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Mechanical, Thermal and Morphological Analysis of 4-Hydroxycoumarin Doped Polyvinyl Alcohol Films

Vinayak N. Vanjeri[1], Deepak Kasai[3], Naganagouda Goudar[1], Vishram Hiremani[1], Tilak Gasti[1], Sarala P. Sataraddi[1], Bhagyavana S. Mudigoudra[4], Oshin D'souza[1], Saraswati P. Masti[2], Ravindra B. Chougale[1,*]

[1,*]P. G. Department of Studies in Chemistry, Karnatak University, Dharwad, Karnataka, India.
[2]Department of Chemistry, Karnatak Science College, Dharwad, Karnataka, India.
[3]Department of Basic Sciences, Faculty of Engineering and Technology, Jain (Deemed to-be University), Jakkasandra, Karnataka, India.
[4]Maharani`s Science College for Women, Bangalore, Karnataka, India.
*Corresponding author: Ravindra B. Chougale

Abstract

In this article, new Polyvinyl alcohol/4-Hydroxycoumarin (PHC) films were prepared and characterized using different instrumental techniques. The influence of 4-Hydroxycoumarin (4HC) on the mechanical properties, thermal behaviour, surface morphology and wettability of the Polyvinyl alcohol (PVA) films were studied. The results of mechanical properties revealed that lower compatibility among the PVA and 4HC. The thermal properties of the PVA films slightly increased with incorporation of different concentration of 4HC. This suggests that there is compatibility among components indicating the intermolecular interaction among the PVA and 4HC which is confirmed by the FTIR study. In addition, presence of single glass transition temperature in all PHC films suggests the miscibility among the components. The experimental studies showed that surface roughness increased with increase in the concentration of 4HC in the PVA film. The results of water contact angle study showed that contact angle decreased with addition of 4HC onto the PVA indicating the films were hydrophilic in nature and affinity towards water increased in PHC films when compared to pure PVA. It can be expected that, the best properties of PHC films were recorded in the study may play a vital role in food packaging and coating applications.

Keywords: Polyvinyl alcohol, 4-Hydroxycoumarin, Mechanical, Thermal and Morphological.

Introduction

Polyvinyl alcohol (PVA) is synthetically prepared non-toxic, odourless, tasteless, translucent cream or white coloured granular powder. It is hydrophilic, biodegradable, water soluble polymer with outstanding chemical stability and exhibits good film-forming, adhesive and emulsifying property [1,2].

The physical properties of PVA depends on the degree of polymerization or degree of hydrolysis. It is resistant to oils, grease, solvents and exhibits good mechanical properties. The presence of a large number of hydroxyl groups in the PVA molecule leads to the formation of hydrogen bonding with –OH and NH_2 groups of other polymers [3]. Also, the presence of hydroxyl groups makes polyvinyl alcohol easily soluble in water. PVA acts as the efficient binder for solid pigments, plastic, cement, fibers, ceramic products, woven fabrics, cork compositions and catalyst pellets.

Polyvinyl alcohol has wide applications in industry and it is low cost in manufacture [4]. PVA is widely used in solid polymer electrode, solid state photocells in the production of conducting polymers [5, 6]. Meanwhile, PVA is also used in adhesives, textile, and paper industry, as an emulsifier and in enzyme mobilization [7].

Recently, polyvinyl alcohol has gained increasing attention in the biomedical field, because of its bio-inertness [8, 9, 10, 11, 12, 13]. Polyvinyl alcohol is used in different biomaterials like an artificial pancreas, haemodialysis and in implantable biomaterials. In pharmaceutical and biomedical applications polyvinyl alcohol is used for control drug release, due to its degradability and non-toxicity [14]. Pure polyvinyl alcohol is used to prepare films because of its compatibility and ability to tailor the properties in water [15]. Individual polyvinyl alcohol film itself offers good tensile strength, excellent flexibility, toughness and barrier property [16]. Polyvinyl alcohol films are prepared for food packaging, tissue engineering, and drug delivery applications [17, 18, 19, 20].

The 4-hydroxycoumarin (4HC) represents a significant precursor in the field of organic synthesis. Interest in it has been amplified because, not only they are significant synthetic endpoints [21], but it constitutes the structural nucleus of many natural products [22]. These derivatives have shown a remarkably broad spectrum of pharmacological and physiological activities and they are used as anticoagulant [23], antibacterial [24], antifungal [25], antitumor [26], insecticidal [27], antimutagenic [28], antioxidant, anti-inflammatory agents [29]. Also, in recent years there are references to derivatives with HIV protease inhibitors [30].

4HC is an important fungal metabolite, and its production leads to further fermentative production of the natural anticoagulant dicoumarol. This happens in the presence of naturally occurring formaldehyde, which allows attachment of a second 4HC molecule through the linking carbon of the formaldehyde, to the 3-position of the first 4HC molecule, to give the semi-dimer the motif of the drug class. Dicoumarol appears as a fermentation product in spoiled sweet clover silages and is considered a mycotoxin [31].

Materials and Methods

Materials

Polyvinyl alcohol with molecular weight 1,60,000 procured from, Himedia, Mumbai. 4-Hydroxycoumarin AR grade (Sigma Aldrich), Acetic acid (Spectrochem Pvt. Ltd. India) Acetone and Ethanol were used as solvent were procured from SD Fine, Mumbai, India and doubly distilled water was used throughout the experiment.

Preparation of Films

PHC films were prepared by doping different concentration of 4HC onto the PVA solution by casting method. An exactly weighed (2 g) amount of PVA was dissolved in distilled water. To the PVA solution different concentration of 4HC (0.002 g to 0.008 g dissolved in 5 mL of 100 % acetic acid) was mixed and the mixture of PVA and 4HC (PHC) was stirred for 3-4 hour. Then, subsequently, definite volume of homogeneous PHC film solution poured onto the previously cleaned and dried glass petri dishes and solvent is evaporated at room temperature to form films. Finally the petri dishes containing films were dried in hot air oven at 45°C for 2-3 days to ensure complete removal of trace amount of solvent present in the films. After drying, all films were peeled from petri dishes and kept in vacuum desiccators before use.

Methods

Thickness Measurement

The thickness of the film was measured using a digital micrometre. Several thickness measurements were taken at various positions for each film and mean value were found to be around 0.08 mm. The obtained results were used for the measurement of mechanical properties.

Mechanical Properties

The universal testing machine (Dak System series 7200 – 1 KN) was used to measure tensile strength, young's modulus and percentage elongation at break. The tests were carried out according to American Society for Testing and Materials (ASTM) D-882 standard test (ASTM, 1992) at room temperature in air and mechanical properties were calculated using TEST BENCH-3 software. The rectangular shaped sample of films (25×100 mm) was taken for the study of tensile properties. Two metallic grips were attached for griping 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 1 mm/min keeping constant initial grip separation 50 mm for all samples.

Thermogravimetric Analysis

A thermogravimetric analysis technique (SDT Q600 V20.9 Build 20**)** was used for the study of thermal stability of pure PVA and PHC films. Samples with masses between 5 and 6 mg were heated in an inert nitrogen atmosphere at a heating rate of 10°C/min from ambient temperature to 600°C. The weight losses at different stages were analysed from the curves of TGA.

X- Ray Diffraction

X-ray diffraction patterns were obtained using D2 PHASER Brucker, Cu-K alpha 1.504 A° wavelength made in Germany. The radiation was generated from Cu K_α source at a voltage 30 kV and 20 mA in the $2\theta = 0^\circ$ to 80° with a scanning speed of 2°/minute. The effect of 4HC on the degree of crystallization was investigated. Crystallinity was calculated from the diffracted intensity data.

Fourier Transform Infrared Spectroscopy

The interaction among the blend components was successfully examined with an attenuated total reflection (ATR) method of IR spectrometer (FT-IR-ATR, Prestige 21, Shimadzu, Japan). Measurements were conducted between 400 cm^{-1} to 4000 cm^{-1} at 4 cm^{-1} resolution.

Atomic Force Microscopy

The surface morphology of the film was recorded using Nanosurf Flex AFM System (Switzerland) via Nanosurf Easyscan2 software. Topographic images were obtained in contact mode using aluminium coated cantilever. The images were captured at different positions and roughness of the films was calculated.

Water Contact Angle

The changes in the hydrophobic or hydrophilic nature of the films were evaluated by using contact angle meter Model DMs-401 (Kyowa Interface Science Co. Ltd., Tokyo). All the measurements were performed under room temperature. The size of the drop was constant for all the measurements. At least three measurements per sample were taken and averaged.

Results and Discussion

Mechanical properties

The mechanical properties of the PVA films were tuned with addition 4HC and major contribution of 4HC on final properties of the PVA films are analysed with the help universal testing machine. The results are summarized in Table 1 and stress-strain curve is presented in Figure 1. The films of PVA/4-Hydroxycoumarin (PHC) displayed highest tensile strength of 29.5 MPa, young's modulus 547.9 MPa and elongation at break 56.7 % for PHC-2. Addition of 4HC to the PVA has triggered the negative effect on PVA, indicating the decrease in the mechanical properties of PHC films. Similarly at higher concentration, dispersion of 4HC reduced the interaction leading to the decreased mechanical properties.

Table 1: Mechanical properties of pure PVA and PHC films

Figure 1: Stress-strain curve of pure PVA and PHC films

This could be due to the lower compatibility among the PVA and 4HC. The stress-strain curves of PVA and PHC films indicated that films are less elastic in nature and with increase in the concentration of 4HC elasticity goes on decreasing compared to pure PVA film. The results of mechanical properties confirmed that PHC films were brittle in nature.

Thermogravimetric Analysis

The thermal stability of the prepared films was determined by thermogravimetric analysis method. The thermograms of the films are shown in Figure 2. The thermal degradation of the PVA film showed three step weight losses. The initial weight loss observed in the temperature range 30-105.1 °C. This is due to the evaporation of physically absorbed water molecules. The second major weight loss started at 257-304°C (78%) in PVA, due to the thermal degradation of PVA molecule. The third weight loss occurred in the range of 411-466 °C (16%), corresponds to the release of by-product generated during thermal degradation of PVA.

The incorporation of 4HC has slight influence on PVA film, indicating the increase in the stability of the PHC films. The PHC films also presented three step weight losses. The initial weight loss observed in the range of 38-136 °C (6.3-9.1 %) in PHC-1, PHC-2, PHC-3 and PHC-4 films due to the evaporation of water molecules. The second weight loss observed in the range of 257-359 °C, due to the degradation of films and major weight loss (73-84%) identified at this range corresponds to the thermal decomposition of the films. The third weight loss occurred in the range of 421-473 °C with weight loss of 19-22 %, this is attributed to the complete degradation of films. Notably, slight differences in weight loss were observed in the PHC, indicating the degradation temperature increased in all films with higher weight loss compared to PVA film. The addition of 4HC in to the PVA slightly influenced on thermal stability of PHC films indicating the increase in the overall degradation temperature when compared to that of pure PVA film.

Figure 2: TGA thermograms of pure PVA and PHC films

X-Ray Diffraction Studies

The diffraction pattern of pure PVA exhibits two peaks observed at $2\theta=13°$ and 24°-31°, indicate that semicrystalline nature of the PVA. Owing to the inclusion of 4HC in the PVA films, the diffraction pattern of PHC films showed initially same peak for the composition PHC-1 (13.6°) and PHC-2 (13.9°), later the peak value changed significantly for the composition PHC-3 (14.1°). However, a slight change in the 2θ value leads to an increase in the crystallinity of the films.

Table 2: 2Theta value and percentage of crystallinity of PVA and PHC films

It is obvious that, the structure of the PVA film was influenced by the addition of 4HC resulting from increase in the percentage of crystallinity. Thus, increase in crystallinity and decrease in the amorphous behaviour was observed for the composition PHC-1, PHC-2 and PHC-3 (65 %, 60 %, and 67 %). Moreover, the presences of broad and flat amorphous peaks in blend film confirm the molecular miscibility and considerable interaction among the components and semicrystallinity in the films. The percentage of crystallinity and 2θ values listed in Table 2.

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR analysis was performed in order to study the interaction among the components. The FTIR spectra of 4HC powder, PVA and PHC-1 films are shown in Figure 3. The FTIR spectra of pure PVA presented peak at 3268 cm^{-1} due to non-bonded stretching of –OH group. The C–H broad alkyl stretching band occurred at 2943 cm^{-1}. The peak observed at 1330 cm^{-1} and 845 cm^{-1} is due to the C-C stretching and C-H rocking. The absorption band occurred at 1086 cm^{-1} is assigned to the C-O of PVA. The FTIR spectra of 4HC shows peak at 1705 cm^{-1} attributed to the –C=O stretching. The peak occurred at 1161 and 1593 attributed to the –C-O and –C=C stretching vibration. The peak observed in the range of 3113 is assigned to the –O-H stretching and peak at 2981 attributed to the aromatic –C-H stretching.

Figure 3: FTIR spectra of pure PVA and PHC films

In the FTIR spectra of PHC films, slight change in the peak value was observed indicating that interaction among the PVA and 4HC. The –OH observed in the PVA is shifted to the lower value (3268 cm^{-1} to 3288 cm^{-1}) in all films. This might be due to the intermolecular interaction through hydrogen bonding in the films. Also peak observed in the 4HC (2981cm^{-1}) shifted to the lower level and peak appeared at 1705 cm^{-1} shifted to the higher level (1732 cm^{-1}) in all films. This could be due to the interaction between the PVA and 4HC and disappearance of 1161 cm^{-1} in the film confirms the interaction in the films. The shift in the peak value and change in the peak intensity confirms that there is interaction among the components.

Atomic Force Microscopy

The surface morphology of the pure PVA and PHC films are analysed by using atomic force microscopy and topographic images are shown in Figure 4. The results of AFM study indicates that, films of PHC initially showed decrease in roughness (PHC-1) when compared to that of pure PVA film but as the concentration of 4HC (0.004 g to 0.008 g) increased, roughness begins to alter and showed rougher surface than pure PVA film. This could be due to the distribution of 4HC in PVA which influenced lot on viscosity of the PVA film solution by reducing the interaction among the PVA and 4HC. Meanwhile, at higher concentration of 4HC (0.008 g), the roughness significantly increased which confirmed that higher concentration of 4HC is not compatible with PVA. The similar influence was observed in the mechanical properties indicating the decrease in the mechanical properties at higher concentration of 4HC.

Figure 4: AFM topographic images, 3D view and line graphs of PVA and PHC films

Water Contact Angle

The wetting property of the pure PVA and PHC films was determined by water contact angle measurements. It is well known that lower value of contact angle (less than 90^{o}) suggests the material is hydrophilic in nature and higher value (more than 90^{o}) indicates the material is hydrophobic in nature. The results of contact angle showed that incorporation of 4HC onto PVA did not influenced on hydrophilic nature of PVA film (θ =74.8^{o}). On the other hand, decrease in contact angle from θ=68.7^{o} (PHC-2) to θ=44.9^{o} (PHC-4) were observed with increase in the content of 4HC (0.004 g to 0.008 g) in PVA film. The results obtained from the contact angle measurement confirmed the films were hydrophilic nature. The decreased contact angle θ=74.8^{o} (PVA) to θ=44.9^{o} indicates the affinity of water was significantly increased with incorporation of 4HC.

Conclusion

The results obtained from the study showed that, mechanical properties of the PVA films did not influenced with incorporation of different concentration of 4HC. This suggests that lower compatibility among the intermolecular interaction among the PVA and 4HC indicated by the FTIR study. In addition, variations were observed in some functional properties including surface morphology, thermal properties and water contact angle measurement which is confirmed by the AFM, TGA, and water contact angle measurements. The results of AFM study showed that the surface morphology become uniform and surface roughness increased with increase in the concentration of 4HC in the PVA film. The slight rise in the thermal stability of the PVA films were observed with incorporation of 4HC confirmed in the TGA results. The result of X-ray diffraction study confirmed that films were amorphous in nature. Finally, water contact angle measurement confirmed all the films were hydrophilic in nature. The present study concludes that study can be extended to the application level and the prepared films may play a vital role in food packaging and biomedical applications.

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Manuscript Figures

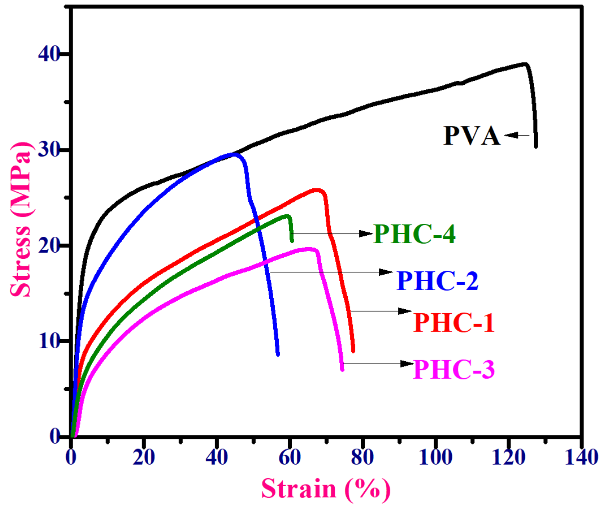

Figure 1: Stress-strain curve of pure PVA and PHC films

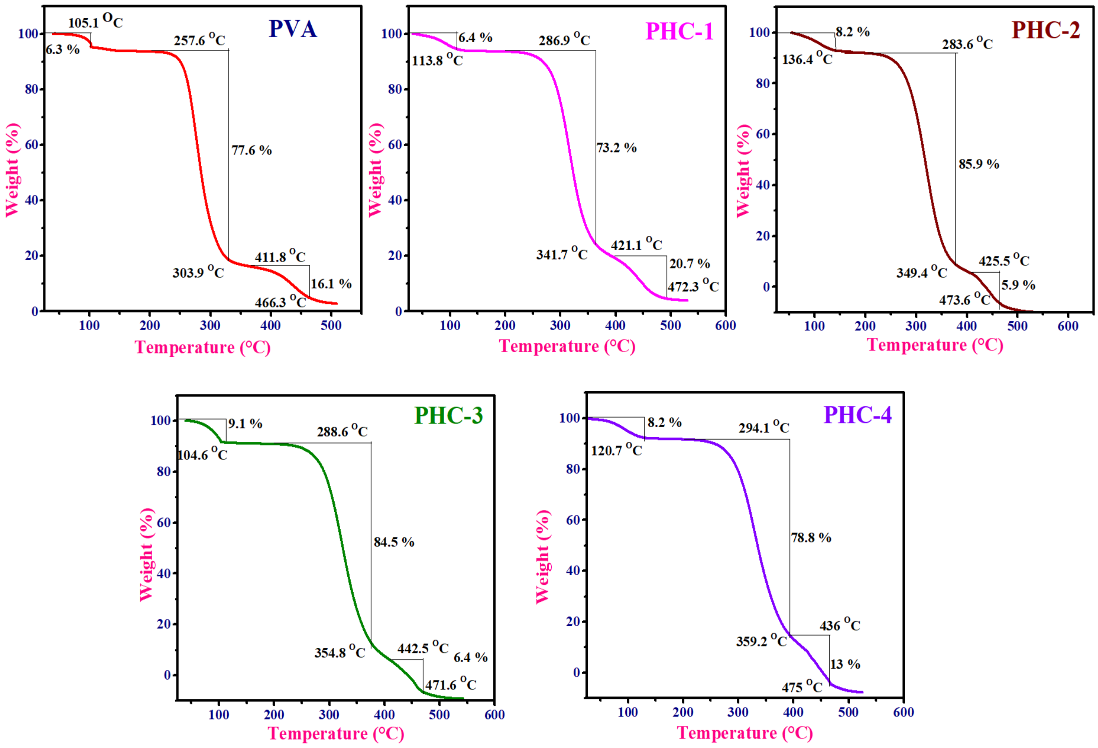

Figure 2: TGA thermograms of pure PVA and PHC films

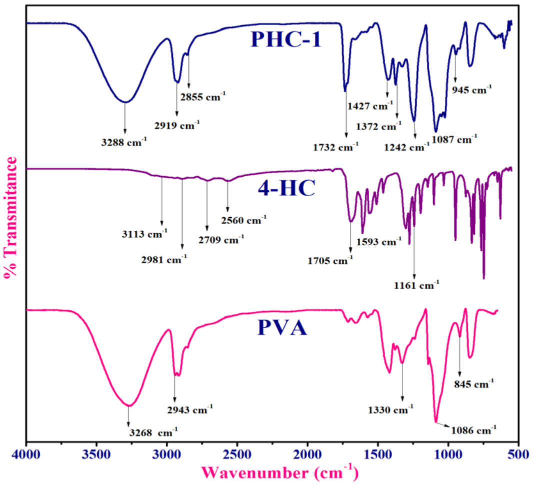

Figure 3: FTIR spectra of pure PVA and PHC films

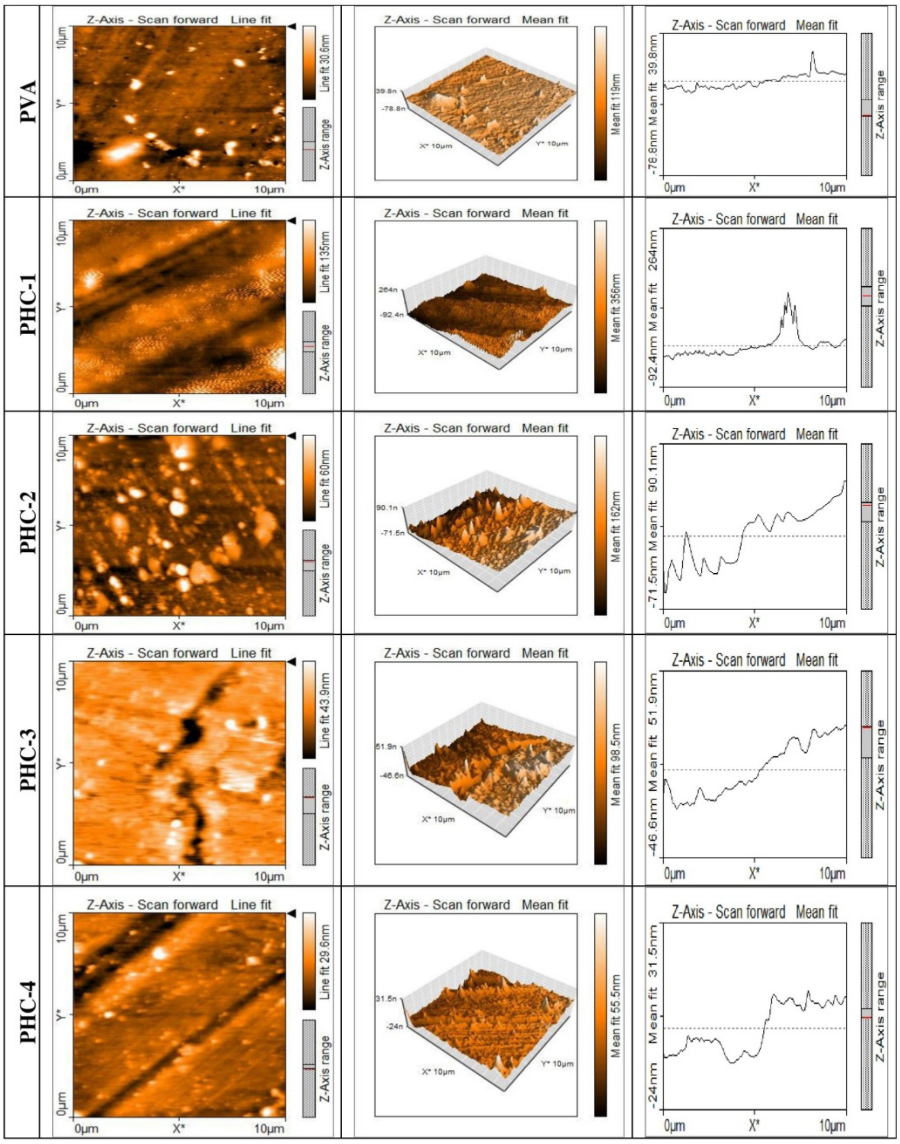

Figure 4: AFM topographic images, 3D view and line graphs of PVA and PHC films

Tables

Table 1: Mechanical properties of pure PVA and PHC films

Sample code	Thickness (mm)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
PVA	0.08	37.64	677.08	118.40
PHC-1	0.05	25.8	352.5	77.3
PHC-2	0.07	29.5	547.9	56.7
PHC-3	0.05	19.6	200.5	74.3
PHC-4	0.06	23.1	235.4	60.5

Table 2: 2Theta value and percentage of crystallinity of PVA and PHC films

	PVA	PHC-1	PHC-2	PHC-3	PHC-4
2 Theta value	13.3	13.6	13.9	14.1	13.1
	24.6	19.5	19.1	19.1	24.6
	29.3	28.7	28.6	2.6	29.3
	31.2	33.2	32.3	31.1	31.2
	39.0	39.7	40.9	40.4	39.0
% of crystallinity	58	65	60	67	32