Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **11(1),** 15-24, February **(2021)** *Res. J. Chem. Sci.*

Influence of potassium hydrogen phthalate on thermal, mechanical, structural and surface properties of Chitosan/PVA blend films

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Available online at: www.isca.in, www.isca.me
Received 13th August 2020, revised 2nd November 2020, accepted 10th January 2021

Abstract

The Potassium hydrogen phthalate (KHP) doped Chitosan/Polyvinyl alcohol (CPK) blended films were prepared by solution casting technique. The different instrumental methods were utilized to investigate the influence of KHP on Chitosan/Polyvinyl alcohol blended films. The interaction and miscibility of prepared blend films were confirmed by Infrared Spectroscopy and Differential Scanning Calorimetry (DSC) analysis. The CPK blend films showed higher thermal stability than the Chitosan/Polyvinyl alcohol (CP) blend film. The mechanical properties of the CP blend films were improved after the addition of KHP. Increased amorphous nature of CPK blend films was observed through the X-ray diffraction (XRD) patterns. The surface roughness was analyzed by Atomic Force Microscopy (AFM) suggest that the KHP exists in the films owing to strong interactions. The hydrophobic nature of the CP blend was enhanced after the addition of KHP, which is verified by measuring the water contact angles. These investigated properties fitted with the properties which are applicable for the packaging and coating applications.

Keywords: Thermal, mechanical, surface properties, potassium hydrogen phthalate, chitosan, polyvinyl alcohol, blend films.

Introduction

The improvement in the packaging and coating materials brings the finest advantages. However, several challenges were come out to develop such materials. These days, polymer blending has been the most helpful technique for the change of the physicochemical properties or improvement of polymer materials[1]. Presently their potential applications in various fields are becoming more and more evidently[2].

Chitosan (CS) is a copolymer[3] obtained by chitin[4] and has antimicrobial activity[5], biocompatible, biodegradable properties and film-forming ability[6-8]. It is a hydrophilic polymer, solvable in acidic solutions especially in the diluted hydrochloric acid[7, 9], formic and acetic acids[6, 10]. Polyvinyl alcohol (PVA) is a polar, synthetic polymer, soluble in water[6, 11-12]. This polymer is used for the preparation of membrane[13], blend and composite films[14-16], because of the hydroxyl groups present on the PVA backbone causes for the hydrogen bonding[17] and hence helpful for good film formation. It is used in the field of drug delivery and drug coating[18-19]. PVA and chitosan are used for the preparation of blend films because of their film-forming ability[5,19-20], and its utilization is growing steadily in recent years.

Potassium hydrogen phthalate (KHP) or potassium acid phthalate crystal is an acidic salt[21]. It exhibits the properties of nonlinear, piezoelectric, pyroelectric and superior physical properties. Also, the single crystals of KHP show the elastic properties[22-23]. KHP crystals can be used as a substrate in the oriented polymers and organized materials for their epitaxial and the hierarchical growth respectively. M. Enculescu[25] studied the structural, morphological and optical properties of KHP crystals by doping with rhodamine and polyvinyl-pyrrolidone polymer. Also, the growth kinetics and mechanical properties of KHP crystals have been studied[22]. Hafez and El-Khiyami studied the effect of copper nitrate on the properties of PVA film, which suggests that inorganic salt can be used for the study of polymer films[24].

Various researchers have reported on the study of CS/PVA binary blend films[13,15], membranes[26], etc. But there is no report have found on the KHP doped CS/PVA blend film still to date. Hence, we focus on the CS/PVA/KHP blend system and the influence of KHP on thermal, mechanical, structural and surface properties was discussed. Figure-1 shows the chemical structure of PVA, Potassium hydrogen phthalate and Chitosan.

Materials and methods

Materials: Chitosan with viscosity 200-600 mPa was purchased from TCI Tokyo Japan. PVA (Mol. wt 1,25,000) was procured from Thomas Baker Pvt. Ltd. Mumbai. Potassium hydrogen phthalate and Acetic acid were purchased from Spectrochem Pvt. Ltd. Mumbai. Double distilled water was utilized until the end of experiment.

Preparing the blend solutions: To preparing the blended solutions, the 100 ml of 2% PVA solution was poured into a 50 ml of 2% CS solution, and the mixture was stirred up to 24 hours with the help of the magnetic stirrer at a speed of 180 revolutions per minute (rpm), then the KHP solution (from 0.02 g to 0.06 g weight in 10 ml of Millipore water) was added to the CS/PVA blend. The weight proportion (1:2) of CS and PVA was kept constant, and KHP was varied from 0.02 g to 0.06 g for CPK-1 to CPK-3 blend films respectively.

Preparation of blended films: The total volume of 160 ml blended solution was cast onto clean and dried glass petri dish (200 X 20mm) and allowed to dry for two weeks under room temperature. Then the dried films were peeled off and stored in a desiccator for further analysis. In the same way, film of pure CP was prepared. The obtained blend films seem homogeneous and transparent. The procedure for the preparation of blend films was graphically represented in Figure-2.

Methods: Thickness measurements: The thickness of the film was measured with the help of a digital micrometer. For each film, five readings were taken and averaged. The averaged values were recorded and used for the study of mechanical properties and to calculate the density.

Density measurements: Film samples with size 2.5cmx1.5cm were weighed and used for density measurement. The weight of the sample was divided by the volume to calculate density. The volume of each rectangular-shaped sample was calculated by multiplying the area and the thickness.

FT-IR spectroscopy: The FT-IR spectra were obtained at a resolution of 4cm^{-1} in the range 550–4000cm^{-1}.

DSC measurements: For DSC measurements the 1-2mg weight for each sample was taken according to the instrument standard. The analysis was performed between the temperature of 25°C and 250°C under the nitrogen atmosphere at a heating rate of 10°C/min.

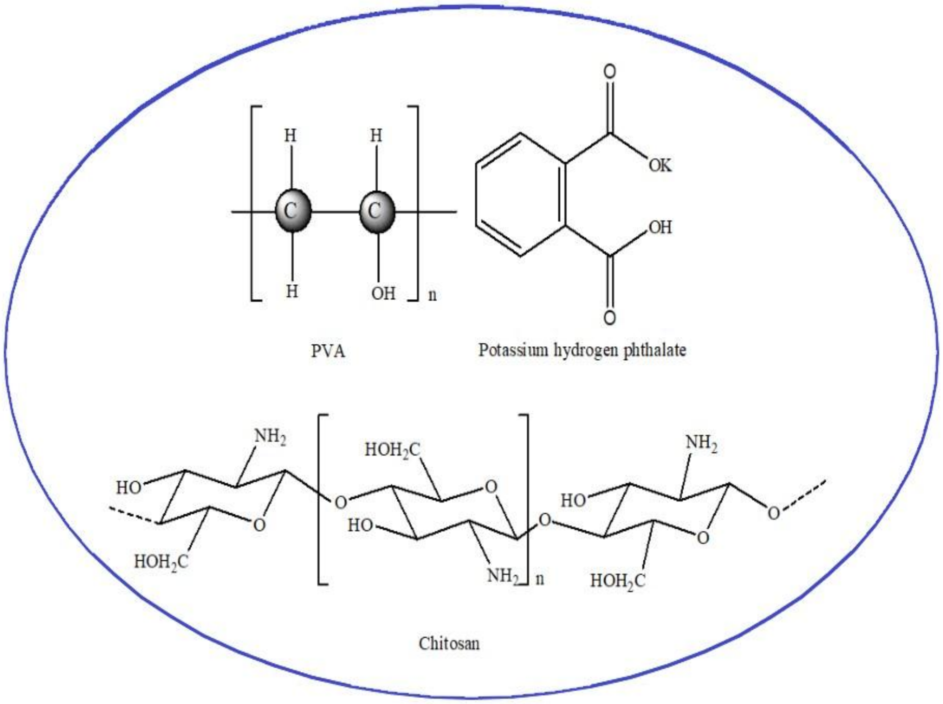


Figure-1: Chemical structure of PVA, Potassium hydrogen phthalate and Chitosan.

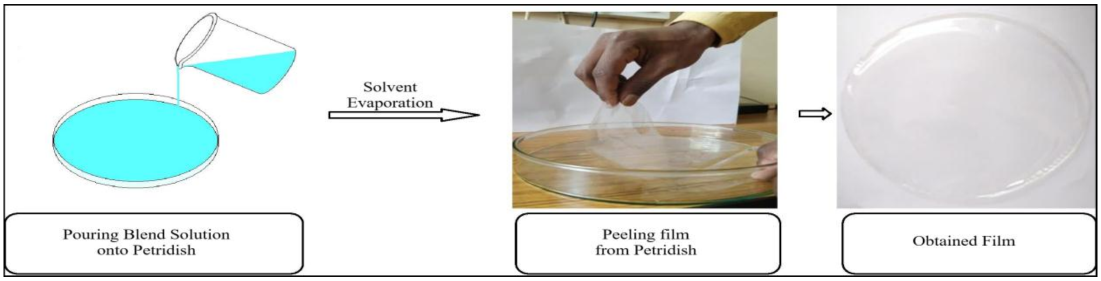


Figure-2: Procedure to obtain blend film.

TGA measurements: The TGA measurements of blend films were done by using 5–6 mg sample for every test. The samples were analyzed under N_2 atmosphere by heating from 25 ºC to 600 ºC at a rate of 10 ºC/min.

Mechanical properties: The UTM was used to measure the mechanical properties. Specimen of size 100mm x 25mm was used for testing by keeping crosshead speed at 1 mm/min. The average value of the three specimens for each sample was recorded by testing.

XRD measurements: XRD measurements were performed on a Rigaku SmartLab X-ray Diffractometer (Tokyo, Japan) with Cu K-beta radiation (λ=0.154 nm). The samples were scanned in the range of 2θ = 5-80° at a scanning rate of 5°/min with working voltage 40 kV and current 30 mA.

AFM imaging: AFM images were acquired by dynamic force operating mode under the air environment using a Nanosurf Flex AFM System. The image size 5µm X 5µm was chosen for the blend series to gain a clear picture of the large-scale morphology of each sample. Area root mean square (RMS) roughness values were calculated using the Nanosurf Easyscan 2 control software.

WCA measurements: A contact angle meter (Model DMs-401) was used to measure the angles of water contact. To measure contact angles a water drop was dropped on the surface of film with the help of syringe. Three readings were taken from each sample and were averaged.

Results and discussion

Density measurement: The density was calculated by dividing the weight of the sample by the volume, as reported by Gomez-Aldapa et al.[27]. The measured density values were shown in Table-1. All the films have a density greater than 1 g/cm^3 hence the film samples were settled down into the water-bodies[28].

Table-1: Density values of films.

Sample code	Density (g/cm^3)
CP	1.32
CPK-1	1.33
CPK-2	1.29
CPK-3	1.27

FT-IR spectroscopy: FT-IR is a powerful tool to identify functional groups in a molecule and for the investigation of the hydrogen bonding. The recorded FT-IR spectra of CP, CPK films and KHP powder were analyzed and the resulted graphs are shown in Figure-3.

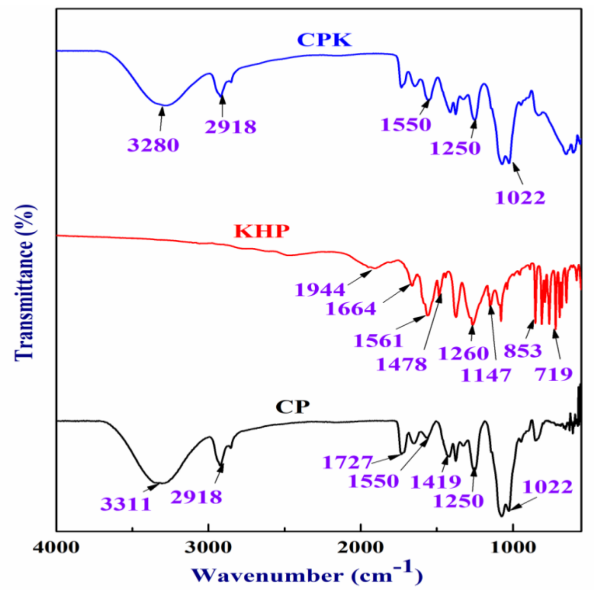


Figure-3: FT-IR spectra of CP, CPK films and KHP powder.

From the spectra of pure CP film the peak at 3311cm^{-1} corresponding to OH group, 2918cm^{-1} corresponding to CH_2 asymmetric stretching vibration and 2850 cm^{-1} corresponding to CH stretching. FT-IR spectra of KHP shows the peaks, 1664 cm^{-1} carboxylic acid C=O symmetric stretching, 1561cm^{-1} C=O carboxylate ion asymmetric stretching, 1478cm^{-1} C=C ring stretching, 1374cm^{-1} C=O carboxylate ion symmetric stretching, 1260cm^{-1} C-O stretching, 1147cm^{-1} and 762cm^{-1} C-C stretching, 1077cm^{-1} C-C-O stretching, 853cm^{-1} and 805cm^{-1} C-H out of plane bending, 719cm^{-1} =C-H out of plane deformation, 688 C-O wagging[29]. From the CPK blend, peak at 3280cm^{-1} is broaden and intensity decreases, peak at 1664cm^{-1} of KHP and 1642cm^{-1} of CP shifts to 1658cm^{-1}. Also the values 1374cm^{-1} of KHP and 1370cm^{-1} of CP shift to higher wave number 1397cm^{-1} in the CPK blend. These observations confirm that KHP interact chemically and thus miscible with Chitosan/PVA blend. The probable chemical interaction among Chitosan, PVA and KHP is shown in Figure-4.

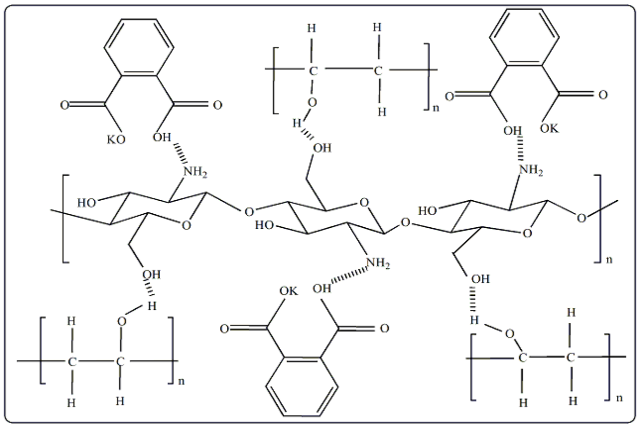


Figure-4: Schematic presentation of probable chemical interaction among Chitosan, PVA and KHP.

DSC measurements: The glass transition temperature (T_g) is an important criteria to check the miscibility of components in blends[30]. The DSC Q20 instrument was used to examine the T_g, T_g breadth and melting temperature (T_m) of the blend films. Figure-5 shows the DSC thermograms of the films. The glass transition temperature of each blend film was taken at the midpoint of the onset temperature (T_o) and endset temperature (T_e) as shown in Figure-5 and similar T_g range is reported by Nassima El Miri et al.[31]. T_g breadths were calculated according to the formula T_g breadth as $\Delta T_g = T_g$ endset - T_g onset define by John M. Torkelson et al.[32]. A single glass transition temperature observed for all the blends shows that added components were miscible. The higher T_g values for the Chitosan/PVA blend were observed by adding the KHP and the T_m values were decreased compared to CP as shown in Table-2, similar trend was observed by Manisara Peesan et al.[33].

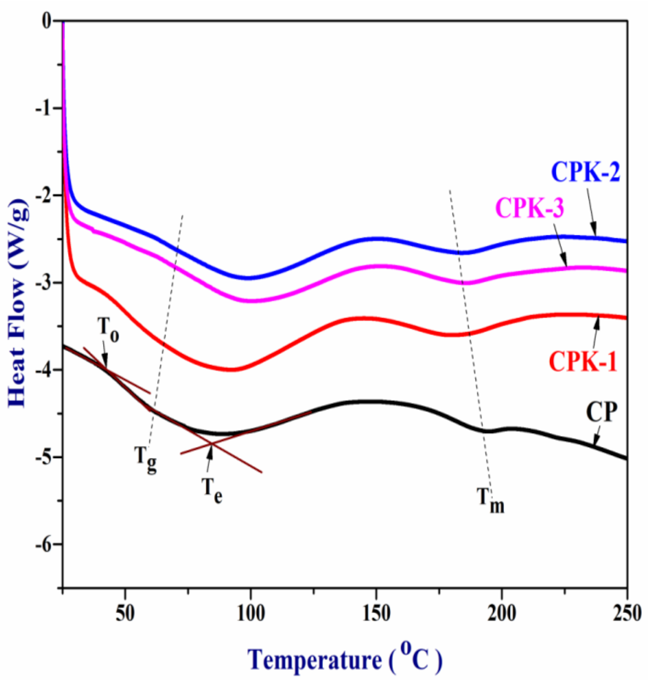


Figure-5: DSC thermograms of CP and CPK films.

TGA measurements: Thermal stability of pure CP and CPK blend films were estimated by utilizing TGA. The TGA thermogram of blend film as a function of temperature demonstrates the weight loss as shown in Figure-6. Table-3 tabulated the thermal stability analysis data from TGA thermograms. The weight loss within 135ºC is because of the removal of volatile material present in the films[34].

Three-stage weight losses are seen for CP blend film, weight loss in the first stage at 45–114ºC is due to evaporation of the moisture and water molecules. The second stage weight loss at 263–339ºC is because of the thermal degradation of chitosan and PVA. And, the last stage weight loss at 408–431ºC is due to the by-product generated by chitosan and PVA. The maximum weight loss and decomposition rate was observed for CPK blend films at the temperature of 267–351°C. An increased temperature range was observed for weight reduction of CPK blended films as shown in Table 3. Besides, slightly increased residual is observed at 600°C with the increase of the KHP component. This suggests that due to the presence of KHP higher thermal stability was observed for CPK blend films.

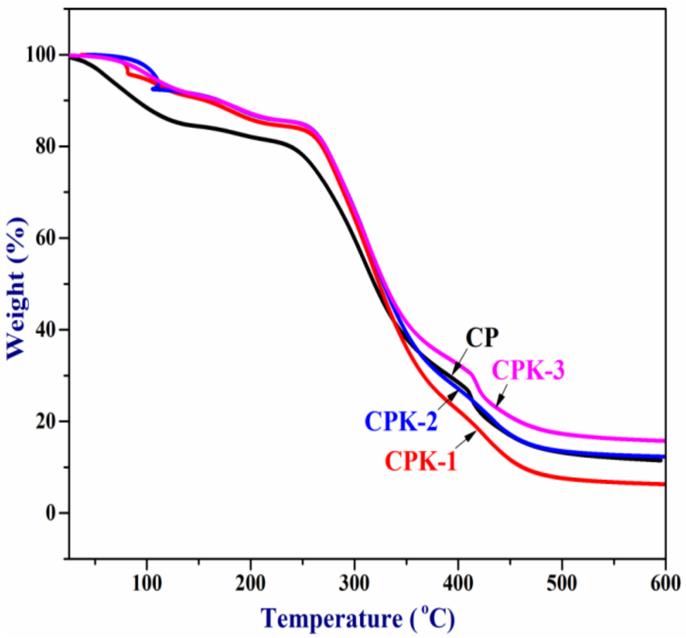


Figure-6: TGA thermograms of CP and CPK blend films.

Mechanical properties: Understanding the mechanical behavior is important for the packaging purpose[35]. Figure-7(a) shows the stress-strain curve, which is used to calculate the tensile properties for CP and CPK blend films in keeping with the ASTM-D882 standard test (ASTM, 1992) and obtained results are summarized in Table-4. It tends to be seen from Table-4 and Figure-7 that the tensile strength (TS) increased for CPK films. Looking at the TS between films of varied content of CPK, it might be seen that there was an expansion in tensile strength of CPK-1 film (consist of 0.02g of KHP). The high TS assessment of these films could be attributed to the arrangement of intermolecular hydrogen bonding. The amino groups (NH_2) of CS are protonated to NH_3^+ in the acetic acid solution, while the arranged structures of KHP atoms are demolished with the solubilization procedure, coming about in the $-COO^-$ groups being presented to promptly frame hydrogen bonds with NH_3^+ of the CS. However, a noticeable decrease in the tensile strength was seen for CPK-2 to CPK-3 blend films (containing 0.04 to 0.06g KHP) but remains higher than the pure CP film. The Young's modulus (YM) of films exhibited a similar pattern as that of TS, but the percentage of elongation at break (EB) was decreased as compared to CP blend film. The changes in the TS and EB were shown in Fig. 7(b). These results indicate that the KHP contributed to altering the mechanical properties of the CP blend films. Among them CPK-1 film had better properties.

Table-2: DSC parameters of pure CP and CPK blend films.

Sample codes	T_g (°C)	T_o (°C)	T_e (°C)	T_g breadth	T_m (°C)
CP	63.99	44.19	83.79	39.60	192.93
CPK-1	64.63	41.17	88.09	46.92	176.76
CPK-2	78.92	59.76	98.08	38.32	180.68
CPK-3	79.7	61.32	98.08	36.76	183.08

Table-3: Observation data from TGA analysis.

Sample Code	Temperature range (ºC)	Weight loss (%)		Residuals weight (%) at 600 ºC
		Partial	Total	
CP	45-114 263-339 408-431	15.81 53.20 17.03	86.04	13.96
CPK-1	78 - 83 160 - 205 270 - 351 416 - 465	9.22 6.39 60.99 17.48	94.08	5.92
CPK-2	104 - 112 163 - 205 270 - 349 424 - 465	8.24 6.09 56.84 17.31	88.48	11.52
CPK-3	75 - 117 170 - 203 267 – 342 412 - 445	8.12 5.84 50.73 20.52	85.21	14.79

Table-4: Mechanical properties of CP and CPK blend films.

Sample Code	Thickness (mm)	TS (MPa)	YM (MPa)	EB (%)
CP	0.09	22.34	241.98	61.85
CPK-1	0.11	46.80	636.98	56.90
CPK-2	0.14	30.23	594.83	30.64
CPK-3	0.13	29.24	312.68	47.36

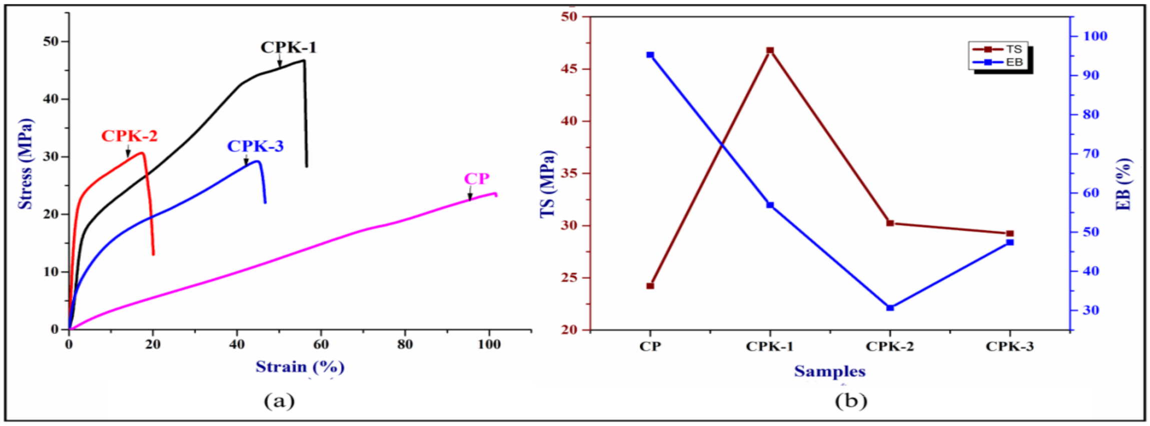


Figure-7: Stress-strain curves (a) and tensile properties (b) of films.

XRD measurements: X-ray diffraction was performed to study the crystalline nature of films. Figure-8 shows the XRD patterns of the films. The CP blend film shows two distinct peaks at 11.59º and 19.48º. The peak at 11.59º attributed to the hydrated crystalline and amorphous structure of chitosan and peak at 19.48º attributed to semicrystalline nature of PVA. After the addition of KHP in the CP blend, the peak 11.59º is diminished and the intensity of diffraction peak at 19.48º becomes flat and broad. It illustrates that the existence of KHP into the CP blend, the crystallines of CS and PVA are decreases. This may be due to the presence of KHP into the polymer backbone, which hinders the dense chain packing of polymer chains, resulting in the amorphous nature of CPK blend films. Also, the absence of any new diffraction peaks for CPK blend films reveals a complete dissociation of KHP on the CS/PVA matrix.

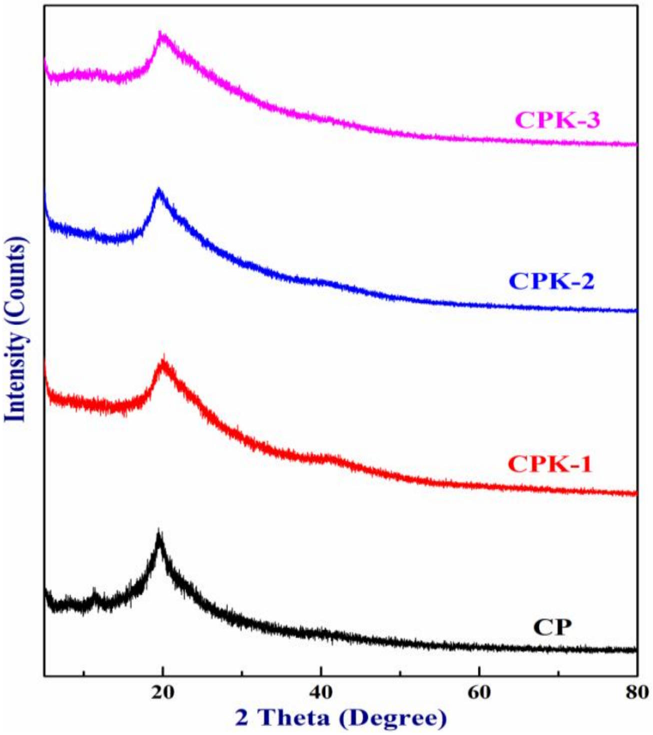


Figure-8: XRD patterns of CP and CPK films.

AFM imaging: The surface roughness in terms of area root mean square (RMS) roughness of blend films was investigated using an atomic force microscope technique and the resulting images are shown in Figure-9. The area RMS roughness measured was tabulated in Table-5. The surface roughness 3.57 nm was found for the topographic image of CP film. From the topographic image of the CPK-1 blend film, the surface roughness 12.19nm was observed. Further increase in the concentration of KHP in CPK blend system, the surface roughness was decreased from 12.19nm to 5.57nm. It could be attributed to the effect of KHP at higher concentration was good. This clearly suggests that the KHP exists in the films owing to strong interactions. This may be due to hydrogen bonding as discussed in the mechanical properties section.

Table-5: Area RMS roughness and water contact angle measurements of the films.

Sample code	Area RMS Roughness (nm)	Contact Angle (degree)
CP	3.57	83.4
CPK-1	12.19	88.5
CPK-2	9.39	96.3
CPK-3	5.57	95.8

WCA measurements: In packaging application the hydrophilicity of the material to resist wet ability is one of the most important and widely used properties. The surface wettability of blend films was analyzed using a contact angle meter by measuring contact angles. The contact angles results of CP and CPK blend films were summarized in Table-5.

Figure-10 shows the water drop images on CP and CPK blend films. The water contact angle of the CP film is 83.4°, it indicates the hydrophilic nature. For the CPK blend films, water contact angles are increased (up to 0.04g of KHP content) as compare to CP film. Further increasing KHP content in the CPK blend film, the slight decrease in the contact angle was observed. Overall, the contact angle of CP blend films was increased after the addition of KHP in the blend system and CPK-2 blend film shows the highest contact angle.

Conclusion

A new KHP doped Chitosan/Polyvinyl alcohol blend films were prepared via solution casting technique. Different instrumental techniques such as DSC, FTIR, TGA, UTM, XRD, AFM and Contact angle measurement were utilized for the characterization of blend films. The completion of interaction is confirmed by analyzing changes in FT-IR spectra. Also, the completion of interaction and miscibility is concluded from the evidence of melting temperature and a single glass transition temperature obtained by DSC analysis. From TGA analysis, increased thermal stability is observed for CPK blend films than the CP film. Also, the mechanical properties of the CPK blend films were increased as compared to CP film. This may be due to the intermolecular hydrogen bonding between KHP and Chitosan/PVA blend. AFM has contrasted the surface morphology of blend films with varied contents; both pitted and granular topographies have been observed. The addition of KHP reduces the crystallinity of the CS/PVA blend film. At a lower weight of KHP in CS/PVA blend film, the roughness was more, while at a higher weight lesser roughness was observed. Water contact angle measurements show that the CPK blend films have a higher water contact angle than CP blend film. These results indicate that prepared series films based on KHP have improved water resistance, which have a potential application as packaging and coating materials.

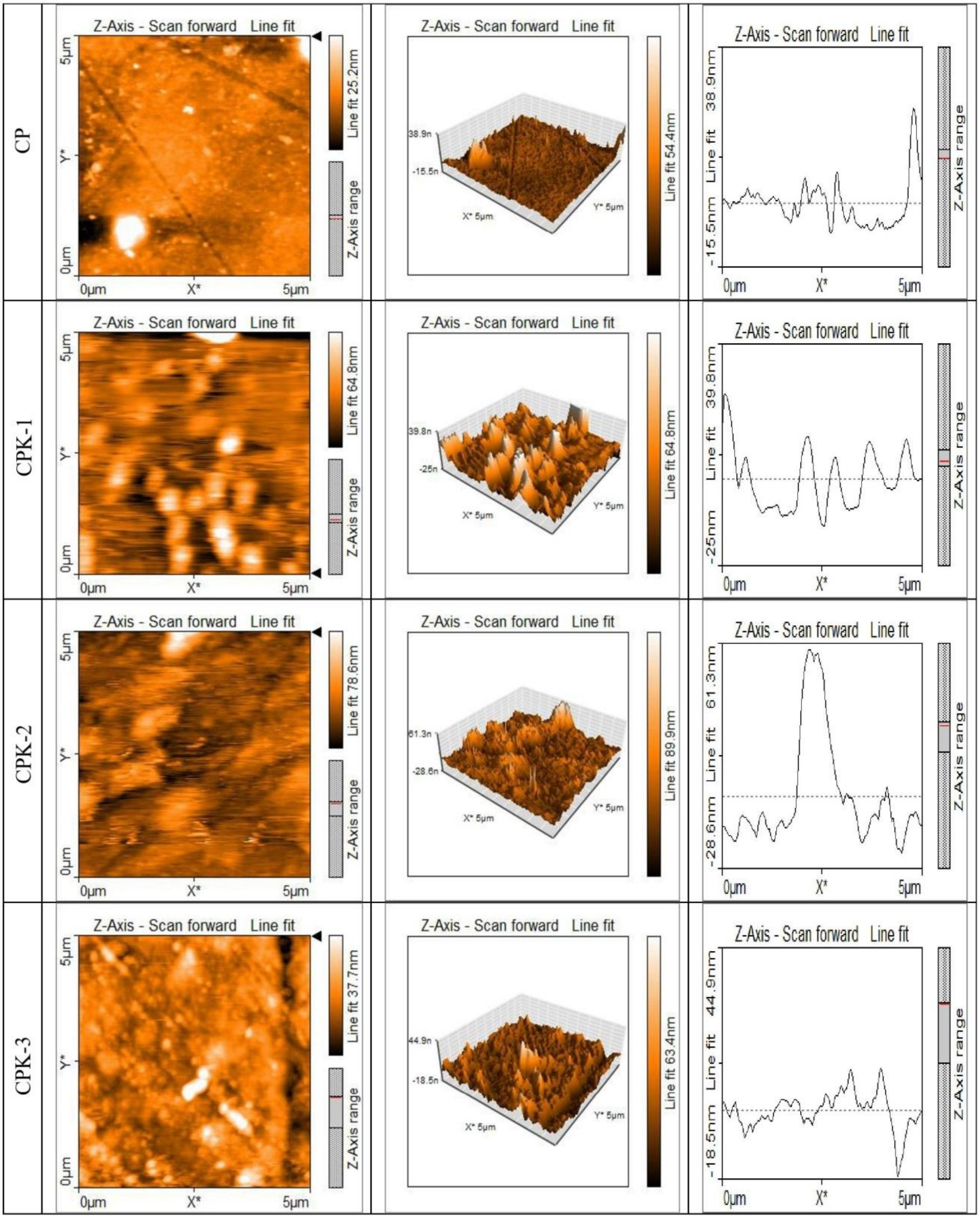


Figure-9: AFM topography images (left), line graphs (right) and three-dimensional view of the topography (middle) of CP and CPK blend films.

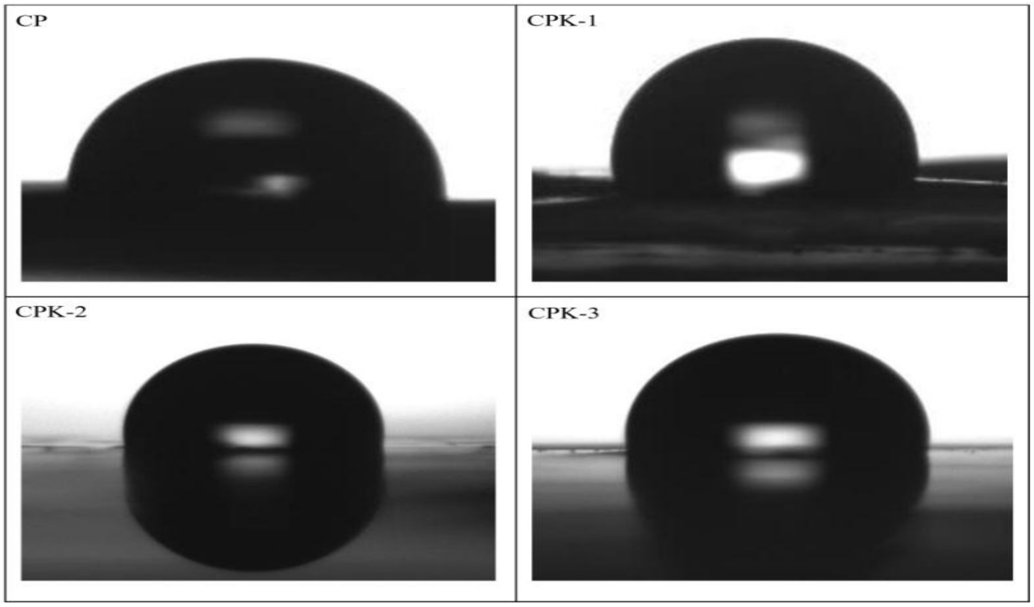
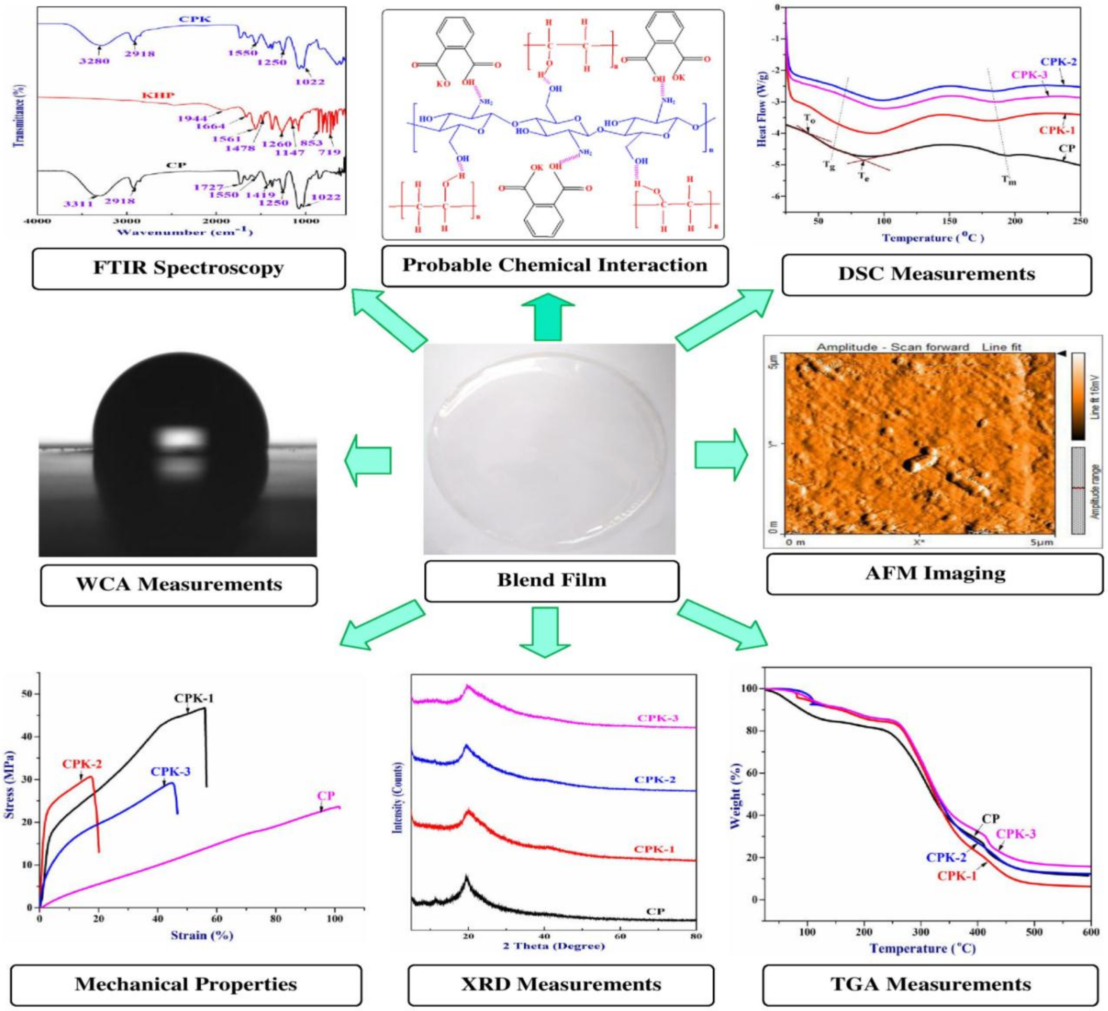


Figure-10: Water drop images on CP and CPK blend films.

Graphical Abstract



Abbreviations: CS – Chitosan, PVA - Polyvinyl alcohol, KHP - Potassium hydrogen phthalate, CP - Chitosan/Polyvinyl alcohol, CPK - Chitosan/Polyvinyl alcohol/Potassium hydrogen phthalate, FT-IR - Fourier Transform Infrared Spectroscopy, DSC - Differential Scanning Calorimetry, UTM - Universal Testing Machine, XRD - X-ray diffraction, AFM - Atomic Force Microscopy, WCA - Water Contact Angle, T_g - Glass transition temperature, T_m - Melting temperature, TS - Tensile strength, EB - Elongation at break, YM- Young's modulus.

Acknowledgments

The authors gratefully acknowledge the facilities provided by University Science Instruments Center (USIC) and DST PURSE Phase-II Program, Karnatak University, Dharwad. One of the authors would like to thank Dr. Saraswati P. Masti Principal investigator DST-SERB Project, No. SB/EMEQ-213/2014, Department of Chemistry, Karnatak Univesity's, Karnatak Science College, Dharwad, for providing Universal testing machine to study the mechanical properties.

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