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Synergistic Antimicrobial Effect of Xylitol with Curcumin: Water vapor barrier, Mechanical and Thermal Properties of PSS/PVA Packaging Films

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Abstract

The present work aims to investigate the synergistic effect of xylitol with curcumin concentration on antimicrobial properties of polystyrene sulfonate/ polyvinyl alcohol active packaging film. Polystyrene sulfonate/ polyvinyl alcohol/curcumin films (PSS/PVA/C) with xylitol concentrations of 6% and 8% showed antimicrobial activity versus *Pseudomonas aeruginosa*, *Candida albicans* and *Staphylococcus aureus* and no antimicrobial activity recorded against the fungus *Aspergillus niger*. The effect of xylitol content on physical, mechanical and thermal properties was investigated also. With increasing xylitol, the equilibrium moisture content increase clearly.The monolayer was affected by xylitol increasing content. WVP values of PSS/PVA /curcumin films without and with xylitol were in the range 1.574 and 16.894 $g.m^2.h^{-1}. m^{-1}$ Pa and were affected by xylitol content. The effects of xylitol contents on mechanical and physical properties were evaluated. The elongation at break was enhanced however; elastic modulus and tensile strength were decreased. Thermal behavior studies reflect an increase of weight loss rate with increasing xylitol percentage.

Keywords: Curcumin, Active packaging, Water vapor permeability, Xylitol

INTRODUCTION

Packaging manufacturing depends mostly on petroleum based polymers [1]. Plastics are one of the most famous petroleum based polymers. They have superior barrier and mechanical properties. These features are the key reason which assisted plastic to be the most widely used packaging material [2]. Nevertheless, the non- biodegradability nature is the main reason for massive environmental pollution. Hence, many considerations have been paid to develop plastic materials of eco-friendly and biodegradable [3].

Its microbial contamination has been documented as the main spoilage cause of food products. Prolonging shelf-life, accompanied by delivering a high quality food product in proper flexible packaging, is necessary in order to address issues such as economical yield, customer satisfaction, global supplier demands, and more prominently, reduction of food wastage. Active packaging [4] offer solutions to this problem presented in the form of antimicrobial-active packaging.

Review of literatures demonstrates that the relevant research has principally focus on metallic nanoparticles (NPs) as antimicrobial agent such as silver oxide and zinc oxide nanoparticle. They suggest many advantages, like superior antimicrobial ability, no impacts on the food sensory properties, and compatibility with harsh polymer manufacturing conditions [5]. Naturally-occurring active antimicrobial substances offer many potential benefits with respect to food packaging applications [6].

Curcumin is a yellow polyphenol extracted from the plant Curcuma longa, commonly called turmeric [7]. It has been widely used as a spice and it also has attracted a significant attention because of its extensive spectrum of biological activities. Extensive research over the last decades on the medical applications of curcumin has shown its powerful antimicrobial, anticancer, antioxidant and anti-inflammatory [8].

Also, xylitol is categorized as naturally occurring a polyalcohol or sugar alcohol. It was found that fibers of various vegetables and fruits have small percentage of xylitol. Xylitol is considered as a famous type of extensively used plasticizer that enhances flexibility as well as gases permeability in addition to water permeability [9]. A significant study was conducted to determine antimicrobial activity of xylitol and many different plasticizers as glycerol, glucose, mannitol, mannose, and sucrose [10].

Moreover, polyvinyl alcohol is widely used as a nontoxic and synthetic packaging film as a result of its biodegradability and water solubility. It has outstanding chemical stability and good film-forming capacity. Additionally, Polystyrene sulfonate is a hydrophilic polymer and it was extensively used as perm selective membrane under semi- interpenetrating polymer networks form [11].

Since, there is global attention towards antimicrobial active packaging films, primarily the prevalent reason of antimicrobial films to be a promising solution to food spoilage during long-term storage periods. Thus, the aim of this study was to develop active packaging films of PSS/PVA with two types of naturally occurring antimicrobial agents. Synergetic antimicrobial concentration of xylitol with curcumin was optimized against *Staphylococcus aureus, Pseudomonas aeruginosa, Candida albicans,* and *Aspergillus niger.* The effect of different xylitol content on water vapor barrier properties (water vapor permeability was verified. The effect of xylitol content on the mechanical and thermal properties was also investigated.

EXPERIMENTAL

Materials

Poly (sodium-4-styrene sulfonate, average M_w= 7000) delivered from Aldrich, Germany. Polyvinyl alcohol, DP≈1700-1800 purchased from Qualikems, New Delhi. Xylitol (Sigma, USA). Turmeric powder was obtained from the local market. The other chemicals were used as received.

Extraction of curcumin

Curcumin was extracted as will be described; fine turmeric powder (15g) was suspended in acetone (150 ml) under moderate stirring for 72 hours at 30 ^oC. The mixture was simply filtered and was heated up to evaporation temperature to get semi-dried oily form. This oily form was weighed and then was dissolved in 50 ml of dimethyl sulfoxide (DMSO) that provides a reddish brown curcumin solution [12].

Film preparation

The polystyrene sulfonate/polyvinyl alcohol (PSS/PVA)/curcumin blended films were prepared as the following: PVA (2g) and PSS (1g) were dispersed in 40 ml of water and stirred at room temperature for 24 hours until complete solubility of the components. Then fixed amount of curcumin (0.05g) was added with different amounts of xylitol (2%, 4%, 6%, and 8%) based on the total solid content of the film. The mixture was continuously stirred to obtain homogeneous solution, then fixed amount of the mixture was casted into 14 cm petridish to obtain film thickness of 11.2 micrometers. Finally, the films were dried in vacuum oven at 50 ^oC.

CHARACTERIZATION OF PSS/PVA-CURCUMIN FILM

Antimicrobial test by the zone inhibition method

Agar plate method has been recognized to evaluate the antimicrobial activities of the prepared PSS/PVA⁄curcumin films plasticized with different amounts of xylitol [13-15]. Four different test microbes; *Staphylococcus aureus* (Gram positive bacterium), *Aspergillus niger* (fungus), *Candida albicans* (yeast) and *Escherichia coli* (Gram negative bacterium) were chosen to assess the antimicrobial activities. The bacterial and yeast test microbes were grown on a nutrient agar medium (DSMZ1). On the other hand, the fungal test microbe was cultivated on Czapek-Dox medium (DSMZ130). The culture of each test microbe was diluted by distilled water (sterilized) 10^7 to 10^8 cell/ml and then 1ml of each was used to inoculate 1L-Erlenmeyer flask containing 250ml of solidified agar media [15]. These media were poured onto previously sterilized Petri dishes (10 cm diameter having 25ml of solidified media). PSS/PVA⁄curcumin films discs (5 mm Ø) were placed on the surface of the agar plates seeded with test microbes and incubated for 24 hrs at the appropriate temperature of each test organism. Antimicrobial activities were recorded as the diameter of the clear zones (including the gel film itself) that appeared around the gel films [14].

Physical properties

Film thickness

Film thickness was measured using a thickness gauge tester (Kalfer GmbH, Germany) accurately 0.01 mm reading and maximum 10 mm reading in accordance with ISO 534-2005. Five replicates were done on each sample.

Water vapor permeability (WVP)

ASTM method E96 (1996) was used to evaluate WVP with certain modifications [16]. The films were cut into circles sealed with melted paraffin and stored in desiccator at 25 ^oC with relative humidity zero maintained using anhydrous calcium sulfate in the cups of 2cm diameter. Each cup was placed in a desiccator containing saturated sodium chloride solution to provide a constant relative humidity of 75 %. Water vapor transport was determined by the weight gain of the permeation cup. Changes in the weight of the cups were recorded as a function of time. Slope was calculated by linear regression (weight changes vs. time) and the correlation coefficients (R^2) for all reported data were ≥ 0.99. The water vapor transmission rate (WVTR) was easily calculated as a slope (g/h) division by the transfer area (m^2). After the permeation tests, films thickness was measured and WVP ($g.m^2.h^{-1}.m^{-1}.Pa$) was calculated as:

$$WVP = WVTR/\,P\,(R_1 - R_2).X$$

Where P is the saturation vapor pressure of water (Pa) at the test temperature (25 °C), R_1 is the relative humidity (RH) in the desiccator, R_2 is the RH in the permeation cups, and X is the film thickness (m). Under these conditions, the driving force $P (R_1\text{-}R_2) = 1753.55$ Pa.

Mechanical properties

Mechanical properties include tensile strength (TS), elastic modulus (E) and elongation at break (EAB, %) were estimated by the standard method (ASTM D-882-91, 1996) by the Universal Testing Device (model LLOYD). displayed outstanding antimicrobial To determine the mechanical properties, the samples were cut into rectangle of 20 × 70 mm and fixed on the grip of the device with span distance 50 mm. TS was calculated through the division the greatest force (F) at break by the cross–sectional area (S) of the specified film as showed in equation (1), and it was expressed in Mega Pascal (MPa). The EAB was calculated based on the length extended (ΔL) and the initial length (L_o) of the film and expressed in % as equation (2) [17]. The elastic modulus is defined as the slope of its stress–strain curve in the elastic deformation region as equation (3).

$$TS = F/S \qquad (1)$$

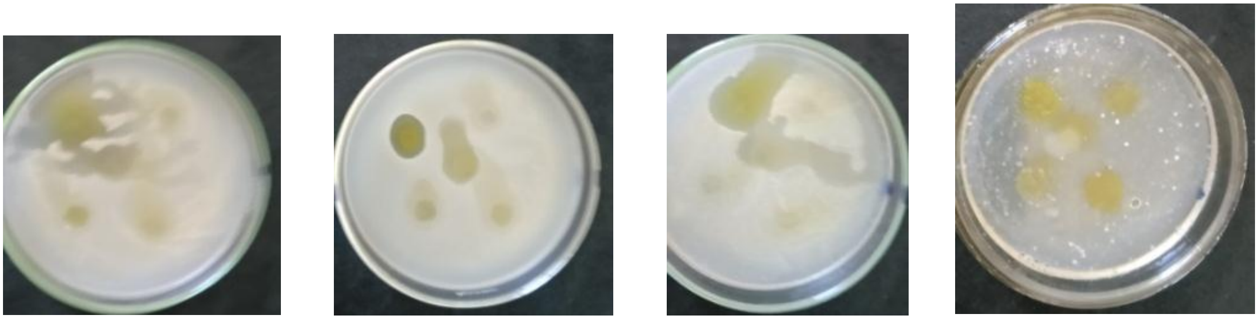
$$EAB = \Delta L / L_o \times 100 \qquad (2)$$

$$\lambda = \text{stress/strain} \qquad (3)$$

RESULTS AND DISCUSSION

The antimicrobial activity

Figure (1) revealed the antimicrobial activity of PSS/ PVA⁄curcumin films (PSS/PVA/C) plasticized with different xylitol concentrations from 0% to 8%. However, Figure 1, showed inhibition zone images of xylitol concentrations of 8%. It has been found that PSS/PVA⁄C films with both xylitol concentrations of 6% and 8% displayed outstanding antimicrobial activity versus *Staphylococcus aureus* (G+ve bacterium), *Pseudomonas aeruginosa* (G-ve bacterium) and *Candida albicans* (yeast) and showed no antimicrobial activity at low xylitol concentrations. On the other hand, no antimicrobial activity has been recorded against the fungus *Aspergillus niger*. Xylitol is considered as five carbon pentahydroxyl alcohol which was naturally found. It has been early reported that xylitol possesses antimicrobial activity against dental pathogens [18]. It was reported in some literatures that, the concentrations of 1% and 5% xylitol were found to inhibit the growth of *Streptococcus pneumonia.* The antimicrobial mode action of xylitol firstly is xylitol metabolism by entry into bacterial cell via fructose phosphotransferase system in presence with fructose, and then xylitol is metabolized to xylitol-5-phosphate which is toxic to bacteria. The cycle of xylitol consumes energy and leads to growth inhibition [19]. From the previous results, it can be concluded that both xylitol concentrations of 6% and 8% are the optimum concentration which has synergistic effect with curcumin concentration. From the previous results, it can be concluded that both xylitol concentrations of 6% and 8% are the optimum concentration which has synergistic effect with curcumin concentration.



S. aureus ***P. aeruginosa*** ***C.albicans*** ***A. niger***

Figure 1: The antimicrobial activity of PSS/PVA⁄curcumin supplanted with 8% xylitol concentration

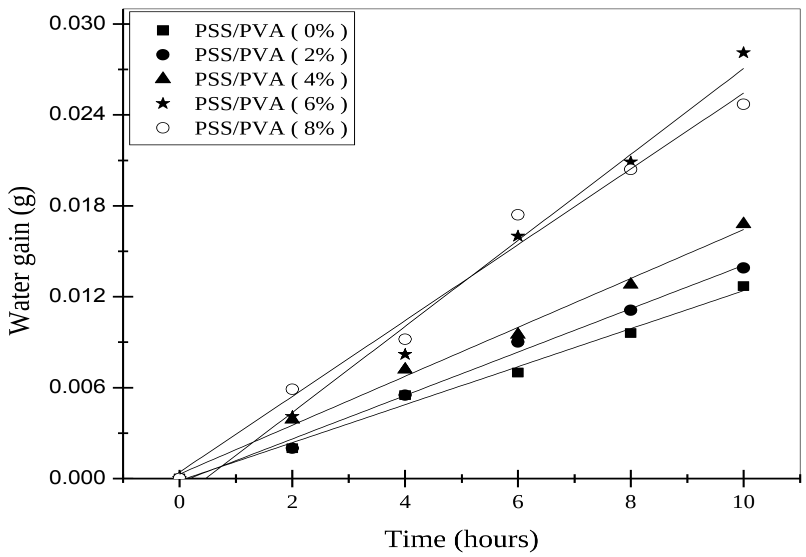


Figure 2: Water gain of PSS/PVA/curcumin blended films with different ratios of xylitol plasticizer

Water vapor permeability (WVP)

Water vapor permeability (WVP) expresses of the amount of water vapor (g) pass through unit area of material per unit time. In this study, WVP was investigated to understand the effect of xylitol plasticizer with different contents on blend films. Figure 2: explains the water gain of PSS/PVA/curcumin blended films with different xylitol plasticizer ratios. As shown in

Figure (2), hydrophilic films (PSS/PVA/C) exhibited linear relationships between water gain and time with somewhat deviation from ideal behaviour. Hydrophilic materials with polar groups in their molecular structures, and the interactions of polar groups with permeating water molecules causes the WVP to deviate from an ideal behavior [20]. The deviation from ideal behavior is attributed to the variation structure of the materials. The deviation was believed to be governed by free volume theory. Water increases the polymer free volume, allowing the polymeric chain segments to increase their mobility. Higher segment mobility results in higher WVP. The increase in plasticizer content is directly proportional to an increase in water gain and consequently in water vapor transmission rate and permeability coefficient. That trend indicates that the increase addition of xylitol increase the ability of PSS/PVA/curcumin films plasticized with different xylitol content to absorb and accept more water. WVP values of PSS/PVA/curcumin films plasticized with different xylitol are in the range of 4.164 to 16.894 ($g.m^2.h^{-1}.\ m^{-1}.Pa$) compared with control 1.574 ($g.m^2.h^{-1}.\ m^{-1}.Pa$). Generally, the addition of plasticizer not only loosened the microstructure of blended films, thus increasing the rate of water molecules diffusion through the films, but also increased the hydrophilicity by exposing their hydroxyl groups to water molecules.

Mechanical properties

Figure 3; demonstrated the mechanical properties of PSS/PVA/C films plasticized with different percentages of xylitol. Tensile strength (TS) and elastic modulus (EM) showed remarkable decline. However, elongation at break (EAB) fulfills increasing values compared to control films. This behavior is mainly due to the incorporation of plasticizer (xylitol). Hence; addition of plasticizer not only loosens the chains of blended films, but also increases the rate of water vapor molecules diffusion through the films creating more flexibility of films.

Since, stiffer material has a higher elastic modulus. Nevertheless, our films under consideration are highly elastic, they obey reverse behavior this is the reason of reduced tensile and elastic modulus according the fact that, elastic modulus stress is a force initiating the deformation divided by the area and strain is the percentage of the variation in length parameter that produced via deformation to the original length parameter.

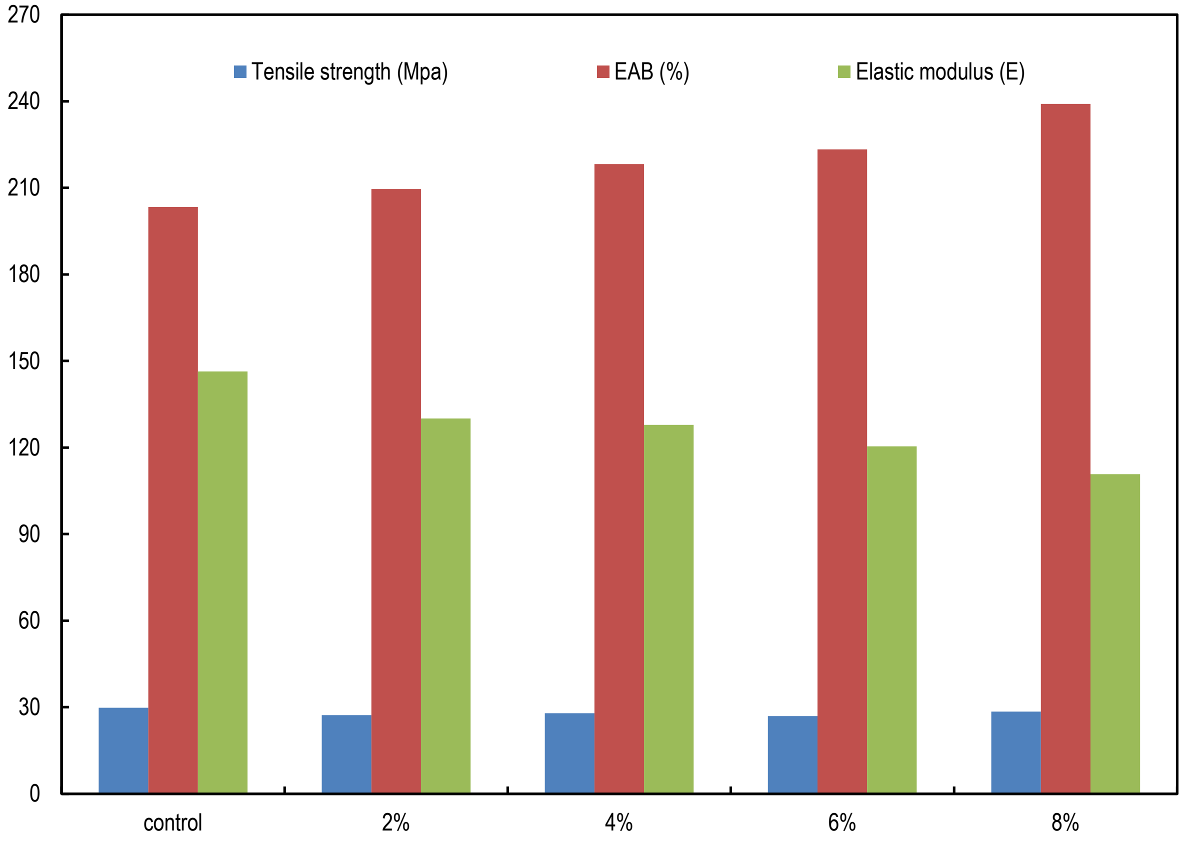


Figure 3: Elastic modulus (E), tensile strength (TS) and elongation at break of specimens

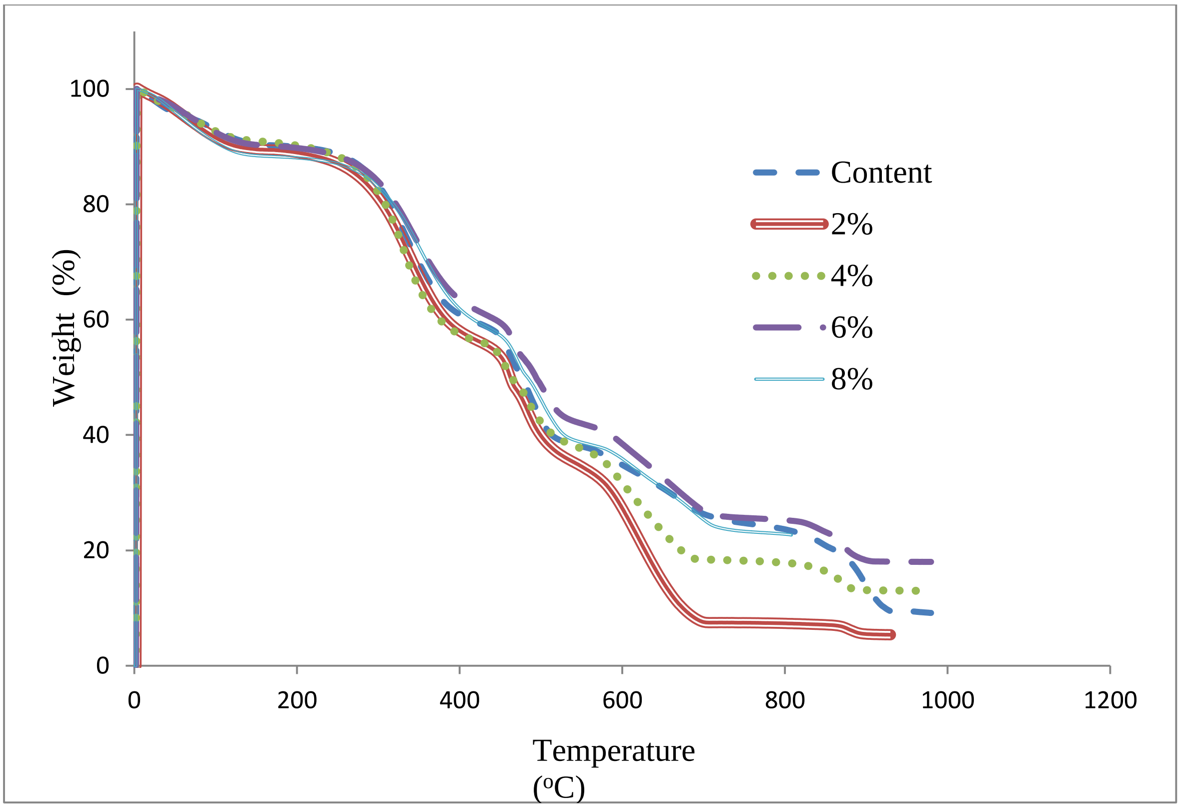


Figure 4: TGA thermograms of PSS/PVA/curcumin blended films with different ratios of xylitol plasticizer.

Thermal behaviour

Figure 4, shows thermogravimetric curves of PSS/PVA/ C plasticized with different amounts of xylitol captured with control (0% plasticizer). There are generally 4 distinct mass loss regions in PSS/PVA/ C plasticized with different amounts of xylitol and control. The first region ranges between 50.0 and 250 ◦C is attributed to the dislocation of loosely bound water, accompanied by the formation of organic volatiles products such as dissociation of the plasticizers in the blend. The second region (250-350 ◦C) is described as the main decomposition step, third region range with (350-450◦C), and the final stage is the carbonization of the organic matter above 500 ◦C [21]. Since, the first degradation step of control (0% xylitol) ranges between 73.69-253.53◦C with weight loss 10.77% , there are shifts in start degradation temperature and weight loss percentages to lower values with further plasticizer addition is an evidence of decreasing thermal stability to PSS/PVA/C plasticized with different amounts of xylitol. Whereas, the first degradation temperatures of samples treated with xylitol range between 50-250◦C with weight loss percentages ranges between 11.20-13.24%.

CONCLUSION

Polystyrene sulfonate/ polyvinyl alcohol/curcumin active packaging films (PSS/PVA/C) was successfully prepared with xylitol concentrations of 6% and 8% that showed antimicrobial activity versus *Pseudomonas aeruginosa*, *Candida albicans* and *Staphylococcus aureus* and no antimicrobial activity noted at low xylitol concentrations (0-4%) and against the fungus *Aspergillus niger*. The influence of xylitol concentration on physical, mechanical and thermal properties was explored. The equilibrium moisture content was found increased with xylitol increasing. WVP values of PSS/PVA /curcumin films were 1.574 - 16.894 $g.m^2.h^{-1}.\ m^{-1}$ Pa. The elongation % at break was found enhanced, but elastic modulus and tensile strength were decreased. Thermal properties of plasticized films showed less thermal resistance with increasing xylitol concentration.

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