Miscibility and Thermal Study of PVA/Chitosan/Papaya Latex Blend Films

Chougale Ravindra B.[1*], Masti Saraswati P[2]., Mudigoudra Bhagyavana S[3]., Kasai Deepak R[4]

[1]P. G. Department of Studies in Chemistry, Karnatak University, Dharwad - 580 003, Karnataka, India.*
[2] Department of Chemistry, Karnatak Science College, Dharwad - 580 001, Karnataka, India.
[3] Department of Computer Science, Maharani Science College for Women, Bangalore, Karnataka, India.
[4] Department of Materials Science, Mangalore University, Mangalgangotri - 574 199, Karnataka, India.

***

Abstract: Different weight percent of ternary PVA/Chitosan/Papaya latex blend films were prepared by solvent evaporating technique. The glass transition temperature and thermal stability of blend films were investigated using differential scanning calorimetry and thermogravimetric analysis. Fourier transform infrared studies reveal the formation of hydrogen bond. The miscibility of various wt % of papaya latex incorporated blend films were carried out using scanning electron microscopy. Scanning electron microscope micrographs for the blend system showed good miscibility among the blend components. The tensile strength increases with increase in wt % of papaya latex and then decreases.

Key Words: Papaya latex, thermal properties, glass transition.

1. INTRODUCTION

Biomaterials for control drug release and food packaging have gained much interest to develop and modify the polymeric materials to meet desired property [1]. In this context, many types of synthetic and natural polymers have been prepared and subjected to the various applications. The miscibility between the components of polymer mixture is major factor in the development of new polymer material with desired property. In search of new polymeric materials researchers have paid much attention to the study of polymer blending [2-6]. Polymer blending is easy and inexpensive [7] method for modifying properties of polymers. Blending of natural polymer with synthetic which is application oriented lead to the pollution free and biodegradable materials [8-12].

Chitosan is a by-product obtained by deacetylation of chitin [13]. It is a cationic polysaccharide with high molecular mass, good film forming ability and antimicrobial activity. Chitosan it is one of the abundant, renewable, biodegradable carbohydrate polymer. Chitosan is known have various biological activities [14-16]. On the other hand poly (vinyl alcohol) is studied extensively because of its physical properties which are arising from the presence of –OH groups and the hydrogen bond formation [17]. The blends of poly (vinyl alcohol) with chitosan have attracted much commercial interest. On review of literature on polymer blend we came to know that blending of Chitosan with poly (vinyl alcohol) has been already reported in literature [18-23]. Therefore, this study was undertaken to determine the effect of papaya latex on PVA/chitosan blend films and to investigate their morphology, miscibility, stability, interaction and mechanical properties.

2. EXPERIMENTAL METHODS

2.1 Materials

Chitosan was supplied by Tokyo Chemical Industry (TCI) Tokyo, Japan (CAS 9012-76-4) and Poly (vinyl alcohol) (PVA) was procured from central drug house (CDH), New Delhi. Papaya latex was purchased from Sisco Research Laboratories Pvt, Ltd, Mumbai, India.

2.2 Preparation of Blend Films

Ternary polymer blends films containing PVA/chitosan/papaya latex of different compositions were prepared by solution casting method. For the preparation of blend films, exactly weighed amount of two different polymers and papaya latex were dissolved separately. Chitosan solution was prepared in 2% acetic acid and poly (vinyl alcohol) and papaya latex solution was made in distilled water. After allowing those to dissolve, the three solutions were mixed with continuous

stirring on magnetic stirrer for four hours. Subsequently definite volume of all blend homogeneous 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 dish and kept under evacuated desiccators over fresh silica gel until further use. All obtained films were semitransparent, uniform thickness and bubble free.

Table- 1: Composition of Ternary Blend Films

Blend Composition (Wt %)		PVA (Wt %)	Chitosan (Wt %)	Papaya Latex (Wt %)
50/50/0	PL1	50	50	0.0
47.5/47.5/5	PL2	47.5	47.5	5
45/45/10	PL3	454	45	10
42.5/42.5/15	PL4	42.5	42.5	15
40/40/20	PL5	40	40	20

2.3 Scanning Electron Microscopy (SEM)

The phase morphology of the prepared blend films were determined by using scanning electron microscopy (SEM) (JOEL-JSM-6360, Germany). Blend films were sputter coated with gold layer to avoid charging under high electron beam and mounted on a metal stub with double side sticky tape. The images were taken at accelerating voltage 5 kV and a magnification 500 times of origin specimen size.

2.4 Fourier Transform Infrared (FTIR) Spectroscopy

The possible interactions among the prepared blend films were analysed by FTIR spectroscopy (FTIR attenuated total reflection (ATR) method in IR spectrometer, FT-IR-ATR, Prestage 21, Shimadzu, Japan). Samples were analyzed between 400 and 4000 cm-1 with a resolution of 4 cm^{-1}.

2.5 Thermogravimetric Analysis

The thermal properties of pure polymer and its blends films were measured using thermogravimetric analyzer (SDT Q600 V20.9 Shimadzu, Tokyo) from 30°C to 700°C in an inert N_2 environment (flow rate 100 ml/min) at heating rate of 10°C/min. The sample mass was between 5-10 mg.

2.6 Differential Scanning Calorimetry (DSC)

DSC studies were performed using DSC Q20- V24.4 Build 116 (TA Instruments, Walters LLC New Castle, Delaware, USA). Samples were sealed in aluminum crucible and heated from room temperature to 500°C at 10°C min-1in an inert nitrogen gas (50 ml/min^{-1}).

3. RESULTS AND DISCUSSION

3.1 scanning electron microscopy

The morphological structures of the films were studied by a JSM- 6360 scanning electron microscope of JEOL, Germany, and the images were taken at accelerating voltage 5 kV and a magnification 500 times of origin specimen size. Figure 1 shows scanning electron microscope micrographs of the top surface of the pure PVA/chitosan blend film and PVA/chitosan/papaya latex blended films.

The result of scanning electron microscope indicates that, on surface of PVA/chitosan/papaya latex film there are many non-spherical granules with varying sizes and these kinds of granules are not seen in the films prepared from 10 wt %, 15 wt % and 20 wt % of papaya latex displayed clear and homogenous surfaces. The formation of homogeneous blends of PVA/chitosan/papaya latex was could be due to the interactions of hydrogen bonds among the functional groups of the blend component. However, the ratio 47.5% PVA/47.5% chitosan/5% papaya latex blend film showed a little rougher surface indicating more hydrophilic top surface than the other blend films.

According to Chen *et al*. [28] the blend film a shows rough surface attributed because of the reorientation of polar functional groups in the direction of 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.

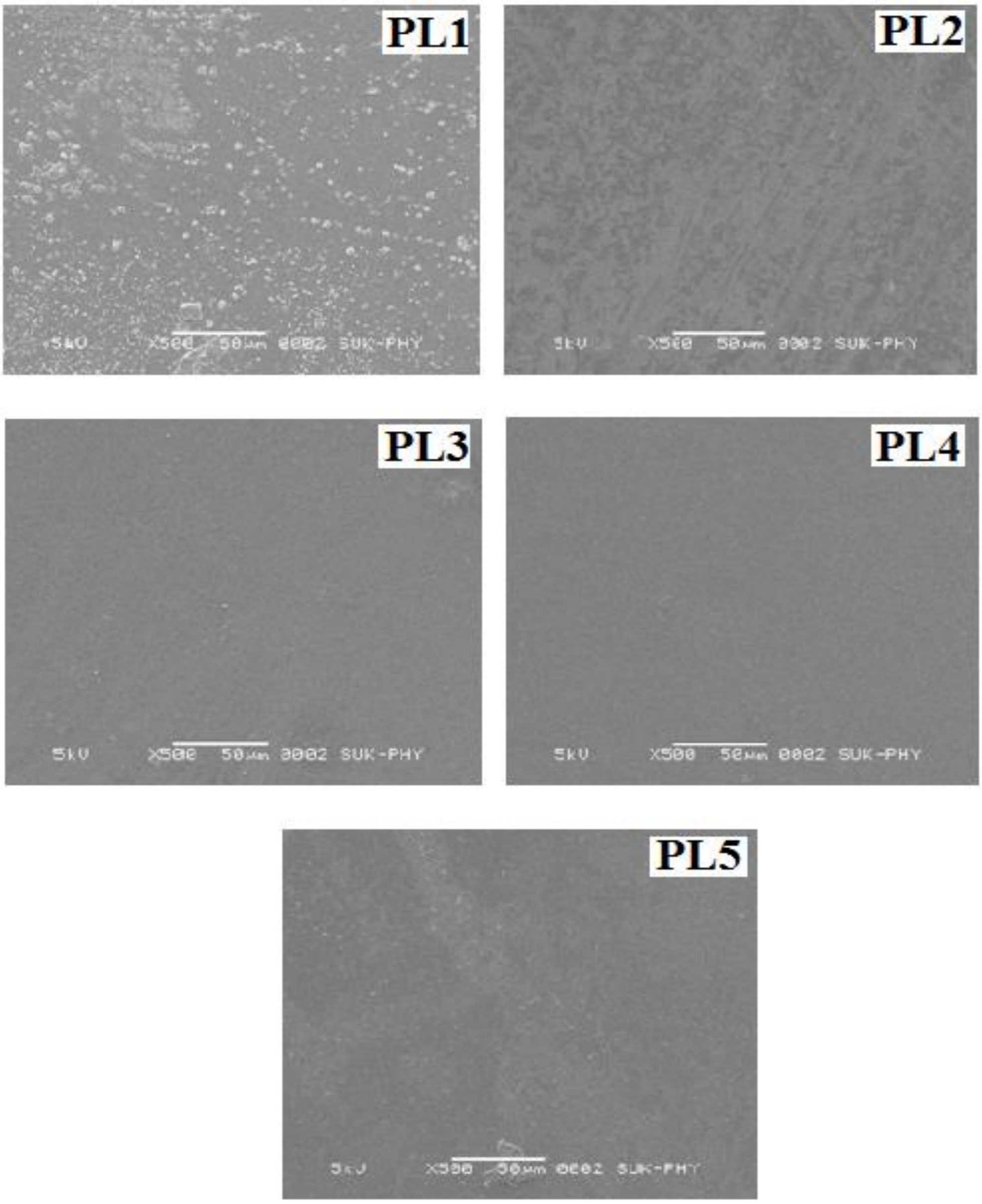


Fig-1: Scanning electron microscope micrographs PVA/chitosan/papaya latex blend films

3.2 Fourier Transform Infrared Spectroscopy

The Fourier transform infrared spectra of PVA/chitosan/papaya latex are depicted in Figure 2. FTIR spectra were used to identify interaction in polymer blend films. FTIR spectra of blend films were shown in Table 2 and 3. Pure PVA and equal weight percent of (wt %) PVA/chitosan blend and blend filled with different wt % papaya latex also showed various distinct and predominant peak around 3450-3225 cm^{-1}. The peak occurred at 3292 cm^{-1} due to O-H & N-H stretch in secondary N-substituted amide. Different concentration of papaya latex (0,5,10,15,20) at room temp in region of 500 to 4000 cm^{-1} and absorption band listed in Table 3.3 and Table 3.4.

The weak peak occurred at 2921cm^{-1} due to C-H stretching, medium band observed at 1600-1500 cm^{-1} due to C-C and peak around 837 cm^{-1} due to p-substituted aromatic C-H deformation of aromatic residues of tryptophan or tyrosine. The peak observed at 1429 cm^{-1} is due to C-H deformation of alkyl substituted amino acids. 1654.2 cm^{-1} due to C=O stretch of carboxylate anion and amide group and strong peaks between 1150-1050 cm^{-1} and 705-570 cm^{-1} due to C-S stretch of sulphides and disulfides. The spectra of papaya latex loaded enteric polymer micro spheres showed peaks at 3386.2 cm^{-1}

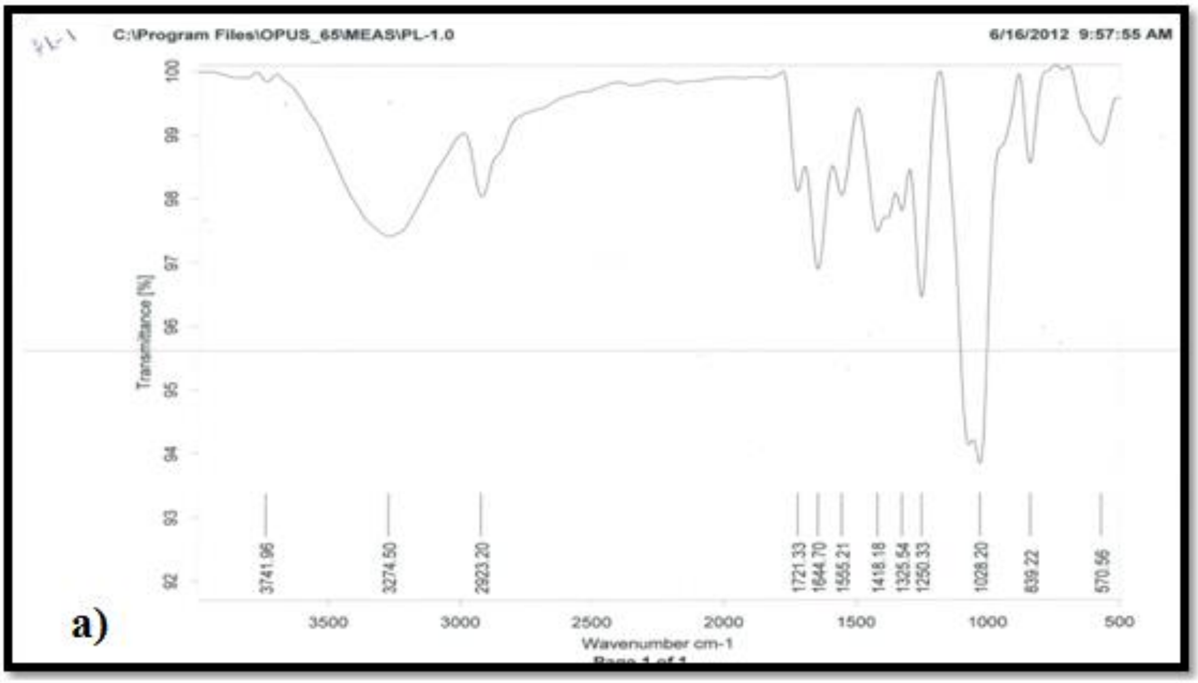
for substituted secondary amide, 1145 cm^{-1} and 600 cm^{-1} due to C-S Stretch of sulphides and disulfides. In poly (vinyl alcohol)/chitosan blending spectra of different concentration of papaya latex indicate clear increasing in the intensity of the peak around 3292 cm^{-1} was attributed to a hydroxyl group of stretching vibration of poly (vinyl alcohol) with a secondary amide (- NH_2) of papaya latex and chitosan. The results of FTIR spectra indicated that presence of stronger intermolecular hydrogen bond, between amide, hydroxyl and amino groups of the components of blend.

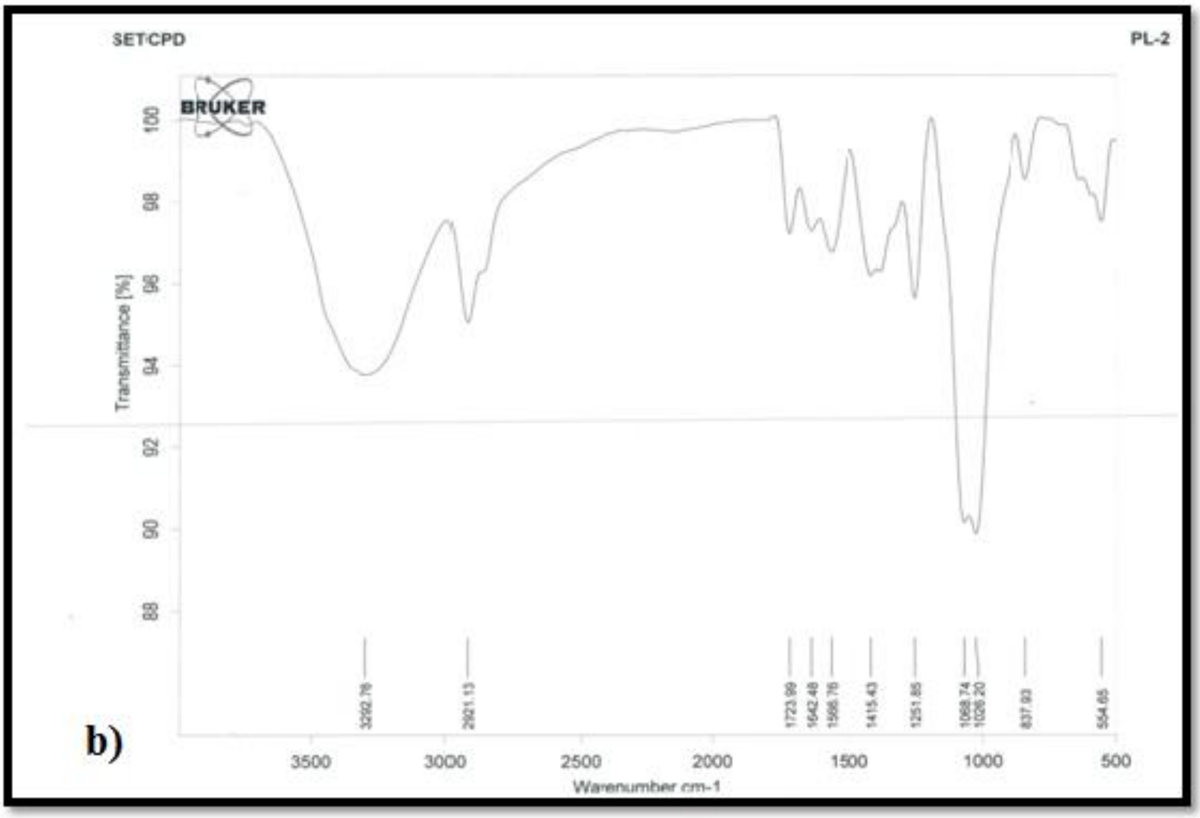
Table-2: Assignments of the FT-IR Characterization Pure PVA, Pure Chitosan and PVA/Chitosan Blend Films

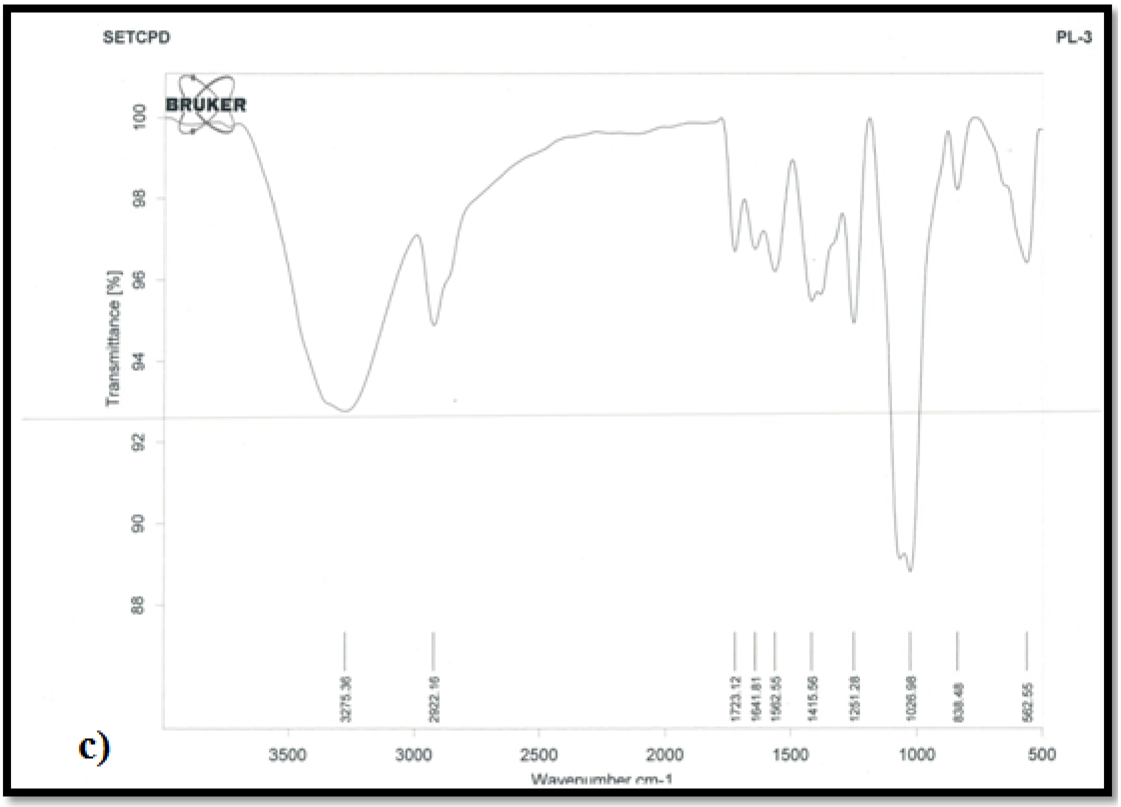
Pure PVA		Chitosan		Pure Blend PVA+ Chitosan)	
Wave Number (cm^{-1})	Assignment	Wave Number (cm^{-1})	Assignment	Wave Number (cm^{-1})	Assignment
3455	O-H Stretching	3480	C6-O-H Stretching	Around 3741	O-H Stretching of alcohols
2924	CH_2 Asymmetric stretching	3300-2950	N-H stretching for secondary amide	3274	N-H Stretching
2892	CH_2 symmetric stretching	1721	C=O stretching	2924	CH_2 $_A$symmetric stretching
1664	C = C Stretching	1660	Amide I band of chitosan	Around 1721	C=O stretching
1461	CH_2 bending	1558	Amide II band of chitosan	Around 1644	C=O stretch of carboxylate anion and amide group
962	C-H out of plane bending	1250	Amino Group	Around 1555	O-H and C-H bending
-	-	1166	Amino group	Around 1418	O-H and C-H bending
-	-	---	-	Around 1250	Amino Group
-	-	--	-	Around 1028	CO symmetric stretching

Table-3: Assignments of the FT-IR Characterization Pure Papaya latex and PVA/Chitosan/Papaya Latex Blend Films

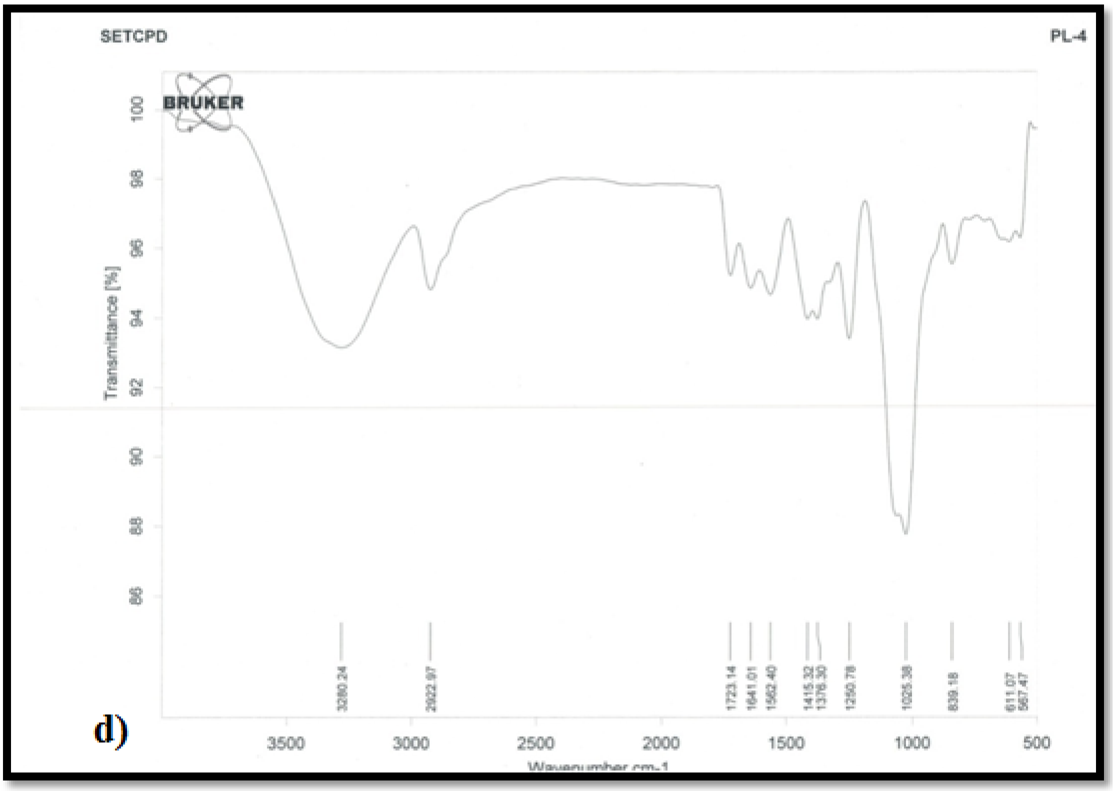
Pure Papaya latex		(Poly (vinyl alcohol)/Chitosan) + Papaya Latex	
Wave Number (cm^{-1})	Assignment	Wave Number (cm^{-1})	Assignment
3450-3225	N-H Stretching of N substituted secondary amide	3741	O-H stretching
2981	C-H stretching	3274	N-H Stretching of N substituted secondary amide
1600-1500	C-C Stretching	2922	C-H Asymmetric stretching
865-850	p-Substituted aromatic out of plane	Around 1721	C=O stretching
1420-1430	C=H deformation of alkyl chain of amino acids	Around 1642	C=O stretch of carboxylate anion and amide group
1650	C=O stretch of carboxylate anion and amide group	Around 1572	C - C Stretching
1150-1050 & 700-550	C=S stretch of sulphide, disulphides	Around 1418 and 1321	C-H deformation of alkyl chain of amino acids
1635	-CONH amide band II	Around 1251	Amino Group
1555	-NH amide band II	Around 1026 to 1068 & 554 to 570	C=S stretch of sulphide, disulphides
		Around 837 to 839	p-substituted aromatic out of plane


PL-1
C:\Program Files\OPUS_65\MEAS\PL-1.0
6/16/2012 9:57:55 AM
Transmittance [%]
100
99
98
97
96
95
94
93
92
3741.96
3274.50
2923.20
1721.33
1644.70
1555.21
1418.18
1326.54
1250.33
1028.20
839.22
570.56
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
Page 1 of 1
a)


SETCPD
PL-2
BRUKER
Transmittance [%]
100
98
96
94
92
90
88
3292.76
2921.13
1723.99
1642.48
1566.76
1415.43
1251.85
1068.74
1026.20
837.93
554.65
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
b)


SETCPD
PL-3
BRUKER
Transmittance [%]
100
98
96
94
92
90
88
3275.36
2922.16
1723.12
1641.81
1562.55
1415.56
1251.28
1026.98
838.48
562.55
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

c)


SETCPD
PL-4
BRUKER
Transmittance [%]
100
98
96
94
92
90
88
86
3280.24
2922.97
1723.14
1641.01
1562.40
1415.32
1376.30
1250.78
1025.38
839.18
611.07
567.47
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

d)

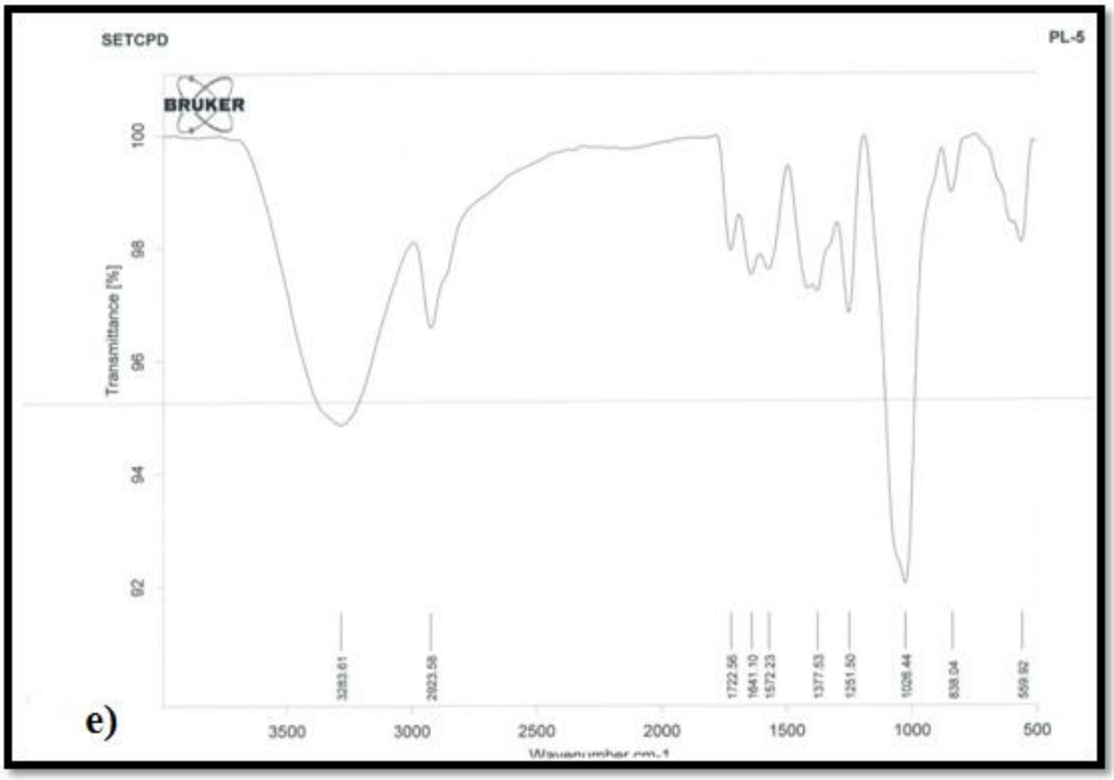


Fig-2: FTIR Spectra of PVA/Chitosan/Papaya Latex PL1, b) PL2, c) PL3, d) PL4, e) PL5

3.3 Thermogravimetric Analysis

Thermal behavior of the prepared blend films was analyzed by thermogravimetric analyzer from 20°C to 400°C. Thermogravimetric curves of PVA/chitosan and blend films in different atmospheres were shown in Figure 3. Different different weight percent of papaya latex blended with PVA/chitosan blend films showed first weight loss at 30-130^{o}C, due to evaporation of solvent molecules and shows about 9.63% loss. The mass loss in first decomposition process could be attributed to the splitting or volatilization physically absorbed water [29]. The wide degradation occurred at 130-230^{o}C, attributed to the melting point of poly (vinyl alcohol) and 15% of mass loss observed in the PVA/chitosan/papaya latex blend films. Therefore, higher values of mass loss in second decomposition step suggests bond scission (carbon-carbon bonds) in the polymeric backbone. The third weight loss observed in the temperature range of 377.88^{o}C, could be thermal degradation of polymeric chain with vaporization of voltaic compounds and cross linking reaction occurring with destruction of amino group.

Table-4: Thermal properties of T_g, T_m and T_d of PVA/Chitosan/Papaya Latex Blend Films

Blend Composition (Wt %)		T_g ^{o}C	T_m ^{o}C	T_d ^{o}C
50 PVA/50 CS/0	PL1	95.66	332.07	373.22
47.5 PVA/47.5 CS/5 PL	PL2	89.12	311.71	371.42
45 PVA/45 CS/10 PL	PL3	87.13	305.43	374.76
42.5 PVA/42.5 CS/ 15 PL	PL4	86.35	303.13	377.88
40 PVA/40 CS/ 20 PL	PL5	68.70	302.24	374.16

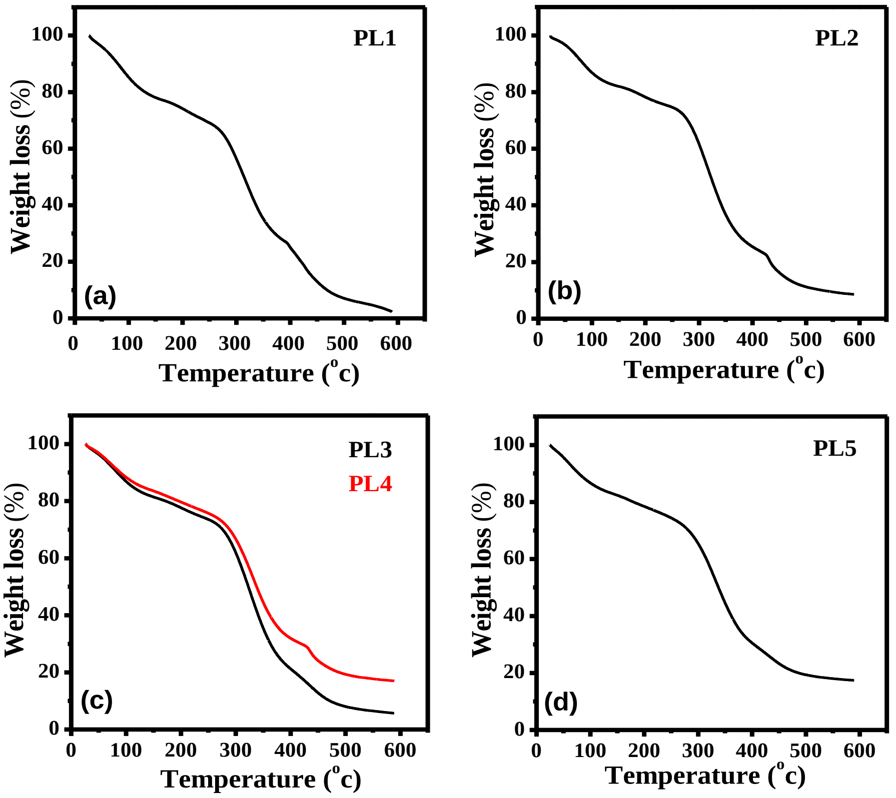


Fig-3: Thermogravimetric Analysis of PVA/Chitosan/Papaya latex Blend Films Blend films a) PL1, b) PL2, c) PL3 & PL4, d) PL5

3.4 Differential Scanning Calorimetry

The glass transition temperature (T_g) of blend films containing PVA/chitosan blend films were affected by adding the various wt % of papaya latex as shown in Figure 4 and Table 4. The glass transition temperature of the blend films decreased as the concentration of papaya latex increased. Glass transition temperature values shifted to lower values, this could be attributed to the weak interaction among the PVA/chitosan/papaya latex. The blend films showed maximum glass transition temperature for PVA/chitosan of equal wt %, but glass transition temperature value decreases with different concentration of (wt %) papaya latex. From these studies, it is clear that, addition of papaya latex decreased glass transition temperature as well as melting temperature and concludes that addition of papaya latex acts as plasticizer.

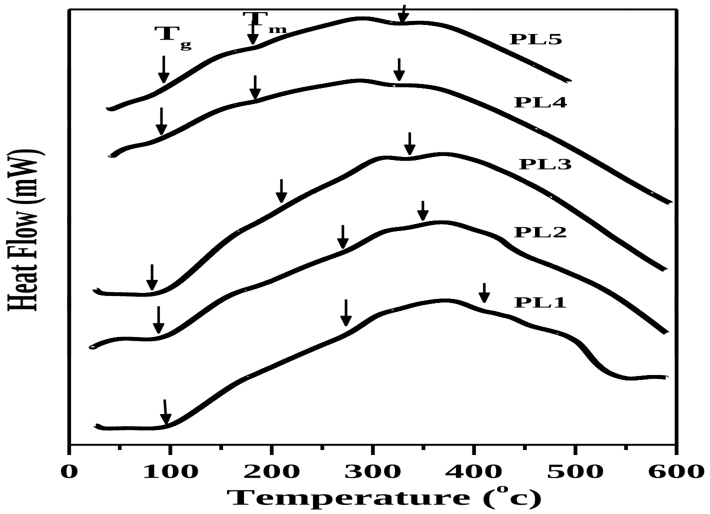


Fig-4: Differential Scanning Calorimeter of Poly (vinyl alcohol)/Chitosan/Papaya latex Blend Films Blend films

4. CONCLUSIONS

In the present work, ternary blend films of PVA/chitosan/papaya latex were prepared by solution casting. The films were analyzed with SEM, FTIR, TGA and DSC. The SEM micrographs confirmed the miscibility among the PVA/chitosan/papaya latex, due to interaction existed among the blend components. The Fourier transform infrared study concludes that presence of strong intermolecular hydrogen bond, between amide, hydroxyl and amino groups of the blend components. From thermogravimetric analysis it is clear that, the blend films were not stable and the degradation of the blend films can be observed with respect to the heating temperature. Glass transition temperature, T_g and melting temperature, T_m decreased with addition of papaya latex has been proved in DSC studies. This confirms the plasticizing behavior of the papaya latex.

REFERENCES

[1] Ezequiel, CJ. S.; Edel, B-S. F.; Alexandra, A.P. M.; Wander, L., V.; Herman, S. M. *Carbohyd. Polym. 2009*, 76, 472-481.
[2] Barsbay, M.; Guner, A. *Carbohyd. Polym. 2007,* 69 (2), 214-224.
[3] Gure, G. S.; Prasad, P., H.; Siva, Kumar R.; Rai, S. K.; *J. Polym. Env.* 2010, 18 (2), 103-135.
[4] Mruthunjayaswamy, T. M.; Ram Raj, Siddaramaiah, M. *J. Appl. Polym. Scie.* 112(4), 2235-2240.
[5] Kondo, T.; Sawatari, C. *Polym.* 1994, 35 (20), 4423-4428.
[6]. Nishio, Y.; Manley, R.S. *Polym. Eng. Sci.* 1990, 30 (2),71-82.
[7]. Kolahchi, A. R.; Ajji, A.; Pierre, J. C., J. Phys. Chem. 2014, 118, 6316-6323.
[8]. Lipscomb. G. G.; Banerjee, T. Polym. Adv. Technol. 1993, 5 (11), 708-723 (1993).
[9]. Pinnau, I. Polym. for Advanced Technologies, 1994, 5(11), 733-744.
[10]. Stadler, R.; Auchra, C.; Bekmann, J.; Krape, U.; Voigt-Martin, I.; Leibler, L. *Macromolecules*, 1995, 28 (9), 3080-3097.
[11]. Gagnon, K. D.; Lenz, R. W.; Farris, R. J. Polym., 1994, 35(20), 4368-4375.
[12]. Ohya, Y.; Okawa, K.; Murata, J.; Ouchi, T. Macromol. Mat. Eng. 1996, 240 (1), 263-273.
[13]. Babiker, E.E. Food Chem. 2002, 79 (3), 367–372.
[14]. Qin, C.; Du, Y. M.; Xia, L.; Li, Z.; Gao, X. H. Int. J. Biolog. Macromol. 2002, 31 (1–3), 111–117.
[15]. Roller, S.; Covill, N. Int. J. Food Microbiol. 1999, 47 (1-2), 67-77.
[16]. Zheng, L. Y.; Zhu, J. F. Carbohyd. Polym. 2003, 54 (4), 527–530.
[17]. Abdelrazek, E.M.; Elashmawi, I.S.; Labeeb, S. Phys. B: Condensed Matter, 2010, 405 (8), 2021–2027.
[18]. Kim, J.H.; Kim, J.Y.; Lee, Y.M.; Kim, K.Y. J. Appl. Sci. 1992, 45 (10), 1711-1717 (1992).
[19]. Kim, J.H.; Kim, J.Y.; Lee, Y.M.; Kim, K.Y. J. Appl. Sci. 1992, 44(10), 1823-1828.
[20]. Nakatsuka, S.; Andrady, A. J. Appl. Polym. Sci. 1992, 44 (1), 17-28.
[21]. Kweon, D.K.; Kang, D.O. J. Appl. Polym. Sci. 1999, 74(2): 458-464.
[22]. Chuang, W.Y.; Young, T.H.; Ya, C.H.; Chiu, W.Y. Biomat. 1999, 20(16): 1479-1487.
[23]. Sakurai, K.; Maegawa, T.; Takahashi, T. Polym. 2000, 41 (19): 7051-7056.
[24]. Guo, H. F.; Packirisamy, S.; Gvozdic, N. V.; Meier, D. J. Polym. 1997, 38 (4), 785-*794.*
[25]. Luzinov, I.; Pagnoulle, C.; Xi, K.; Huynh-Ba, G.; Jerome, R. Polym. 1999, 40 (10), 2511.
[26]. Hobbs, S. Y.; Dekkers, M. E.; Watkins, V. H. Polym. 1988, 29 (9), *1598.*
[27]. Asadinezhad, A.; Yavari, A.; Jafari, S.; Khonakdar, H. A.; Boehme, F.; Haessler, R. Polym. Bull. 2005, 54 (3), 205-213.
[28]. Chen, C. H.; Wang, F. Y.; Mao, C. F.; Liao, W. T.; Hsieh, C. D.; Int. J.Biol. Micromol. 2008, 43(1), 37-42.
[29]. Jellinek, H. H. G. J. Polym. Sci. 1949, 4 (1), 13-36