



Research Article

# Mechanical, optical and antioxidant properties of 7-Hydroxy-4-methyl coumarin doped polyvinyl alcohol/oxidized maize starch blend films



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## Abstract

In the present study, the different weight ratios of 7-hydroxy-4-methyl coumarin (7H4MC) mixed polyvinyl alcohol (PVA)/ oxidized maize starch (OMS) blend films were achieved by the solvent casting method and coded as PSC. The prepared film samples were characterized by employing techniques such as FTIR, UTM, and SEM. The film samples were also subjected to their wettability, biodegradation and migration rate studies. Experimental outcomes showed that strong intermolecular hydrogen bonding between components of the blend films contribute to increase the mechanical properties, smoother surface morphology, increase in surface hydrophobicity, improvement in biodegradability, and exhibited migration rates below the overall migration limit (OML). Furthermore, moisture content, density, optical properties, water absorption, water solubility, water vapour transmission rate and antioxidant properties are discussed in detail. With all these properties, PVA/OMS/7H4MC blend films have the potential to use as packaging material.

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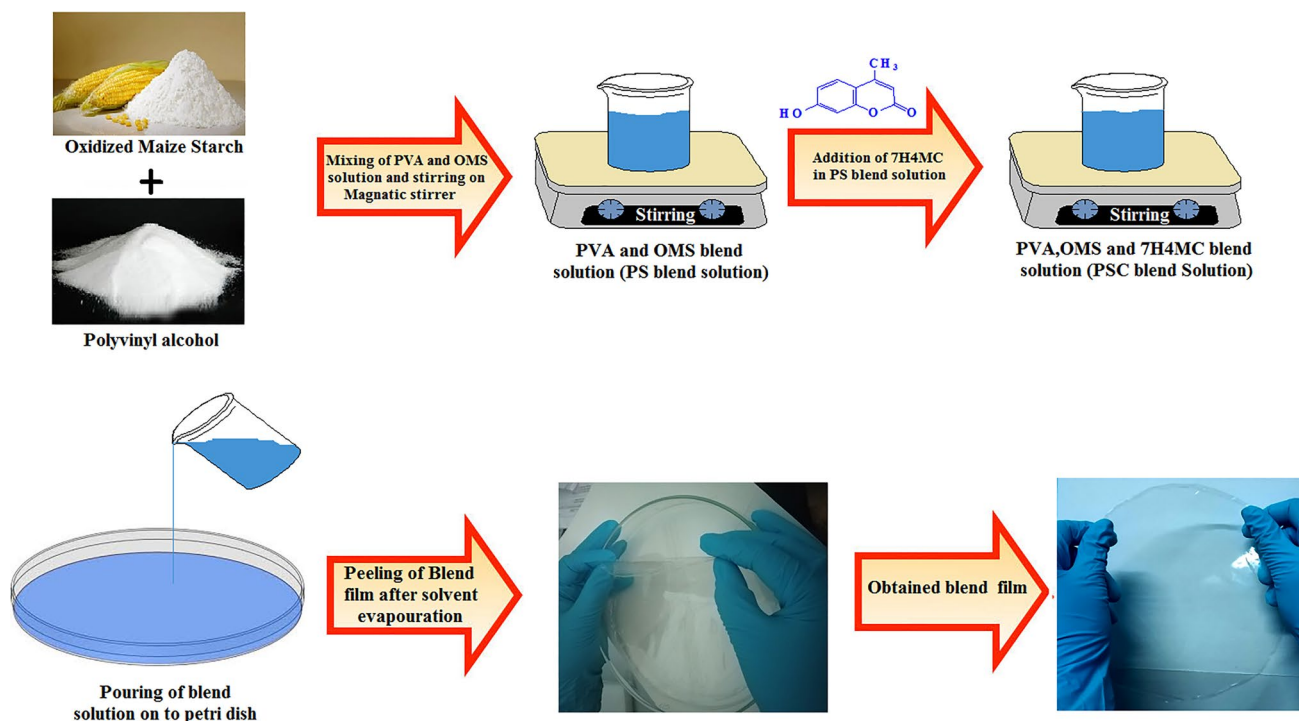
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## Graphic abstract



**Keywords** Mechanical · Antioxidant · Wettability · Biodegradation

## 1 Introduction

In the recent decades, increasing use of petroleum based plastics and their non-biodegradability have raised genuine environmental pollution, and hence, there is a demand for the development of environmentally friendly degradable polymer materials [1]. Therefore, the current trends encourage the improvement of active biodegradable plastics from renewable materials to exchange non biodegradable polymers in various applications. Polyvinyl alcohol and polysaccharides viz starch, pectin, and alginate are biopolymers, which are advantageous for the expansion of packaging films [2].

Polymer blends have become prominent in scientific research and practical applications, as they offer a key option in solving emerging application requirements. Polymer blending can be illustrated as a physical combination of two or more different polymers which interact through secondary forces and result in the formation of new material with improved mechanical and physico-chemical properties [3]. Solution casting is a simple and inexpensive technique to prepare polymer blends because it requires easy tools and without contain any complicated process [4].

Starch is a naturally occurring biodegradable biopolymer. It is non-toxic and is of low cost. It consists of two main polysaccharides linear amylose and branched amylopectin (about 72% in wheat and maize starch). However, starch is modified to overcome its weak film-forming capacity, hydrophilicity and less compatibility with other polymers [5]. The hydroxyl groups of native starch can be readily involved in different types of the modification process, such as esterification, oxidation, and etherification [6]. Oxidation generally involves the chemical modification in which carboxyl and carbonyl group functional groups can be introduced to the starch chain by subsequent depolymerisation of starch [7]. The oxidized starch is more advantageous due to low viscosity, more stability, high transparency, good film forming and binding properties [8, 9]. Polyvinyl alcohol (PVA) is a synthetic, non-ionic water soluble, biodegradable and biocompatible polymer [10, 11], with good film forming capacity, flexibility [12], non-toxicity [13], transparency [14], and barrier properties [15]. In view of all these PVA is widely used in various fields such as packaging industry [16], pharmacy [17], and biosensor [18].

Coumarins are the class of compounds of both natural and synthetic origin [19]. The polymers containing

coumarin are well studied and broadly applied in various fields such as medicinal, biochemical, electrooptical materials, and liquid crystalline materials [20, 21]. Organic compounds containing coumarin moiety exhibit useful and diverse pharmaceutical and biological activities such as anticoagulant, anti-inflammatory, antibacterial, antifungal, antiviral, anticancer, antihypertensive, antitubercular, and antioxidant properties [22]. 7-hydroxy coumarins have great importance as natural fragrances possess a characteristic odour like vanilla beans and their hydroxyl group at 7th position has importance in biosynthesis [23].

Both PVA and starch are hydrophilic, biodegradable and readily dominated by microorganisms in the natural environment. Starch/PVA blend plastics have been one of the most popular biodegradable plastics widely used in packaging and agricultural applications [24–26]. Blending of 7H4MC in PVA/OMS a biodegradable blend is favorable because, all of them have polar hydroxyl and carbonyl groups in their chemical structure. These highly polar hydroxyl groups tend to form intermolecular and intramolecular hydrogen bonds and hence promote the properties of the blend films [27].

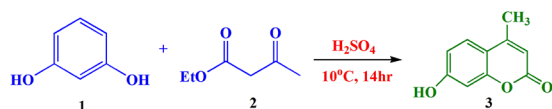
To the best of our knowledge, this is the first report in the literature relevant to 7-Hydroxy 4-methylcoumarin (4-Methylumbelliferone) is used to prepare polymer blend with PVA/OMS. In this regard, we have undertaken this study to evaluate the effect of different amount of 7H4MC on the blend film for their mechanical, morphological, optical, biodegradation, migration, water vapour transmission rate, and antioxidant properties.

## 2 Experimental

### 2.1 Materials

Oxidized maize starch (OMS) was obtained from Millennium Starch India Pvt. Ltd., Athani, Karnataka, India. Polyvinyl alcohol (Degree of polymerization  $1700 \pm 50$ , 99% hydrolysed, and Molecular weight 1,15,000) was procured from Loba Chemie Pvt.Ltd., Mumbai, India. Resorcinol, ethylacetate, sulphuric acid were purchased from Sigma Aldrich. All the chemicals used are analytical grade.

#### 2.1.1 Synthesis of 7-Hydroxy 4-methylcoumarin



The 7-Hydroxy 4-methylcoumarin is synthesized according to method described by Kiskan et al. [28] Conc. sulphuric

**Table 1** Quantities of PVA, OMS, 7H4MC used in the preparation of blend films

Samples	PVA (g)	OMS (g)	7H4MC (g)	Remarks
PVA	2	0.05	–	Good Film
PS	2	0.05	–	Good Film
PSC I	2	0.05	0.002	Good Film
PSC II	2	0.05	0.004	Good Film
PSC III	2	0.05	0.006	Good Film
PSC IV	2	0.05	0.008	Good Film

acid (20 mL) taken in RB flask was cooled in an ice bath at 0 °C. A solution of resorcinol (1) (2.0 g, 18.16 mmol) in ethylacetate (2) (2.4 mL, 19 mmol) was added dropwise to the flask with constant stirring at 0 °C. Then the mixture was stirred overnight at room temperature. After completion of the reaction (TLC), the reaction mixture was poured into crushed ice with vigorous stirring. The white solid separated was filtered and washed with cold water. The crude product was recrystallized from absolute ethanol to obtain the pure white solid of 7-Hydroxy-4-methylcoumarin (3) with an approximately 75% yield.

#### 2.1.2 7-Hydroxy-4-methyl-2H-chromen-2-one (3)

Yield: 85%, mp 189–190 °C, IR (KBr, cm<sup>-1</sup>): (C=O), (O–H); <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 400 MHz) δ ppm: 2.32 (s, 3H, –CH<sub>3</sub>), 6.08 (s, 1H), 6.65 (d, 1H, Ar–H, J = 2.4 Hz), 6.74–6.77 (dd, 1H, Ar–H, J<sub>a</sub> = 2.8 Hz, J<sub>b</sub> = 9.2 Hz), 7.54–7.57 (d, 1H, Ar–H J = 8.8 Hz), 10.57 (s, 1H, –OH).

<sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, 75 MHz) δ ppm: 18.65, 102.67, 110.74, 112.55, 113.41, 127.21, 154.21, 155.32, 160.91, 161.65.

### 2.2 Preparation PVA/OMS/7-Hydroxy 4-methylcoumarin (PSC) Blend Films

Polyvinyl alcohol was dissolved in double-distilled water at 90 °C by stirring on magnetic stirrer to obtain a clear solution (2%). The Oxidized maize starch was added in of double-distilled water (50 mL) at 95 °C with constant stirring to obtain a clear solution. The various weight ratio of 7-hydroxy 4-methylcoumarin viz 0.002, 0.004, 0.006, and 0.008 g were dissolved in suitable quantities of hot water and stirred up to get a clear solution (Table 1).

Prepared OMS solution was added slowly to the previously prepared polyvinyl alcohol solution with constant stirring and kept it for 30 min with constant stirring on a magnetic stirrer. Then the different ratio of the 7-hydroxy 4-methylcoumarin solution was added to the PVA/OMS (PS) blend. The blend solution was stirred for 24 h to get

a clear and homogeneous solution. The solution is cast on a petri dish and placed in a hot air oven at 30 °C. After evaporation of the solvent, the films were peeled out carefully and stored in a desiccator.

### 3 Characterizations

#### 3.1 Moisture content

Film specimens of size 2 cm × 2 cm were weighed ( $W_i$ ) then kept in a hot air oven at 105 °C for 3 h to attain a constant weight. Then the sample was removed from hot air oven and stored in a desiccator for uniform cooling, and then the weight of the film was re-determined ( $W_f$ ). Three measurements were made from each film specimen and the moisture content of the film was determined as follows [29].

$$\text{Moisture content (\%)} = \frac{W_i - W_f}{W_f} \times 100$$

where  $W_i$  is the initial weight of the sample, and  $W_f$  is the final weight of the sample.

#### 3.2 Density

Films density was determined directly by taking film weight and dimensions using the following equation [30]

$$\text{Density} = \frac{M}{A \times T} \text{ g/cm}^3$$

where  $M$  is the mass (g),  $A$  is the area (cm<sup>2</sup>),  $T$  is the thickness of the film (cm).

#### 3.3 Water solubility

To evaluate solubility percentage of all the film in water, the film samples were cut into 2 × 3 cm and these film pieces were stored in desiccators (silica gel, approximately 0% RH) for 7 days. All the samples were initially weighed and placed in a glass beaker containing of deionised water (80 mL). The samples were continuously stirred over magnetic stirrer about one hour at room temperature. Then the contents of beakers were filtered using Whatman No.1 filter paper and the residue is dried in the oven at 60 °C to obtain constant weight. The percentage of the total solubility of films was calculated as follows [31]

$$\text{Solubility(\%)} = \frac{\text{Initially dried weight} - \text{Final dried weight}}{\text{Initially dried weight}} \times 100$$

#### 3.4 Water absorption (WA) capacity

The water absorption capacity of all films samples was performed as described by Ismail et al. [32] Dried films were immersed in deionised water at room temperature (25 °C). After 24 h the film is removed from the water and the final weight of the film is recorded after removing water on the films surface using tissue paper. The amount of water absorbed by all films was calculated using the formula given below:

$$W_A(\%) = \frac{W_F - W_i}{W_F} \times 100$$

where  $W_F$  is the final weight film at equilibrium, and  $W_i$  is the initial weight of film.

#### 3.5 Fourier transform infrared (FTIR) spectroscopy

The Infrared spectra of all films were recorded between 450 and 4000 cm<sup>-1</sup> by placing the films over sample holder with a resolution of 4 cm<sup>-1</sup> by using attenuated total reflection (ATR) equipped IR spectrometer at room temperature in air (FT-IR-ATR, Perkin Elmer spectrum version 10.5.4).

#### 3.6 Mechanical properties

In this study, mechanical properties like tensile strength ( $T_s$ ), young modulus ( $Y_m$ ), and elongation at break ( $E_b$ ) of pure PVA, PS blend film and PSC blended films were evaluated by using Dak system universal testing method (UTM) according to ASTM D882-91 (ASTM, 2009). All the tests were carried out under cross-head speed 1 mm/min<sup>-1</sup> at room temperature in air. Prior to the measurement of tensile strength, the thickness of the films was measured by digital micrometer (Mitutoyo made in Japan) at five different places and the average thickness is considered for testing.

#### 3.7 Water contact angle (WCA) measurement

The water contact angle of pure and blended films was analyzed by using contact angle meter (Kyowa Interface Science Co. Ltd., Tokyo, Model DMS-401). All the measurements are carried out under room temperature. For all the measurement size of the water drop was uniform. From two different places, three measurements per test point were taken and averaged.

#### 3.8 Scanning Electron Microscopy (SEM)

Film specimens of size 2 × 2 mm were cut from Pure PVA, PS blend, and PSC blended films and placed on metal stub using a dual sided gum carbon tape. Then all film specimens

were laminate with a conductive layer of noble metal (10 nm thickness) to avoid charging to the high electron beam. Surface morphology and internal structure of all specimens were examined using a JEOL JSM-6360 scanning electron microscopy (SEM) at an acceleration voltage of 10 kV. SEM micrographs were taken at different magnification.

### 3.9 Water vapor transmission rate (WVTR)

To determine WVTR of all prepared films, the glass bottle having inside diameter 17 mm was taken and 10 ml of deionised water is poured into it, and the mouth of the bottle is capped with prepared films and tightened using Teflon tape then the initial weight ( $W_1$ ) of the bottle was recorded and kept in an oven at 40 °C for 24 h. The bottle was removed from the oven and the final weight ( $W_2$ ) of a bottle is recorded, after 24 h [33]

$$\text{WVTR} = \frac{W_1 - W_2}{A \times T} \text{g/m}^2\text{h}$$

where A is the area of circular mouth of the bottle in  $\text{mm}^2$ ,  $W_1$  initial weight of the bottle,  $W_2$  is the final weight of the bottle.

### 3.10 Optical properties

UV-Visible spectroscopy (Model V-670) was used to determine the transparency and opacity of pure PVA, PS blend and PSC composite films. Each specimen of size 3 cm × 1 cm were cut from pure PVA, PS blend and PSC blended films and directly placed into quartz cuvette and absorbance spectra were recorded in the range of 200 to 600 nm using air as reference. The analysis was done in triplicates and the average was calculated. Obtained results have been expressed in percentage transmission. The transparency of the film is determined by measuring % transmission at 600 nm and was calculated using the following equation [34]

$$T_{600} = \frac{-\log \% T}{b}$$

where % T percentage transmittance and b is the film thickness in mm.

The opacity of the film was determined according to the method reported by Kannat et al. [35]. using the following formula

$$\text{Opacity} = \text{Absorbance at 500 nm} \times \text{film thickness (mm)}$$

### 3.11 Biodegradation test

The biodegradation test of pure PVA, PS blend, and PSC blended films was investigated according to Riyajan et al.

[36]. For this; sample of size 2 × 2 cm was taken and buried under soil at a depth of 5 cm from the surface. The soil was kept moist by sprinkling water at every 3 days for 4 weeks. The weight loss of sample was determined by removing sample and carefully cleaned with distilled water and dried at 45 °C. The degradation of the specimens was calculated according to equation given below:

$$\text{Degradation (\%)} = \frac{W_1 - W_2}{A \times T} \times 100$$

where  $W_1$  is the initial dry weight of the sample and  $W_2$  dry weight of the sample after biodegradation test in soil.

### 3.12 Food compatibility

The analysis of overall migration rate of prepared films into different food simulants like distilled water (A), 50% ethanol (B) and 3% acetic acid (C) (employed to mimic aqueous foods, alcoholic beverages and acidic foods, respectively) was investigated according to IS: 9845-1998 specifications [37]. For this study, approximately 1 cm × 1 cm film samples were immersed into food simulants and kept it in hot air oven at 40 °C up to 10 days. After incubation period the samples were evacuated from food simulants and the simulants were evaporated and the residues were dried overnight at 100 °C and reweighed after cooling to room temperature. The rates of overall migration of components of all the films were estimated gravimetrically. The results were expressed as per kilogram (Fig. 1).

### 3.13 Antioxidant properties

Antioxidant activities of the pure PVA, PS and PSC blended film samples were determined by radical scavenging activity using the 2, 2-diphenyl-1-picrylhydrazyl (DPPH) method. The stock solution of DPPH was prepared by dissolving 3.9432 mg of DPPH in 100 ml of methanol and stored at 4 °C until further use. 2 ml of DPPH was mixed with 1 ml of five various concentrations (20, 40, 60, 80 and 100  $\text{mg mL}^{-1}$ ) of the samples. Ascorbic acid was used as a standard reference. The reaction mixture was mixed and kept in the dark for 30 min to prevent photochemical reaction and incubated at room temperature. The absorbance of reaction mixture (sample absorbance) was recorded spectrophotometrically at 517 nm. An antioxidant activity was calculated by the following equation

Scavenging effect%

$$= \frac{\text{Control absorbance} - \text{sample absorbance}}{\text{Control absorbance}} \times 100$$

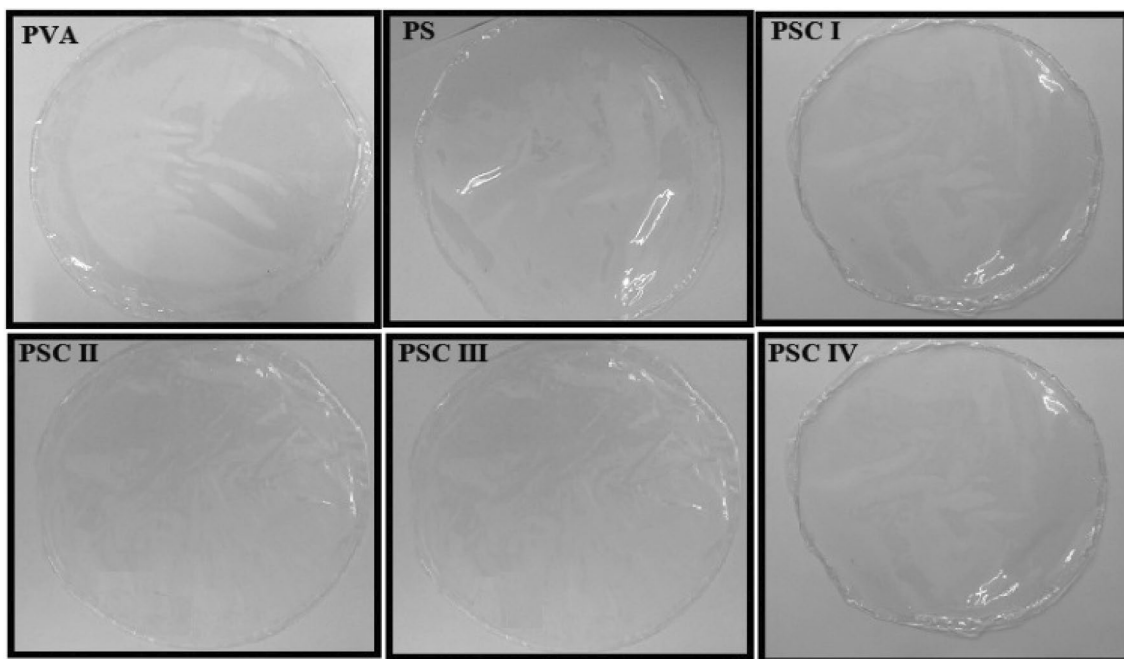


Fig. 1 Images of prepared neat PVA and PS and PSC blend films

## 4 Results and discussion

### 4.1 Characterization of synthesized 7H4MC

$^1\text{H}$ NMR spectrum (Fig. 2a) showed the six different types of proton signals. The chemical shift at 2.32 ppm represents the methyl protons. The chemical shifts 6.08, 6.65, 6.74 and 7.54 ppm represent the aromatic protons and the chemical shift at 10.57 ppm represent the proton of the hydroxyl (-OH) group.  $^{13}\text{C}$ NMR spectrum (Fig. 2b) showed the 10 carbon signals which are equal to the number of carbon atoms present in the 7-hydroxy-4-methyl-2*H*-chromen-2-one. The signal at 18.65 ppm represents the methyl carbon, 102.67, 110.74, 112.55, 113.41, 127.21, 154.21, 155.32 and 160.91 signals represents the aromatic carbons and signal at 161.65 ppm represents the carbonyl carbon. Thus, of the spectroscopy characterizations confirmed the structure of 7H4MC.

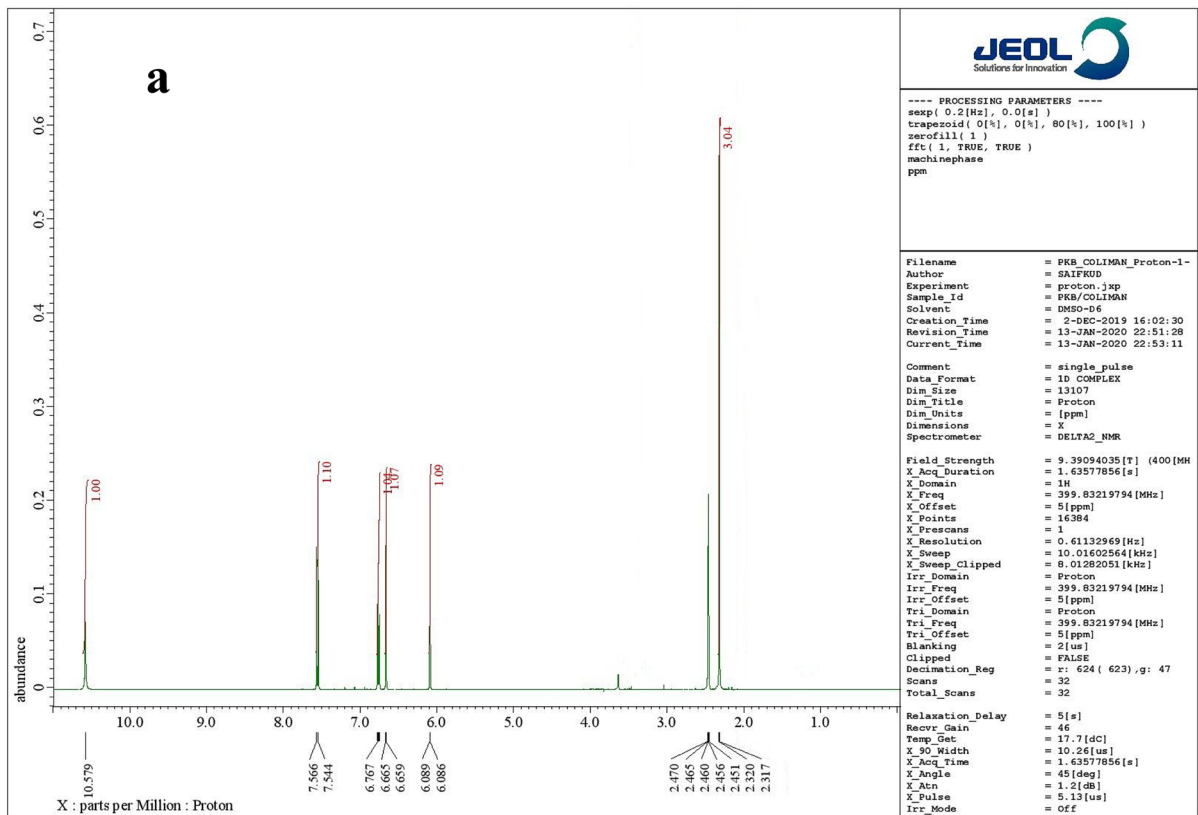
### 4.2 The effect of 7H4MC on density and moisture content of PVA/OMS

In order to prevent the spoilage of food, it is expected that the film must be waterproof. In recent days, there is a need to develop biofilms which can reduce moisture sensitivity of the material. Moisture content and density of all the prepared film samples are presented in Table 2. The moisture content of PVA film decreases slightly after

embodiment with OMS. This is due to both PVA and OMS are polar polymers containing OH groups [38]. After incorporation of different quantity of 7H4MC in PS blend film, a decrease in the moisture content was observed as compared to the control PS blend film. This may be due to the fact that 7H4MC results in the formation of strong hydrogen bonding with starch and PVA and the phenomenon are well supported by the FTIR results that the stretching frequency OH groups in PS blend film are decreased to a lower value after addition of 7H4MC. From the Table 2, it is observed that PS and PSC blend films shown density values lower as compared to pristine PVA this may be due to the interaction between components of the blend films which can reduce the hydroxyl groups per unit mass of the sample causes the reduction in density of the film [39].

### 4.3 The interaction of 7H4MC with PVA/OMS

The polar groups of PVA, OMS and 7H4MC play an extensive role in the formation of strong interaction among the components of the blend film through hydrogen bonding. The FTIR spectrum (Fig. 3) of 7H4MC showed vibration of OH groups at  $3500\text{ cm}^{-1}$  corresponds to stretching vibration of =C-H, a sharp band at  $1671\text{ cm}^{-1}$  corresponds to C=O stretching vibration and medium intensity bands at the peaks at  $1602\text{ cm}^{-1}$  and  $1394\text{ cm}^{-1}$  are associated with vibration of C=C vibration of symmetrical deformation of methyl group. The spectral data of PVA, PS and



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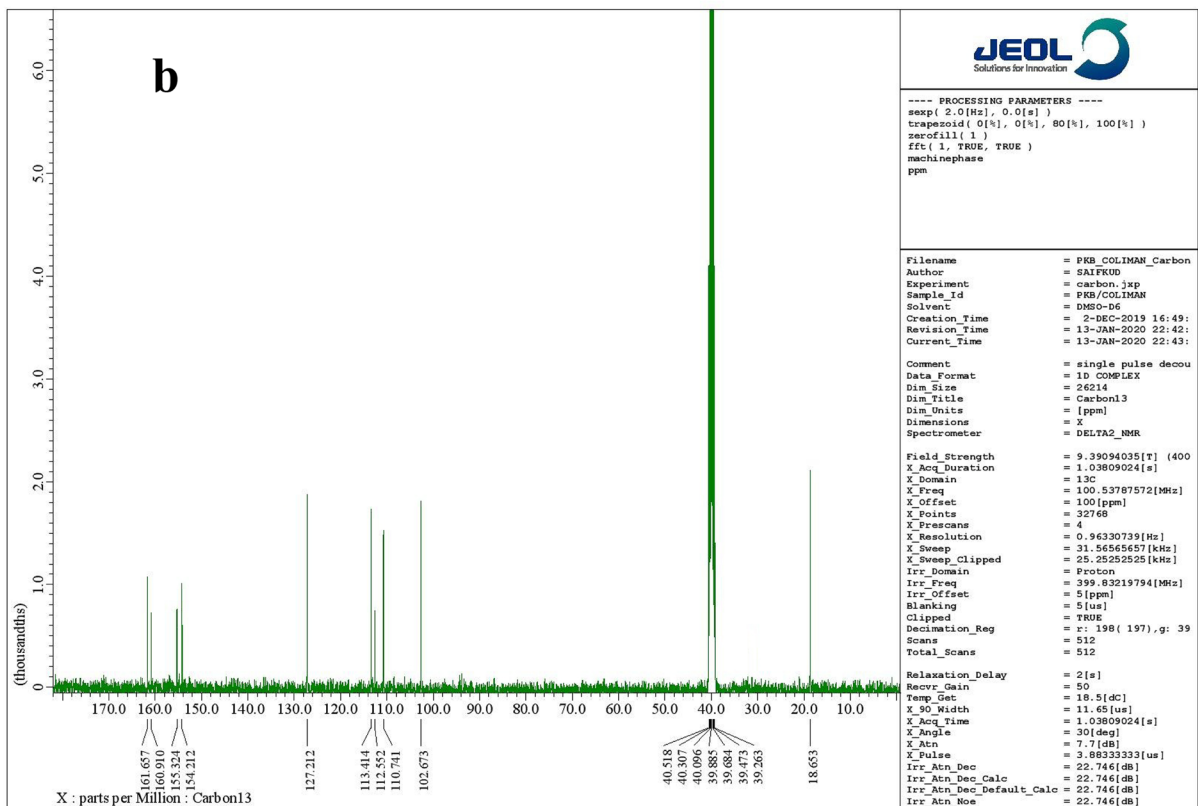
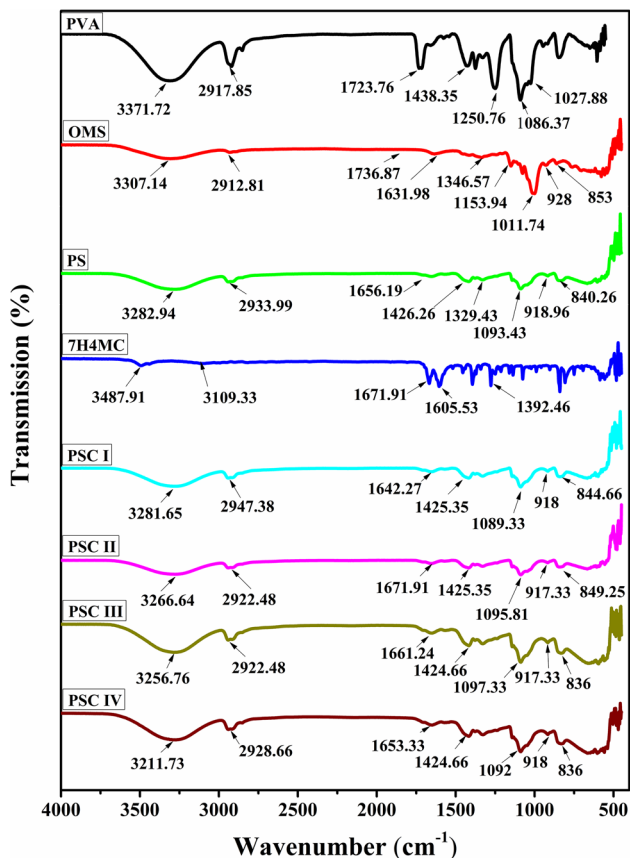


Fig. 2 **a** <sup>1</sup>H NMR and **b** <sup>13</sup>C spectrum of 7-Hydroxy 4-methylcoumarin

**Table 2** The Density, Moisture content and solubility values of prepared films

Sample name	Density (g/cm <sup>3</sup> )	Moisture content (%)	Solubility (%)
PVA	2.75	8.71	28.57
PS	1.35	8.69	43.02
PSC I	1.28	8.31	23.10
PSC II	1.01	7.90	21.00
PSC III	1.97	8.94	20.66
PSC IV	1.44	8.46	26.80

PSC blend films are shown in Fig. 3. The broad absorption peaks observed at 3371 cm<sup>-1</sup> in neat PVA spectra was assigned to -OH stretching frequency, bands at 2917 cm<sup>-1</sup>, 1086 cm<sup>-1</sup>, and 1438 cm<sup>-1</sup> were ascribed to C-H stretching, C-O stretching, and C-H bending, vibrations of PVA respectively, characteristic peak observed at 1723 cm<sup>-1</sup> in PVA was attributed to acetate group exists from hydrolysis of polyvinyl acetate during manufacturing of polyvinyl alcohol. Obtained FTIR data are in good relevant with literature [40, 41].

**Fig. 3** FTIR Spectra of prepared PVA PS and PSC films and OMS, 7H4MC powders

In the spectrum of OMS, the absorption peaks at 3307 cm<sup>-1</sup> and 2912 cm<sup>-1</sup> are correspond to OH and CH<sub>2</sub> stretching vibration of glucose units respectively. The absorption peak observed at 1631 cm<sup>-1</sup> was attributed to the H<sub>2</sub>O bending vibration [42]. The peak located at 1736 cm<sup>-1</sup> was ascribed to the carbonyl (C=O) stretching vibration [43]. The bands observed at 1011 cm<sup>-1</sup> and 1153 cm<sup>-1</sup> were the stretching vibration of C-O in C-O-H groups, and the peak located at 1346 cm<sup>-1</sup> is ascribed to the angular deformation of C-H [44]. The peak at 928 cm<sup>-1</sup> was ascribed to stretching vibration of C-O in C-O-C groups.

After the blending of OMS with PVA, the IR spectra of PS film shows all the specific bands of OMS and PVA with some variations. The position of OH stretching vibration in PVA shifts to lower frequency by the addition of OMS by around 3282 cm<sup>-1</sup> indicating that strong hydrogen bonding interaction occurred between hydroxyl groups of OMS and PVA [45] (Fig. 4). The intensity of carbonyl groups peak observed at 1737 cm<sup>-1</sup> in OMS decreased in PS blend films indicating that carbonyl groups are also involved in the hydrogen bonding with PVA (Fig. 4).

The IR spectra of the PS blend film reflect the modification with the addition of 7H4MC. The absorption peak of OH groups at 3282 cm<sup>-1</sup> in the PS spectra shifts to lower stretching frequency at 3266 cm<sup>-1</sup>, 3256 cm<sup>-1</sup> and 3211 cm<sup>-1</sup> in PSC II, PSC III and PSC IV blend films respectively. This indicated that the 7H4MC has interacted with PS matrix (Fig. 4) and destructed the hydrogen bonding between PVA and OMS, due to which the -OH peaks are shifted to lower wave numbers [46, 47]. From spectral studies, it can be concluded that 7H4MC can forms hydrogen bonding with the OMS and PVA and miscible over the entire composition.

#### 4.4 The effect of 7H4MC on mechanical properties of PVA/OMS

Mechanical properties of films are essential for the proper function of polymer materials and may be altered by the interaction between the components of the polymer blend [48]. Tensile properties such as tensile strength (T<sub>s</sub>), elongation at break (E<sub>b</sub>) and young's modulus (Y<sub>m</sub>) of pure PVA, PS and PSC blended films were measured at room temperature in air and stress-strain curves are shown in Fig. 5a and data obtained from stress-strain curves are presented in Table 3. Due to more hydroxyl group and flexible nature of carbon-carbon backbone, neat PVA film exhibited good mechanical properties [49].

Incorporation of OMS in the PVA matrix revealed weak compatibility between PVA and OMS leads to a decrease in the T<sub>s</sub> and increase in the E<sub>b</sub> of PS blend film. Since



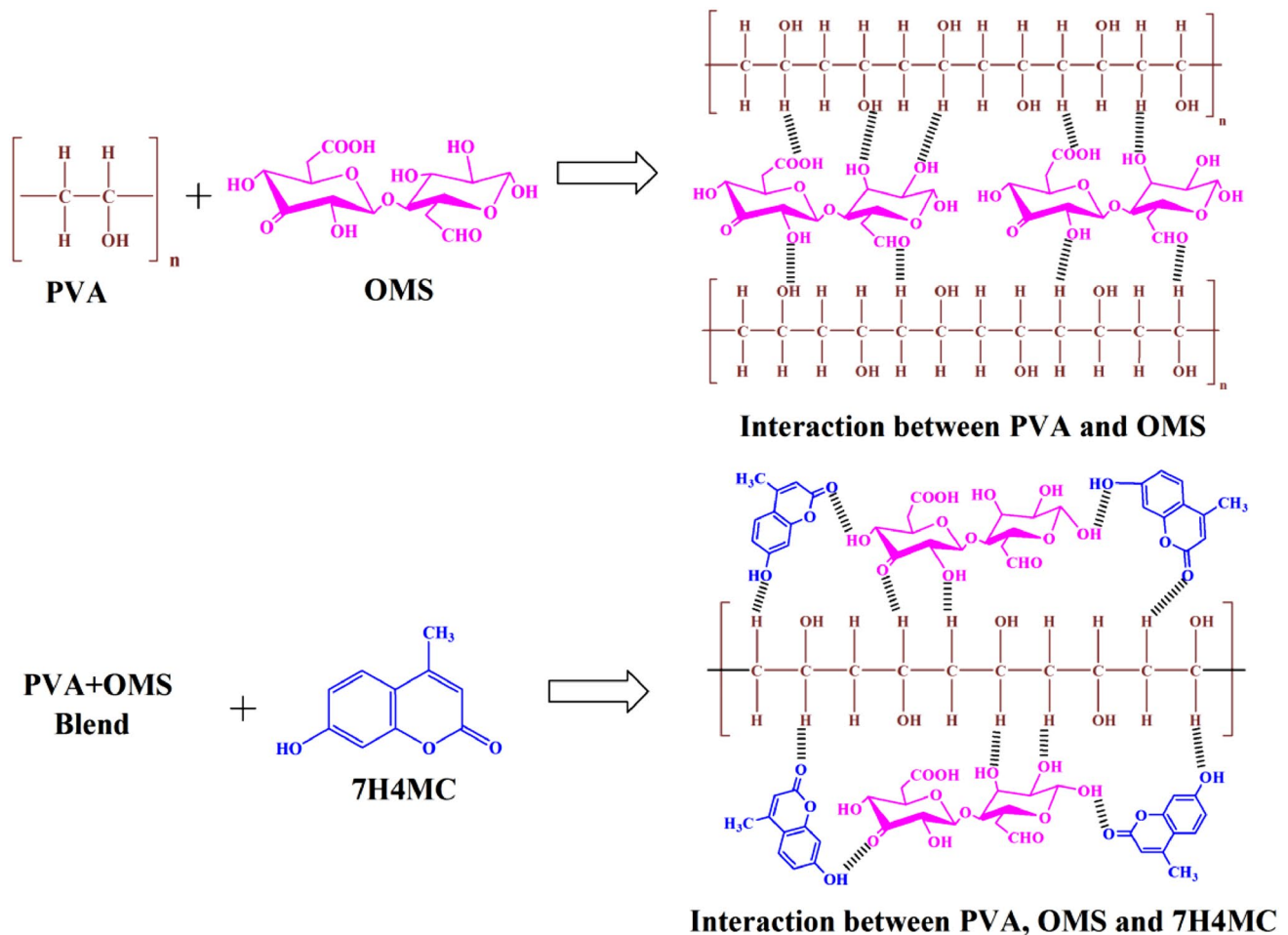


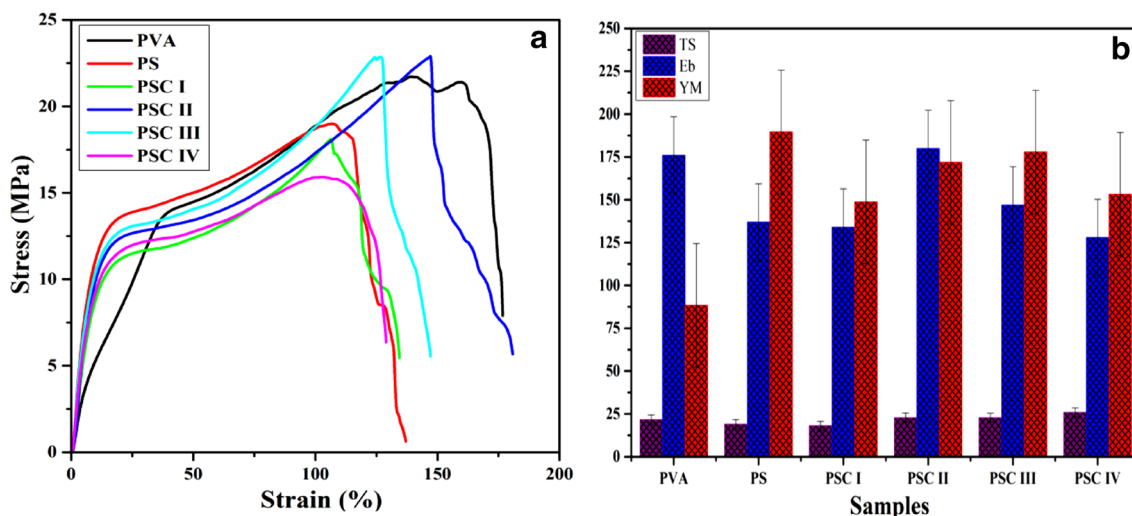
Fig. 4 Plausible Interaction between PVA, OMS and 7H4MC

water is a pervasive plasticizer, higher the water content in the blend enhances the elongation of the film [50]. With increase in the content of 7H4MC in PS blend,  $T_g$  and  $E_b$  increases in PSC I and PSC II films. These observations are in good agreement with the results reported by Domene-Lopez et al. [51]. These maxima in both  $T_g$  and  $E_b$  could be attributed to the strong interaction between the hydroxyl groups of PVA and OMS with the hydroxyl groups of 7H4MC intermolecular hydrogen bonding (Fig. 4). The  $Y_m$  of the blend films varies from 148.85 MPa to 177.89 MPa. However, at a higher content of 7H4MC reduction in both  $T_g$  and  $E_b$  was observed and this could be explained by the thixotropic behaviour of 7H4MC, which causes to reduce the viscosity of the film forming solution [52]. These satisfying results illustrate that the addition of 7H4MC improved the  $T_g$  and  $E_b$  of the blend films.

#### 4.5 The effect of 7H4MC on surface morphology of PVA/OMS

Scanning Electron Microscope (SEM) analysis is a very effective and well known technique to evaluate the surface morphology of polymeric materials as the morphology is a key factor in achieving the desired material properties [53, 54]. Figure 6 shows the SEM micrographs of the surface of neat PVA, PS blend and PS/7H4MC blended films.

The pure PVA film (Fig. 6a) exhibits smooth and homogeneous surface whereas the surface of PVA/OMS blend films (Figure 6b) was found to be rough and irregular surface. The blend film at lower content of 7H4MC (Fig. 6c) exhibits rough surface with short fiber like particles of 7H4MC along with agglomeration of starch particles in the blend films. Further, the agglomeration of starch particles



**Fig. 5** a Stress–Strain curves of prepared films b Tensile properties of PVA, PS and PSC blend films

**Table 3** Mechanical, WVTR, WA properties of PVA and PS, PSC blend films

Sample code	Thickness ( $\mu\text{m}$ )	$T_s$ (MPa)	$E_b$ (%)	$Y_m$ (MPa)	WVTR ( $\text{g}/\text{m}^2\text{h}$ )	$W_A$ (%)
PVA	$60 \pm 1.2$	$21.7 \pm 0.8$	$88.4 \pm 3.2$	$176.8 \pm 1.8$	$31.2 \pm 0.7$	$59.8 \pm 1.2$
PS	$70 \pm 0.5$	$18.9 \pm 1.2$	$137.0 \pm 2.7$	$189.5 \pm 2.2$	$34.8 \pm 0.5$	$81.2 \pm 0.8$
PSC I	$70 \pm 2.1$	$18.1 \pm 1.5$	$134.4 \pm 4.9$	$148.8 \pm 1.7$	$24.9 \pm 0.2$	$52.2 \pm 0.5$
PSC II	$90 \pm 1.7$	$22.8 \pm 1.3$	$180.8 \pm 1.2$	$171.8 \pm 2.3$	$22.0 \pm 0.4$	$48.4 \pm 1.5$
PSC III	$80 \pm 3.7$	$22.8 \pm 2.0$	$147.1 \pm 2.6$	$177.8 \pm 3.1$	$20.2 \pm 0.3$	$44.3 \pm 1.1$
PSC IV	$90 \pm 1.5$	$15.9 \pm 1.5$	$128.9 \pm 4.4$	$153.3 \pm 1.5$	$23.8 \pm 0.5$	$47.1 \pm 1.5$

decreases with an increase in the content of 7H4MC in the PS matrix. This implies the addition of the 7H4MC in the PS matrix improves the compatibility with PVA/OMS and this could be due to strong intermolecular interaction between PVA/OMS. This evidence is good relevance with results reported by Jianga et al. [55].

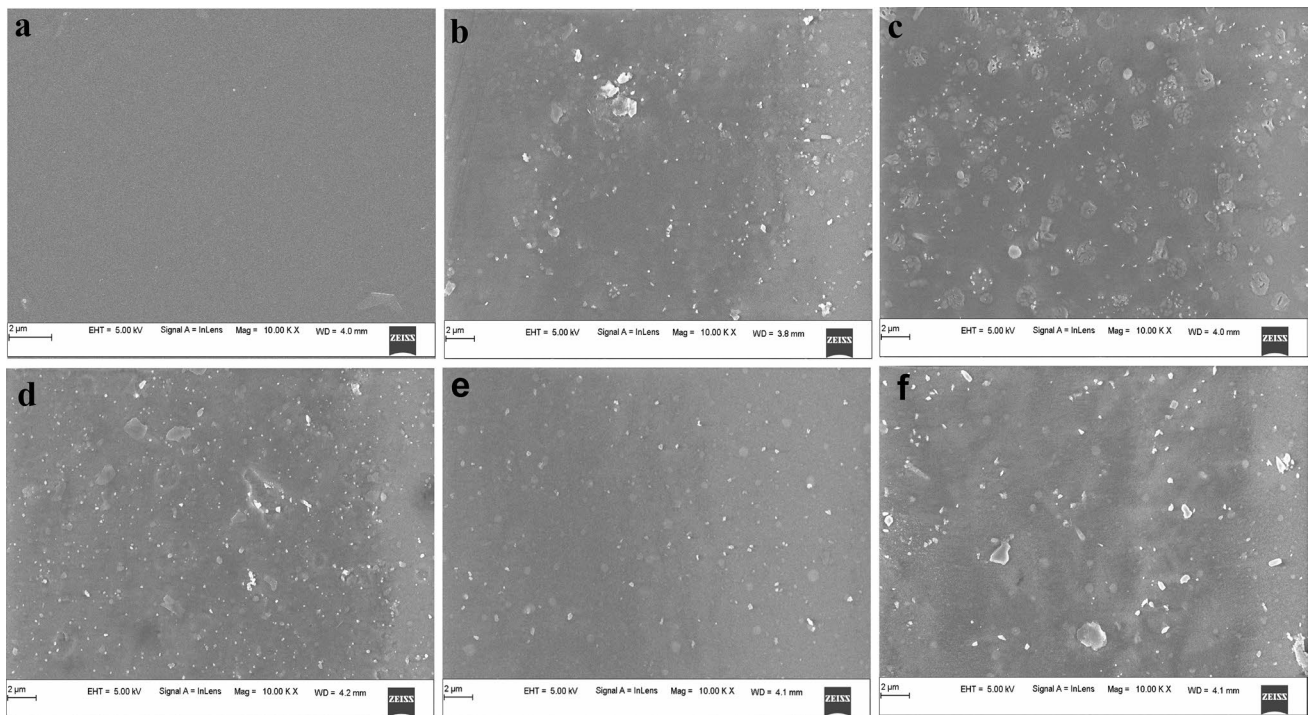
Among all the blend films PSCII and III [Fig. 6d, e] blend films presented smooth surface. The results were correlated with higher values of  $T_s$  and  $E_b$  of these blends films [56]. From the surface morphology of all blend films, it was observed that the PSC blend films were smoother than that PS blend film, this could be due to the better compatibility and strong adhesion between the 7H4MC and PS matrix. These findings have good agreement with the other researchers [57, 58]. These conclusions obtained from SEM are also comparable and in good agreement with FTIR studies.

#### 4.6 The effect of 7H4MC on wettability of PVA/OMS

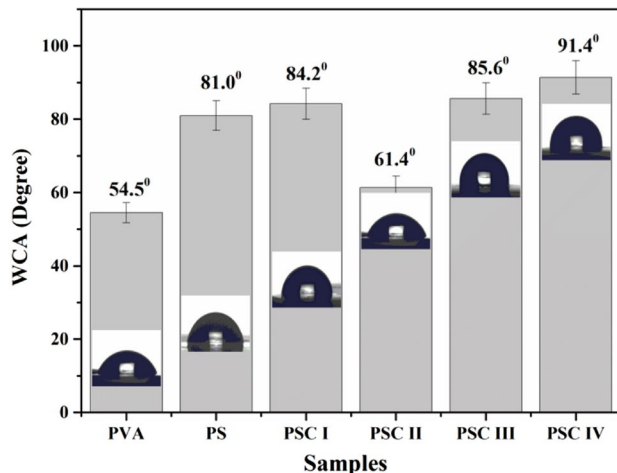
Water contact angle (WCA) measurement is the main criteria to understand the effect of the interaction between the components of the blend on the film hydrophilicity. For the food packaging application of PVA based materials

surface hydrophobicity of film is an important property [59]. The wettability between film surface and liquid can be expressed by contact angle  $\theta$ . When the value of  $\theta$  is smaller than  $90^\circ$  referred to as film is hydrophilic and if the  $\theta$  is greater than  $90^\circ$  correspond to film is hydrophobic [60]. If the film is hydrophilic the liquid can moisturize the surface but in the hydrophobic situation, the liquid can travel on the surface of the film. WCA and the pictures of water drops on the surface of the films of neat PVA, PS and PSC blended films were shown in Fig. 7.

By observing Fig. 7 it is clearly confirmed that all the blended films showed a higher contact angle as compared to neat PVA. PVA film presented fully hydrophilic behaviour with contact angle  $54.5^\circ$  due to water has a stronger interaction with PVA [61]. Moreover the WCA of PS blend film increases by the addition of OMS into PVA, this might be due to interaction between the OMS and PVA reduces the content of hydrophilic groups of PVA film [62]. After incorporation of 7H4MC in PS the matrix a remarkable improvement observed in the WCA. From the figure, we can see that samples with more quantity of 7H4MC found to be hydrophobic. This fact is due to polar groups of PVA and OMS are involving strong hydrogen bonding with 7H4MC (Fig. 4). These consequences are associated with



**Fig. 6** SEM images of **a** neat PVA **b** PVA/OMS **c** PSC I **d** PSC II **e** PSC III **f** PSC IV



**Fig. 7** Water contact angle measurements and Images of water drops

the surface morphology of the films (SEM) that the films with rougher surface shown the higher values of contact angle whereas smoother surface films showed the lower values of contact angle and similar results are reported by Kubiak et al. [63] From the above observation it should be concluded that incorporation of 7H4MC into PVA and OMS blend can change the film wettability from hydrophilic to hydrophobic.

#### 4.7 The effect of 7H4MC on water absorption capacity of PVA/OMS

A water absorption test is carried out to evaluate the percentage of water absorbed by the film under specified situation. It can also give information about the water resistance properties of the films. Reducing water sensitivity and developing water resistance of the starch based material is a highly important concept [64]. Percentage of water absorption capacity of pure PVA, PS and 7H4MC incorporated PVA/OMS blend films are tabulated in Table 3. The incorporation of OMS in the PVA matrix can enhance the percentage of water absorption as compared to pure PVA film. This may due to loading of starch molecules in between PVA chain cause to increase the discontinuity and free volume in the PVA matrix so that water could easily penetrate in the blend through the voids and absorbed by the starch resulting in the higher water uptake [39]. It can be also observed that water absorption of PS blend films decreases after addition of 7H4MC. This observation is attributed to combining 7H4MC with PVA and OMS prevented the water molecule from dissolving and improve the water resistance of the blend film. On the other hand the strong intermolecular hydrogen bonding between 7H4MC, PVA/OMS blend film which forms the network structure that could reduce the penetration of water molecules in a polymer matrix [65, 66].

#### 4.8 The effect of 7H4MC on WVTR of PVA/OMS

For food packaging film water vapour transmission rate is an important criterion that is used to determine the capacity of the moisture getting inside from, surrounding environment of the film. To maintain the freshness of the foods, the value of water vapour transmission should be as low as possible. WVTR across the films takes place through two processes viz adsorption followed by diffusion steps [67]. The calculated values of water vapour transmission of neat PVA and PS, PSC blend films are summarised in Table 3. The neat polyvinyl alcohol film showed WVTR at 31.22 g/m<sup>2</sup>h.<sup>32</sup> With the addition of OMS in the PVA matrix, we observed there was an increase in the water vapour transmission rate of PS blend film. This could be mainly due to hydrophilic behaviour of PVA and water sensitivity of OMS that would cause to enhance the interchain spacing and mobility of water molecules through the films which made positive contributions to increase the WVTR [68, 69]. The incorporation of 7H4MC in PS blend films lowers the WVTR. It might be due to the strong interaction between hydroxyl group of 7H4MC with polar groups of PVA and OMS via hydrogen bonding which made different lanes of direct diffusion of water molecules which creates tortuous path in blend film and thus they blocked the moisture and water vapours passing through the blend film (shown in Fig. 8). The results obtained are good relevance with Fahma et al. [70]. As the percentage of 7H4MC increases in the blend the hydrophilicity of the film is decreases. From the above observation, it can be concluded that the incorporation of 7H4MC in PS caused to decrease in the WVTR of the film up to 20.20 g/m<sup>2</sup>h. All the blend films showed the WVTR value in the range of 31–20 g/m<sup>2</sup>h which are similar to the some polymer used in packaging field (low-density polyethylene—LDPE = 16–23 g/m<sup>2</sup>.day, polyethylene terephthalate—PET = 15–20 g/m<sup>2</sup>.day) [57].

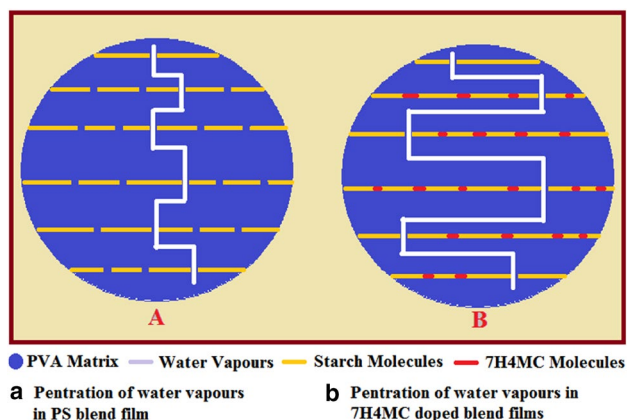


Fig. 8 Penetration of water vapours in PS and PSC blend films

#### 4.9 The Effect of 7H4MC on solubility of PVA/OMS

The percentage of solubility of the film in the aqueous phase is an important criterion to investigate the biodegradability of the films. Lower solubility would indicate high water resistance and vice versa. In some cases the lower the solubility of the film is very useful in the storage applications, higher solubility of the films leads to higher biodegradability [31, 71]. Table 2 shows the solubility values of pure and blend films. Due to the blending of OMS with PVA the solubility of PS blend film increases as compare to polyvinyl alcohol, this result illustrates that strong interaction between the hydroxyl group of PVA and OMS occurred via hydrogen bonding which enhanced the solubility of PS blend film. Furthermore, 7H4MC doped blend films exhibited the reduction in water solubility as compared to PS blend film which is due to improvement in the interfacial adhesion between components of the blend films caused to reduces the water sensitivity of the film [72, 73]. These findings coincided with the decrease in water absorption and water vapour transmission rate of the films.

#### 4.10 The effect of 7H4MC on optical properties of PVA/OMS

The optical properties are one of the important characteristics of packaging films, since it influences the appearance of the product. Generally, a transparent packaging material is desirable for viewing the packed product [74]. In another situation, it is important to protect food from the light, especially from UV radiation in order to reduce catalytically deteriorations [56]. The films were scanned at 200–600 nm wavelength range and the percentage of light transmittance was recorded. The percentage of light transmittance indicates the transparency of films and their structural homogeneity, more the transmittance percentage associated with, more the structural homogeneity and high transparency [75].

The PS blend film shows the reduction in percentage transmission as compared to PVA this could be due to partial miscibility of PVA and OMS [65]. The transmission percentage of PSC blends decreases with an increase in the amount of 7H4MC. The good dispersion of 7H4MC in PS blend film enhances the transmittance (%) whereas the poor miscibility of 7H4MC in blend film reduces the transmission (%) [76]. Apparently, the films with higher content of 7H4MC led to rougher surface due to involvement of highly agglomerated OMS and 7H4MC particles, resulting in enhances the light scattering sites [77]. Lee et al. [78] demonstrated that the reduction in transmittance percentage is an advantage for food packaging application. However, a strong absorption peak arrived

in the wavelength range of 240 to 310 nm, which could be attributed to dipole–dipole interaction between molecules or  $n \rightarrow \pi^*$  transition, because of unsaturated C=O bond break as reported earlier [79, 80].

The transparency and opacity of all the prepared films were calculated and shown in Fig. 9b. Transparency and opacity are inversely related and hence high transparency leads to a low opacity [35]. The transparency values of PS and PSC blend films decreases as compare to control PVA film. This might be due to the coagulation of 7H4MC in OMS and the PVA matrix creates a low miscibility and lowers the value of transparency. Similar results were reported in the PVA/starch films prepared by the incorporation of zinc oxide nanocomposites [66].

Generally, film colour and thickness have a direct effect on its opacity [81]. In the current study, the thickness values Table 3 of the films were different, therefore the thickness affects the opacity of films. The results indicated that blend films produced more opacity values as compared to neat PVA Fig. 9c. An increase in opacity may have been the result of contraction of the film matrix in which the

polymer inter-chain spacing was decreased thus permitting less light to pass through the film [82].

#### 4.11 The effect of 7H4MC on biodegradation of PVA/OMS

In order to evaluate the effect of 7H4MC on the biodegradation PVA and OMS blend films a soil burial biodegradation analysis was performed. The soil burial test is an outdoor experiment and provides a realistic environment, where soil humidity, temperature, and type, and the number of microorganisms are in less control and change with season [83].

Generally, it is demonstrated that two step degradation took place in soil burial biodegradation test first is the diffusion of water into the film samples, resulting in the swelling of the films and allowing the growth of microorganisms on the films. The second step involves enzymatic and other secreted degradation, causing a weight loss and disruption of the film samples [84]. The degradation

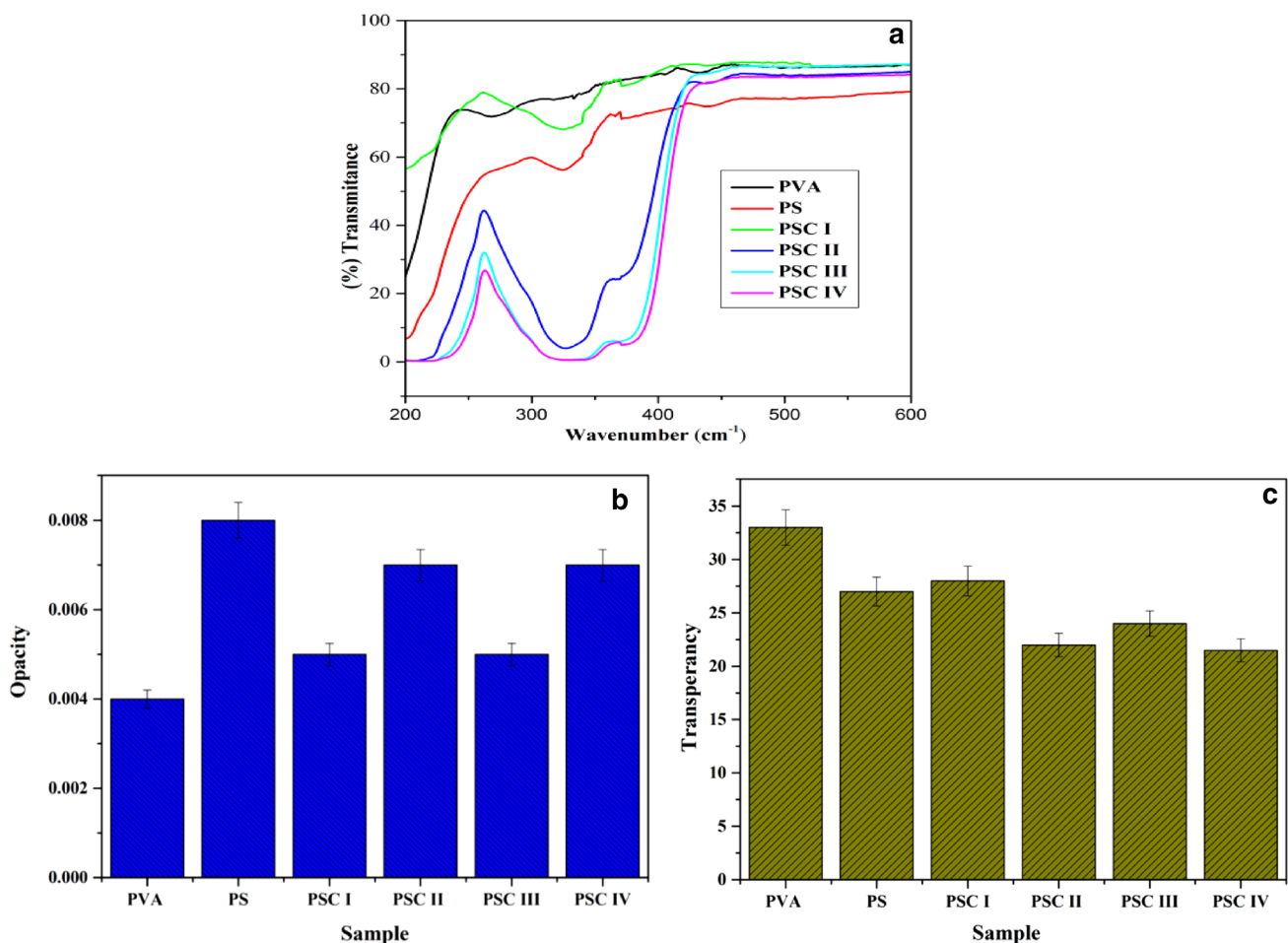


Fig. 9 a % Transmittance, b Opacity and c Transparency properties of prepared blend films

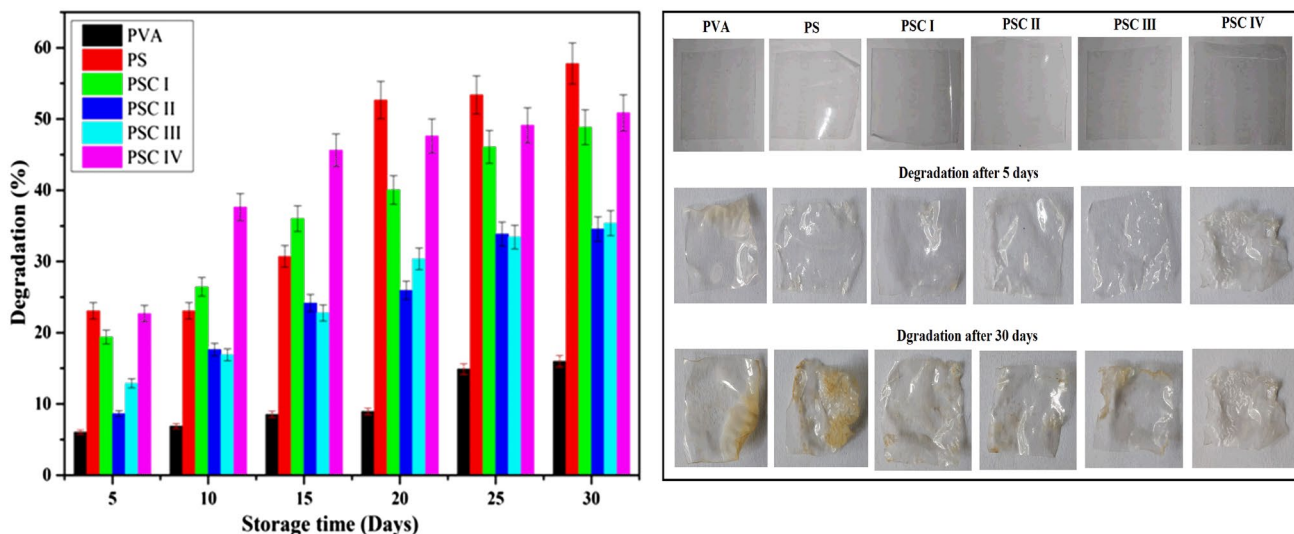


Fig. 10 Degradation (%) of prepared neat PVA and PS, PSC blend films and images of the degradation of films after 5 and 30 days

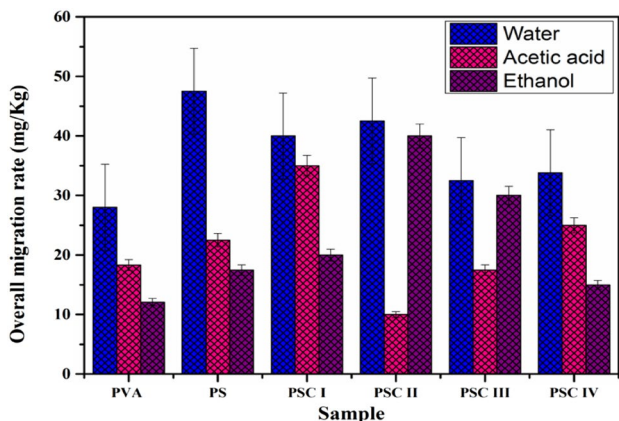


Fig. 11 Migration rates of prepared blend films

percentage of neat PVA and PS, PSC blend films on 1st, 5th, 10th, 15th, 20th 25th, and 30th day were shown in Fig. 10.

In the present work, all the blend films showed the more weight loss as compared to neat PVA film. In contrast, the PVA film results in higher resistance against soil burial biodegradation because of the chemical structure of PVA (unknown stereoregularity of hydroxyl groups) or by the degree of polymerization (comparably high molecular weight) [85]. Further increase in the biodegradation rate is observed up to 56.79% after addition of OMS in PVA matrix (PS blend film) which might be due to the easier microorganism attack to OMS material then those of pure PVA [86]. Concerning biodegradability of PSC blend films, it was manifested that biodegradation rate was dropped after addition of 7H4MC to PS blend this could be attributed to hydrogen bond formation between 7H4MC and blend

matrices so that water diffusion and infiltration speed of microorganism were restricted and similar phenomenon was observed in other results [65]. However the PSC IV blend film shown higher biodegradation rate among, PSC blend films because of agglomeration of 7H4MC in PS blend matrices [87]. The obtained results are related to the solubility and water absorption test.

#### 4.12 The effect of 7H4MC on food compatibility of PVA/OMS

The food compatibility of the prepared pure PVA and blend films were carried out to investigate the total amount additives that might be migrated into foodstuffs from the matrix film [88]. Figure 11 represents migration rates in three different food stimulants like simulant A (distilled water), simulant B (50% ethanol) and simulant C (3% acetic acid). It was observed from the figure that the migration rate of PS blend film is higher for simulant A as compared to PSC blend films. Overall migration results obtained from simulant A have good vibes with the solubility of blend films, with the addition of the 7H4MC into PS matrix reduces the solubility of the blend films as discussed earlier and the similar findings were shown by Mauricio-Iglesias et al. [89]. Moreover, the strong interfacial adhesion between 7H4MC and blend matrix is another evidence for reduction in migration during contact with food stimulant.

While dealing with PSC blend films with respect to simulant B, the migration rate of the blend films were increased at lower dopant levels and subsequently decreases with higher a content of 7H4MC. Finally to mimic the acidic

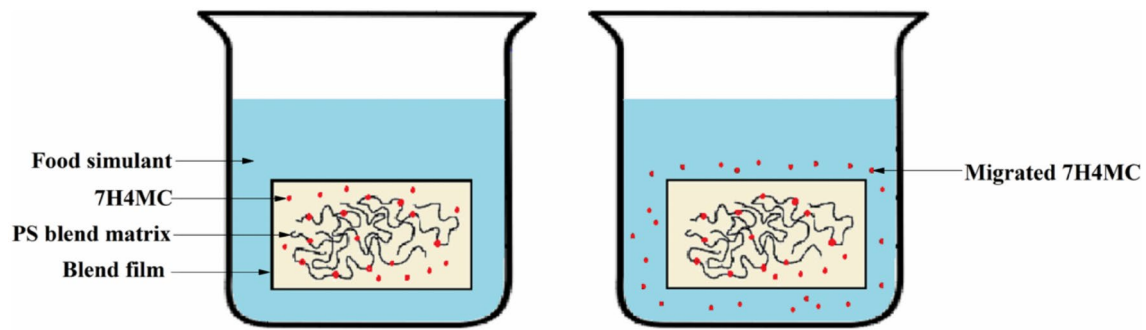


Fig. 12 Schematic representation of migration of 7H4MC from PS blend matrix

foodstuff the overall migration rates were recorded in stimulant C, which shows the increasing trends for overall migration rates.

**Table 4** Antioxidant properties of prepared blend films

Material	Concentration ( $\mu\text{g mL}^{-1}$ )	Scavenging effect (%)	$\text{IC}_{50}$ ( $\mu\text{g mL}^{-1}$ )
Standard ascorbic acid	20	$41.32 \pm 2.12$	35.09
	40	$57.01 \pm 0.96$	
	60	$75.19 \pm 3.05$	
	80	$83.56 \pm 2.02$	
	100	$93.87 \pm 1.90$	
PS	20	$22.2 \pm 0.9$	56.13
	40	$30.3 \pm 1.0$	
	60	$53.2 \pm 1.7$	
	80	$60.9 \pm 1.5$	
	100	$75.4 \pm 2.1$	
PSC 1	20	$33.05 \pm 1.32$	36.52
	40	$40.21 \pm 1.28$	
	60	$58.15 \pm 1.42$	
	80	$77.14 \pm 1.52$	
	100	$92.63 \pm 0.88$	
PSC 2	20	$42.30 \pm 2.15$	48.25
	40	$55.00 \pm 0.99$	
	60	$77.17 \pm 3.06$	
	80	$82.56 \pm 2.03$	
	100	$91.87 \pm 1.91$	
PSC 3	20	$33.24 \pm 1.54$	37.12
	40	$50.37 \pm 1.30$	
	60	$70.24 \pm 1.40$	
	80	$81.95 \pm 1.42$	
	100	$95.73 \pm 0.86$	
PSC 4	20	$42.32 \pm 2.12$	39.52
	40	$60.01 \pm 0.96$	
	60	$80.19 \pm 3.05$	
	80	$88.56 \pm 2.02$	
	100	$97.87 \pm 1.90$	

The blend films possessed a higher sensitivity to water (simulant A), followed by ethanol (Simulant B) and then acetic acid (Simulant C). All the blend films show the migration rates below the overall migration limit (OML) of 60 mg/kg (European Union Commission Regulation (EU) No 10/2011) [90], and hence these films can be used for aqueous, lipophilic and acidic foodstuff packaging (Fig. 12).

#### 4.13 The effect of 7H4MC on antioxidant properties of PVA/OMS

Antioxidant activity of all the prepared films was evaluated by the diphenylpicrylhydrazine (DPPH) scavenging assay. When an absorbance at 517 nm DPPH radical scavenging activity is a violet colour solution, but antioxidants can change the colour of DPPH radical to yellow colour with decrease in the absorbance value [91]. Table 4 represents the scavenging activity of the films. Pure PVA films did not show antioxidant activity [92]. The PS blend films exhibited a lower value of the antioxidant activity, but the addition of 7H4MC increases the DPPH radical scavenging activity of the blend films. Moreover, the activity of the PSC blend films increased with the increase of 7H4MC and similar results were reported by Qin et al. [93]. The antioxidant activity of the PSC blend films mainly due to the 7H4MC since hydroxycoumarins has property similar to phenol or quinol based antioxidants in which hydroxyl groups scavenge the free radicals [94]. All the films have shown good scavenging activity as compared to the activity of ascorbic acid (standard) which indicates that the reported PSC blend films are useful as an antioxidant packaging.

## 5 Conclusion

In the present study, 7H4MC doped PVA/OMS blend films were fabricated successfully by using an inexpensive solution casting technique. The obtained blend films were

characterized by using different instrumental techniques. The experimental finding indicates the incorporation of 7H4MC in the PS blend matrix enhances the mechanical properties due to changes in the structure of blend films. The blend films containing 0.004 and 0.006 g of 7H4MC showed increase tensile strength and elongation at break as compared to control blend film, this could be due to hydrogen bonding interaction between components of the blend films which is confirmed by FTIR spectroscopy. While the Surface morphological studies of 7H4MC doped blend films presented smoother surface as compared to PS blend film and those results are consistent with higher mechanical properties. The PSC IV blend film exposed the hydrophobic nature associated with the rougher surface morphology confirmed by the SEM analysis. The transmission (%) of the films in the UV region reduced after the addition of 7H4MC and also transparency decreases with an increase in opacity values. Meanwhile, the water vapour transmission rate of the films decreased with an increase in the content of 7H4MC and these results of the WVTR, are also in close agreement with reducing values of solubility and water absorption rate. The results obtained from the food compatibility test revealed that migration rates of all the blend films are below the overall migration limit (OML) of 60 mg/kg. All the fabricated blend films are biodegradable and presented good antioxidant properties as compared to the standard sample. An increase in the 7H4MC content in the blend matrix enhances the antioxidant property. Therefore the films with these types of properties have broad prospects in the application of active food packaging.

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## Compliance with ethical standards

**Conflict of interest** On behalf of all authors, the corresponding author states that they have no conflict of interest.

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