymer exhibiting highly polar side groups present in the lactam ring[7]. In addition, it is an amorphous polymer with high T_g due to the presence of rigid pyrrolidone functional group, exhibiting property to form complexes with other polymers[8]. Poly (vinyl pyrrolidone) has adhesive property, excellent physiological compatibility, low toxicity and reasonable solubility in water and most organic solvents[9-10] which can find wide applications in biomedical.

Vanillin (4-hydroxy-3-methoxybenzyldehyde) is an important flavoring agent derived from bean or pod that widely used in industry as a food, drinks and cosmetics. Vanillin has considered as nutraceutical molecule because it possess anticlastogenic, antimutagenic and antitumor property[11-12]. Vanillin has bioactive properties including antioxidant and antimicrobial activity against bacteria, moulds and yeasts[13-16]. The presence of phenolic groups in chemical structure, were responsible for exhibited antimicrobial property in vanillin. In this study we will prepare the PVA/PVP/Vn blend films by using solution casting technique for enhancing PVA properties. Further, the characterization of the films was discussed by means of mechanical and thermal study.

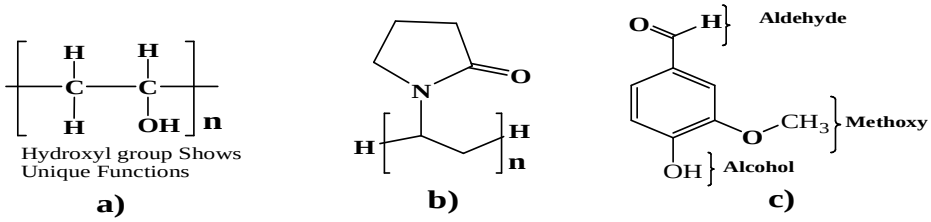


Figure-1
Chemical Structure of a) Poly (vinyl alcohol) b) Poly (vinyl pyrrolidone) and c) Vanillin

Material and Methods

Poly (vinyl alcohol), molecular weight 1, 40,000 and poly (vinyl pyrrolidone) average weight, 40,000 and were procured from, Himedia, Mumbai and Vanillin were obtained from Central Drug House (CDH), New Delhi and used as received. Doubly distilled water was used throughout the experiment.

Preparation of Blend Films: In this study, PVA/PVP/Vn blends films were prepared by solution casting method. PVA solutions of different concentrations were prepared by dissolving an exactly weighed amount of PVA in distilled water and stirred till the solution becomes clear, homogenous and viscous. Simultaneously different concentration (Wt %) of PVP and vanillin solutions were also prepared. Then all the three solutions were mixed and stirred till the solutions become homogenous. Definite volume of all blend solutions poured onto previously cleaned and dried glass petri dishes and solvent is allowed to evaporate at room temperature. After drying, all films were peeled from petri dishes and stored in desiccators until use.

Thermal Analysis: Prepared blend samples with masses between 2 to 10 mg were heated in an inert N_2 atmosphere, at a heating rate of 10°C/min from room temperature to 600°C using SDT Q600 TGA/DTA TA instrument. The glass transition temperature (Tg), melting temperature (Tm) and decomposition temperature (Td) were calculated, from heat flow versus temperature, using the Universal Analysis Software V4.5A (TA Instruments, New Castle, DE, USA).

Tensile Properties: A LLOYD universal testing machine (LLOYDS – 5 KN, London, UK) was used to determine the tensile strength, young's modulus and percent elongation (%). The tests were performed according to ASTM D-882 standard test (ASTM, 1992) at room temperature in air and tensile properties were calculated using NEXYGEN Plus software. Rectangular shaped sample of 25 mm ×100 mm were taken for the determination of tensile properties.

Results and Discussion

Thermal Analysis: Figure-2 shows the thermogram of pure PVA as well as its blend (figure-3a,b,c,d,e) with different ratio. The three step weight loss was observed in the pure PVA. The film is stable up to 250°C. The first weight loss was evaporization of moisture observed at 42–130°C. The second thermal event observed at 220–310°C is due to the thermal degradation of PVA molecule. The byproduct liberated in the degradation of PVA molecule causes the third weight loss at 390–425°C.

According to Hay and Chen et al report[17-18], thermal destruction leads to the formation of aldehyde and alkenes as end-groups and this effect is way to the formation of vinyl ester by the rearrangement reaction.

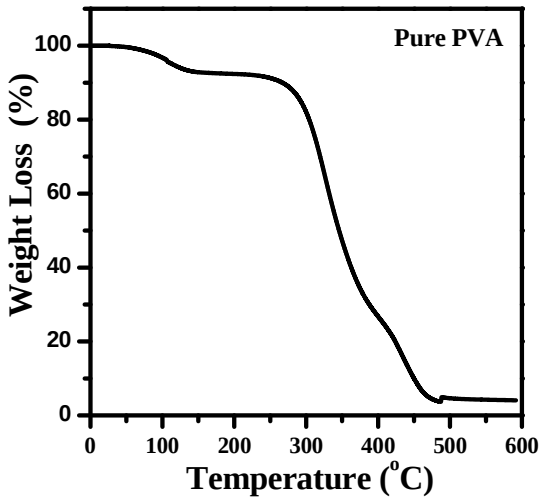


Figure-2
TGA Thermogram of Pure PVA Film

All blend films exhibited three stage weight loss processes. The first initial weight loss occurred between 73°C and 122°C, due to the evaporation of water molecules. The second weight loss occurred at 285°C and continues up to 424°C, corresponding the melting temperature, (T_m) of the blends. The structural decomposition of PVA, PVP and Vanillin occurs at approximately 424 - 466°C. The incorporation of PVP and Vn did not influences thermal stability of these films, as predicted only small variation in the blend film.

The miscibility of the polymer play a key role in the development of novel materials based on blends, as it is directly related to the properties of final product. Figure-4a and 4b shows the DSC thermogram for PVA/PVP/Vn blend films. From the thermogram it is clear that the heat flow observed from 73–135°C is due to the liberation of small amount physically absorbed water molecules. The glass transition and melting temperature of pure PVA were found to be 173°C and 326°C. The decrease in the glass transition temperature (T_g), value is detected by increasing the content of PVP/Vn in PVA matrix. This is due to the added PVP and Vn acts as plasticiser.

Tensile Properties: The tensile properties such as tensile strength (Ts), young's modulus (Ym) and elongations at break (Eb) were determined from the stress-strain curves and are presented in figure-5a, b and summarized in table-3. With incorporation of poly(vinyl pyrrolidone) and vanillin onto the poly(vinyl alcohol) film, the decrease in tensile properties including Ts, Ym and Eb were observed compared to pure PVA film. The decrease in tensile properties of blend films could be attributed to the weak intermolecular interaction and lack of

interfacial adhesion among the components that leads to the reduced tensile properties[19] and brittleness of the blend films.

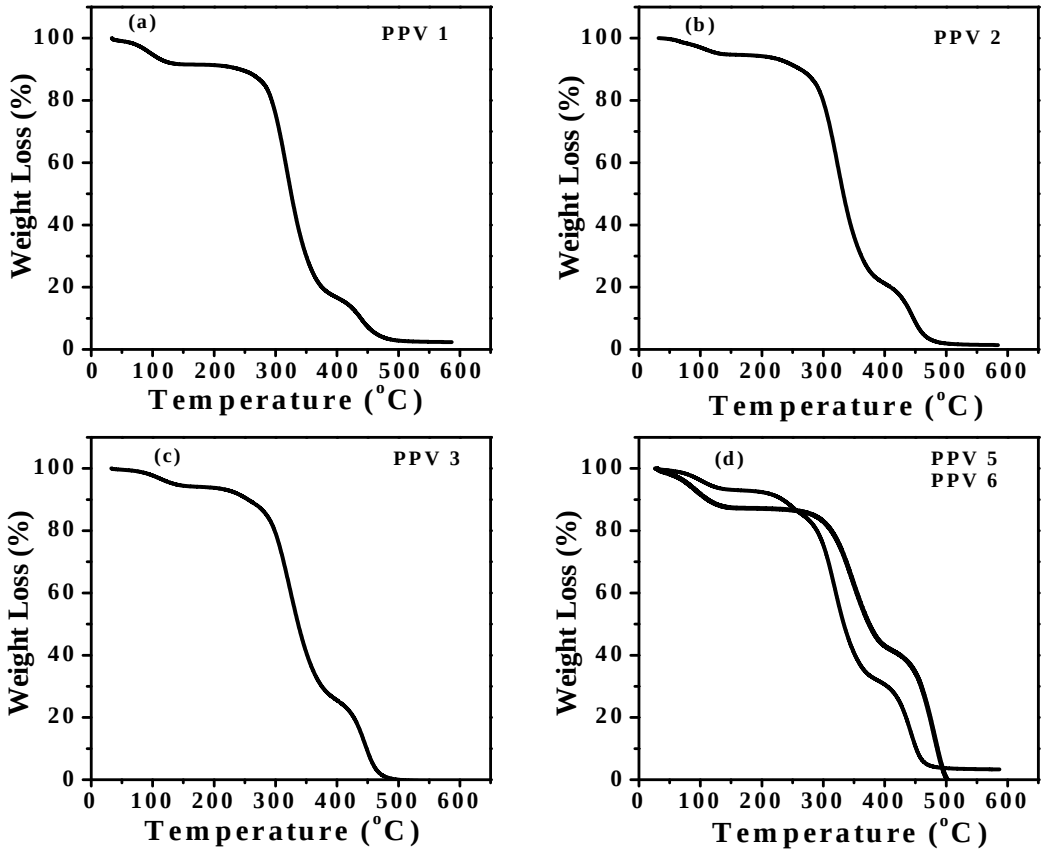


Figure-3
Thermogram of a) PPV1, b) PPV2, c) PPV3, d) PPV4 e) PPV5 Blend Films

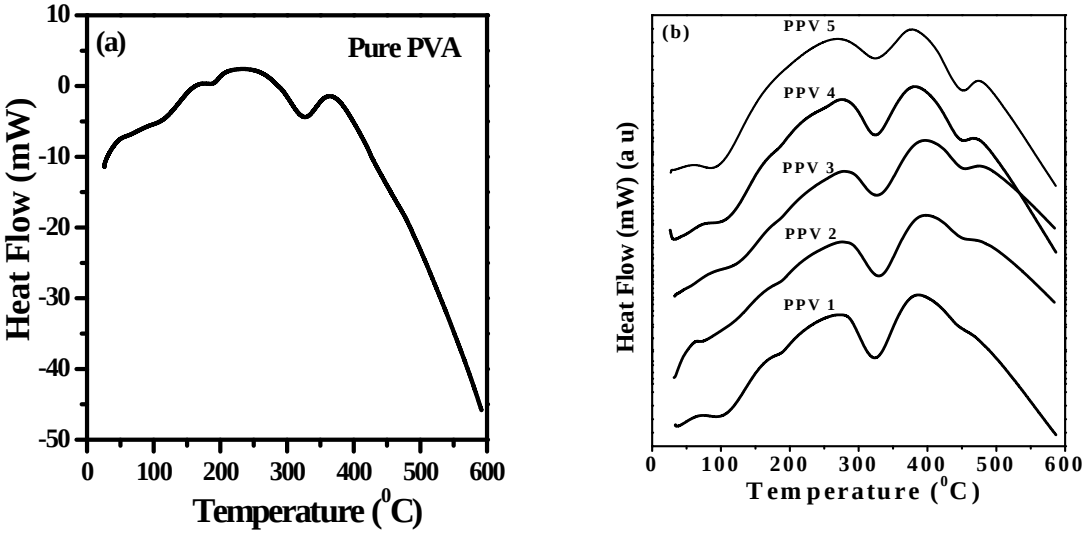
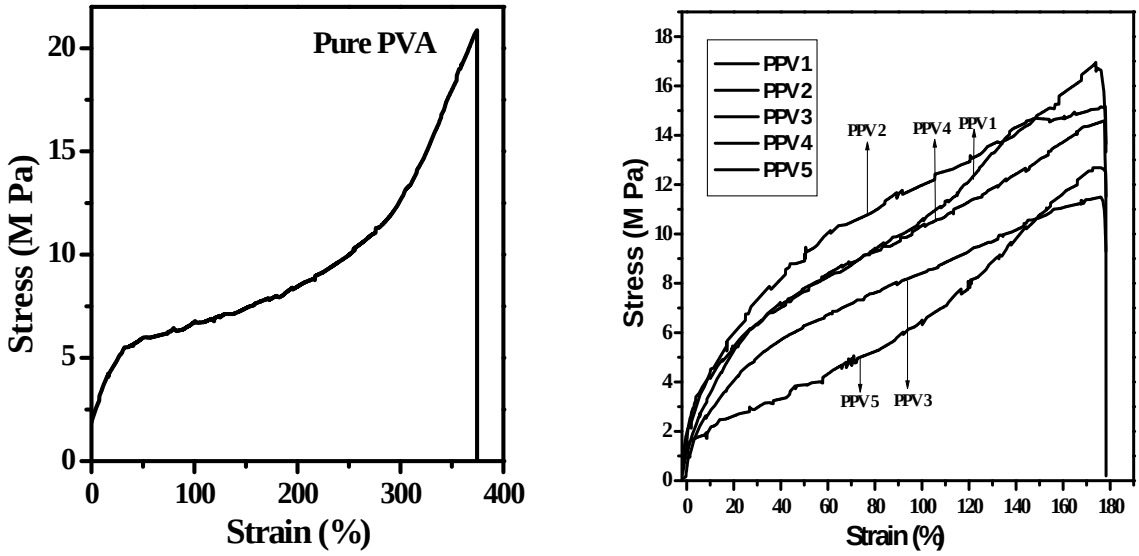


Figure-4
a) DSC Thermogram of Pure PVA Films b) Thermogram of PVA/PVP/Vanillin Blend films



(a) **(b)**

Figure-5
a) Stress-Strain Curve of Pure PVA b) Stress-Strain Curve of PVA/PVP/Vanillin Blend Films

Table-1
Different Composition of PVA/PVP/Vn Ternary Blend Films

Sample Code	Blending Ratios PVA/PVP/Vn	Wt % (PVA)	Wt % (PVP)	Wt % (Vn)
Pure PVA	100/0/0	100	0	0
PPV 1	90/7.5/2.5	90	7.5	2.5
PPV 2	80/15/5	80	15	5
PPV 3	70/22.5/7.5	70	22.5	7.5
PPV 4	60/30/10	60	30	10
PPV 5	50/50/0	50	50	0

Table-2
T_g and T_m Values of Pure PVA and PVA/PVP/Vn Blend Films

Sample code	Blending Ratio	T_g (°C)	T_m (°C)	T_d (°C)
Pure PVA	100	173	330	435
PPV 1	90/7.5/2.5	68.74	325.1	330
PPV 2	80/15/5	75.23	331.7	329
PPV 3	70/22.5/7.5	109.5	325.3	335
PPV 4	60/30/10	91.66	325.22	339
PPV 5	50/50/0	75.98	325.51	334

Table-3
Tensile Properties of PVA/PVP/Vn Blend Films

Sample Code	Blending Ratios PVA/PVP/Vn	Tensile Strength (M Pa)	Young's Modulus (M Pa)	Elongation at Break (%)
Pure PVA	100/0/0	20.87	16.21	374.4
PPV1	90/7.5/2.5	16.77	41.74	174.5
PPV 2	80/15/5	18.63	35.34	145.5
PPV 3	70/22.5/7.5	13.14	65.03	144.2
PPV4	60/30/10	15.69	128.0	173.9
PPV 5	50/50/0	12.68	13.10	192.0

Conclusion

Various proportions of PVA/PVP/Vn blend films were prepared successfully. Tensile and thermal behavior of obtained blend films was determined by using mechanical testing and simultaneous DSC-TGA analysis technique. Results obtained from thermal analysis indicate that all the components in the blend films are miscible showing single glass transition temperature and are stable up to 185^{o}C and mechanical study confirms the tensile strength of various blended films are lower than the pure PVA film.

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