Carbohydrate Polymers 79 (2010) 786–791

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Short communication

Characterization and comparison of chitosan/PVP and chitosan/PEO blend films

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ARTICLE INFO

Article history:
Received 11 September 2009
Accepted 24 September 2009
Available online 9 October 2009

Keywords:
Chitosan
Poly (N-vinyl-2-pyrrolidone)
Polyethylene oxide
Chitosan films
Blend films

ABSTRACT

The objective of this study was to investigate and compare the physical and functional properties of chitosan films prepared with poly (N-vinyl-2-pyrrolidone) (PVP) and polyethylene oxide (PEO). Addition of PVP or PEO reduced yellowish coloration of chitosan-based films and made the films easier to puncture and tear. Contrary to chitosan/PEO films, where addition of PEO had tendency to reduce water vapor permeability (WVP), the chitosan/PVP films with PVP content of 75% had significantly higher WVP compared to pure chitosan films. Chromium binding capacity of the films was not significantly reduced by any of the tested synthetic polymers even when they replaced up to 75% chitosan in the films. Similarly, antimicrobial efficiency was reduced only when 75% PEO or 50% PVP was used in the films. It appears that incorporation of PVP or PEO in chitosan films could significantly reduce production price with no effect on functionality of the films.

1. Introduction

Chitosan films have great potential to be used in the food industry as active packaging material due to their antimicrobial activity and impermeability to oxygen (Butler, Vergano, Testin, Bunn, & Wiles, 1996; Jeon, Kamil, & Shahidi, 2002; No, Meyers, Prinyawiwatkul, & Xu, 2007). However, their wide application is currently limited mainly because of relatively high price compared to plastics, darkening (yellowish color appearance) during storage at elevated temperatures, and relatively poor water vapor barrier characteristics (Butler et al., 1996).

Blending of natural and synthetic polymers is a simple and practical way to produce new materials. The films formed by blending of two or more polymers usually result in modified physical and mechanical properties compared to films made of the initial components. In addition, since synthetic polymers are easily obtained and have low production cost, the blending of natural and synthetic polymers may improve the cost-performance ratio of the resulting films (Fried, 1995, chap. 7). Blending of synthetic polymers, such as poly (vinyl alcohol) (PVA) (Bahrami, Kordestani, Mirzadeh, & Mansoori, 2003), polyethylene oxide (PEO) (Angelova et al., 1995), N-methylol nylon 6 (Shieh & Huang, 1998), polycaprolactone (PCL) (Sarasam, Krishnaswamy, & Madihally, 2006) with chitosan have been reported to improve mechanical properties of chitosan films.

Our previous study has shown that the addition of PEO, a hydrophilic, biocompatible synthetic polymer, to chitosan films alters physical, mechanical and antibacterial properties of the films (Zivanovic, Li, Davidson, & Kit, 2007). In the present work, we studied the characteristics of films formed by blending chitosan with another synthetic polymer – poly (N-vinyl-2-pyrrolidone) (PVP) and compared these films with chitosan/PEO films prepared with the same ratios of the polymers. PVP is a non-toxic polymer with excellent transparency, biocompatibility and film-forming ability and has been utilized in a broad range of areas including in the food industry (Yeh et al., 2006). The miscibility of chitosan and PVP in the films has been reported and it is considered that carbonyl groups in the pyrrolidone rings of PVP interact with amino and hydroxyl groups in chitosan by forming hydrogen bonds and produce materials with novel characteristics (Cao, Shi, & Chen, 1998; Fang & Goh, 2000; Marsano, Vicini, Skopinska, Wisniewski, & Sionkowska, 2004; Sakurai, Maegawa, & Takahashi, 2000). In addition to mechanical characterization, other properties of chitosan/PVP films were also studied, including their surface energy (Caykara, Alaslan, Eroglu, & Guven, 2006), thermoresistance property (Yeh et al., 2006), and methanol permeability for applications in fuel cells (Smitha, Sridhar, & Khan, 2006) but information on functionality important for a potential packaging material for food products is still lacking.

The objective of this research was to evaluate and compare the physical properties and functional performance of chitosan films prepared with various levels of PVP and PEO.

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doi:10.1016/j.carbpol.2009.09.028

2. Materials and methods

2.1. Film preparation

Low molecular weight chitosan (~150 kDa), high molecular weight PEO (900 kDa) and high molecular weight PVP (1300 kDa) were obtained from Aldrich Chemical Co. (Milwaukee, WI). Chitosan solution was prepared with 1% w/w chitosan in 1% v/v acetic acid, stirred overnight at room temperature, and filtered through Miracloth® (Calbiochem-Novabiochem Corp., San Diego, CA) to remove impurities. PVP and PEO were separately dissolved in d.i. water to form 1% w/w solutions. Aqueous solutions of the individual polymers were mixed to prepare series of chitosan/PVP and chitosan/PEO blend solutions with weight ratio of 100/0, 75/25, 50/50, 25/75, 0/100. Aliquots of 10 g of film-forming solutions were poured into 50 mm-diameter polystyrene petri dishes and the solvent was evaporated in a vacuum oven at 38 °C under 17 kPa pressure for 24 h. The dried films were peeled from the petri dishes and conditioned in desiccators at 25 °C and 20% RH prior to testing.

2.2. Film thickness

Film thickness (µm) was determined on six films per ratio treatment averaging measurements at five points for each film using a hand-held microcaliper (Mitutoyo Corp., Kawasaki, Kanagawa, Japan).

2.3. Film color

Hunter color scale of lightness (*L*), *a* (red–green), and *b* (yellow–blue) values of the films were measured using a Hunter colorimeter (Hunterlab, Reston, VA). The colorimeter was calibrated with white and black plates. Color measurements were replicated five times per treatment having one film as a replication.

2.4. Film crystallization

Crystallization of polymers in the films was observed under polarized microscope (Olympus-BX51, Melville, NY) with 100–400× magnification within 24 h after casting.

2.5. Water vapor permeability

Water vapor permeability (WVP) was measured gravimetrically using ASTM E-96 standard method (ASTM. 2005). Fisher permeability cups (Fisher Scientific, Pittsburgh, PA) filled with 5 mL distilled water were sealed by the tested films. Silicon sealant (High Vacuum Grease, Dow Corning, Midland, MI) and the ring covers with three screws around the cup circumference were used for attaching the films to the cups tightly. After measuring the initial weight, the cups were placed in an environment chamber (Yamato Scientific America, Inc., Orangeburg, NY) equipped with a fan for air circulation and set at 25 °C and 50% RH. Steady state was obtained after 2 h and the cups were weighed five times at 1 h intervals. Linear regression analysis of the weight loss versus time curves was performed to obtain the accurate steady state slopes. Since the air gap between film and water surface inside the cup is an important factor for the WVP of highly permeable and hydrophilic films, WVP correction method was used to calculate WVP (g mm/m^2 h kPa) with the following equations (Gennadios, Weller, & Gooding, 1994).

$$\mathrm{WVP} = (G/t)/A \times L/(P_{w1} - P_{w2}) \tag{1}$$

where G/t = the slope of the water weight loss versus time curves (g/h); A = cup mouth area (m^2); L = film thickness (mm); P_{w2} = water vapor partial pressure at film surface outside the cup (Pa); P_{w1} = water vapor partial pressure at film inner surface in cup (Pa), and it is calculated as

$$P_{w1} = P_T - (P_T - P_{w0})exp(N_w \times h_i \times R \times T/(P_T \times D)) \tag{2}$$

where P_{w0} = water vapor partial pressure at water surface (Pa); P_T = total atmosphere pressure (Pa); N_w = measured value of water vapor transmission rate = $(G/t)/A$ (g/h m^2); h_i = air gap height inside cup (mm); R = gas law constant (8.31 Pa m^3/mol K); T = absolute temperature (K); D = diffusivity of water vapor in air at 25 °C (0.26 cm^2/s).

2.6. Mechanical properties

The mechanical properties were determined using a TA.XT*plus* Texture Analyzer (Texture Technologies Corp., Scarsdale, NY/Stable Micro Systems, Godalming, Surrey, UK). Puncture strength (PS) and elasticity (mm) were measured using the TA-108S fixture and 2 mm-diameter needle probe (TA-52) moving with a test speed of 1 mm/s. The PS was calculated by dividing the maximum force at break (N) by the thickness (mm) at the broken areas. The elasticity was determined as the distance the probe traveled before breaking the films. Tensile strength (TS) was determined by following the standard procedures of ASTM D882-02 (ASTM, 2002). Films were cut by specimen cutting die (Qualitest USA LC, Plantation, FL) to the strips with uniform width of 6 mm and were tested using a double clamp (TA-96) at a test speed of 1 mm/s. Initial grip separation was set as 20 mm. The TS was expressed in MPa and was calculated by dividing the maximum load (N) by the cross-sectional area (m^2). PS, TS and elasticity measurements were replicated three times per ratio treatment.

2.7. Film metal-binding capacity

The metal-binding capacity of films was determined as the concentration change of Cr (VI) following NIOSH method (NIOSH Manual of Analytical Methods (NMAM), 1994) before and after addition of films. Chitosan/PVP and chitosan/PEO films with different ratios were pretreated in methanol for 24 h, dried in vacuum oven at room temperature for 24 h, and separately placed into 10 mg/L Cr(VI) solution for 3 h. Aliquots of 1 mL sample solution were taken and mixed with 6 mL of 0.5 N H_2SO_4 in 25 mL volumetric flask followed with addition of 0.5 mL sym-diphenylcarbazide reagent (dissolved in 50% acetone). The volume was adjusted with 0.5 N H_2SO_4 to 25 mL and absorbance was read at 540 nm using a spectrophotometer (UV- 2102PC, Shimadzu, Kyoto, Japan).

2.8. Antibacterial efficiency

Antibacterial test was carried out by submerging films into culture tubes containing 9 mL sterile phosphate buffer (0.05 M, pH 7.08) inoculated with 1 mL of ca. 10^6 CFU/mL *Escherichia coli* K-12, vortexed and incubated for 6 h at 25 °C. The survival of *E. coli* K-12 was determined using the pour plate method on Trypticase Soy Agar (TSA) medium (Swanson, Petran, & Hanlin, 2001).

2.9. Statistical analysis

If not otherwise noted, the measurements were done in triplicate with individually prepared films as the replicated experimental units. Significant differences between groups were determined using Tukey–Kramer HSD test in the JMP program (JMP 2007). On figures with bars, means within the same group with a different letter are significantly different ($p < 0.05$).

Table 1
Thickness, color and water vapor permeability (WVP) of chitosan, chitosan/PVP and chitosan/PEO films*.

Film composition	Thickness (µm)	Film color *L*	*a*	*b*	WVP (g mm/m^2 h kPa)
Chitosan (Chi)	39.91 ± 1.78	$88.36 \pm 0.25^{\mathrm{df}}$	$-2.50 \pm 0.10^{\mathrm{E}}$	5.54 ± 0.67^{b}	$3.53 \pm 0.45^{\mathrm{bcd}}$
Chi/PVP (75/25)	42.22 ± 2.27	$87.87 \pm 1.17^{\mathrm{f}}$	$-2.29 \pm 0.04^{\mathrm{D}}$	4.01 ± 0.58^{c}	$4.43 \pm 0.41^{\mathrm{b}}$
Chi/PVP (50/50)	37.02 ± 2.56	$89.05 \pm 0.17^{\mathrm{bcde}}$	$-2.08 \pm 0.04^{\mathrm{C}}$	2.33 ± 0.26^{d}	$4.30 \pm 0.68^{\mathrm{bc}}$
Chi/PVP (25/75)	38.89 ± 2.26	$89.11 \pm 0.06^{\mathrm{bcde}}$	$-1.95 \pm 0.02^{\mathrm{BC}}$	1.53 ± 0.03^{de}	$6.36 \pm 0.49^{\mathrm{a}}$
PVP	32.78 ± 1.84	$89.71 \pm 0.55^{\mathrm{bc}}$	$-1.75 \pm 0.02^{\mathrm{A}}$	0.56 ± 0.03^{e}	$8.06 \pm 1.69^{\mathrm{a}}$
Chi/PEO (75/25)	37.81 ± 3.63	$88.35 \pm 0.23^{\mathrm{def}}$	$-2.77 \pm 0.06^{\mathrm{F}}$	9.42 ± 0.55^{a}	$3.82 \pm 0.79^{\mathrm{bcd}}$
Chi/PEO (50/50)	35.74 ± 0.81	$89.10 \pm 0.20^{\mathrm{ce}}$	$-2.37 \pm 0.06^{\mathrm{D}}$	5.27 ± 0.64^{b}	$2.42 \pm 0.14^{\mathrm{cd}}$
Chi/PEO (25/75)	34.93 ± 2.08	$89.93 \pm 0.35^{\mathrm{b}}$	$-2.02 \pm 0.03^{\mathrm{C}}$	2.15 ± 0.19^{d}	$2.68 \pm 0.62^{\mathrm{bcd}}$
PEO	35.66 ± 0.56	$91.78 \pm 0.25^{\mathrm{a}}$	$-1.84 \pm 0.04^{\mathrm{AB}}$	0.53 ± 0.08^{e}	$1.81 \pm 0.31^{\mathrm{d}}$

* Values reported are means and standard deviation. Superscript letters indicate significant difference at $p < 0.05$ by Tukey–Kramer HSD test (JMP 2007).

3. Results and discussion

3.1. Film appearance and thickness

Films formed from chitosan/PVP and chitosan/PEO blend solutions and were easily removed from the petri dishes and had thickness of 32–42 µm (Table 1). The Hunter color scale of *L* (lightness), *a* (+red/−green), *b* (+yellow/−blue) values of the films are shown in Table 1. According to the change of *b* values, significant reduction of yellow tones in the chitosan-based films was accomplished with 25% or more PVP but required the minimum of 75% PEO. Chitosan and all chitosan/PVP films were transparent with *L* values ranging from 87.87 to 89.71. *L* values of chitosan/PEO films were slightly higher (88.35–91.78), increasing with increased PEO content. This whitish coloration of the films was result of opacity that occurred due to crystallization of PEO. Since the lack of transparency in the films may be a problem, especially in the food application, films with high PEO content may not be suitable.

3.2. Film crystallization

Polymer crystallization has a significant effect on the structure and physical properties of the films. Fig. 1 illustrates the shape and distribution of the crystals within chitosan/PVP and chitosan/PEO

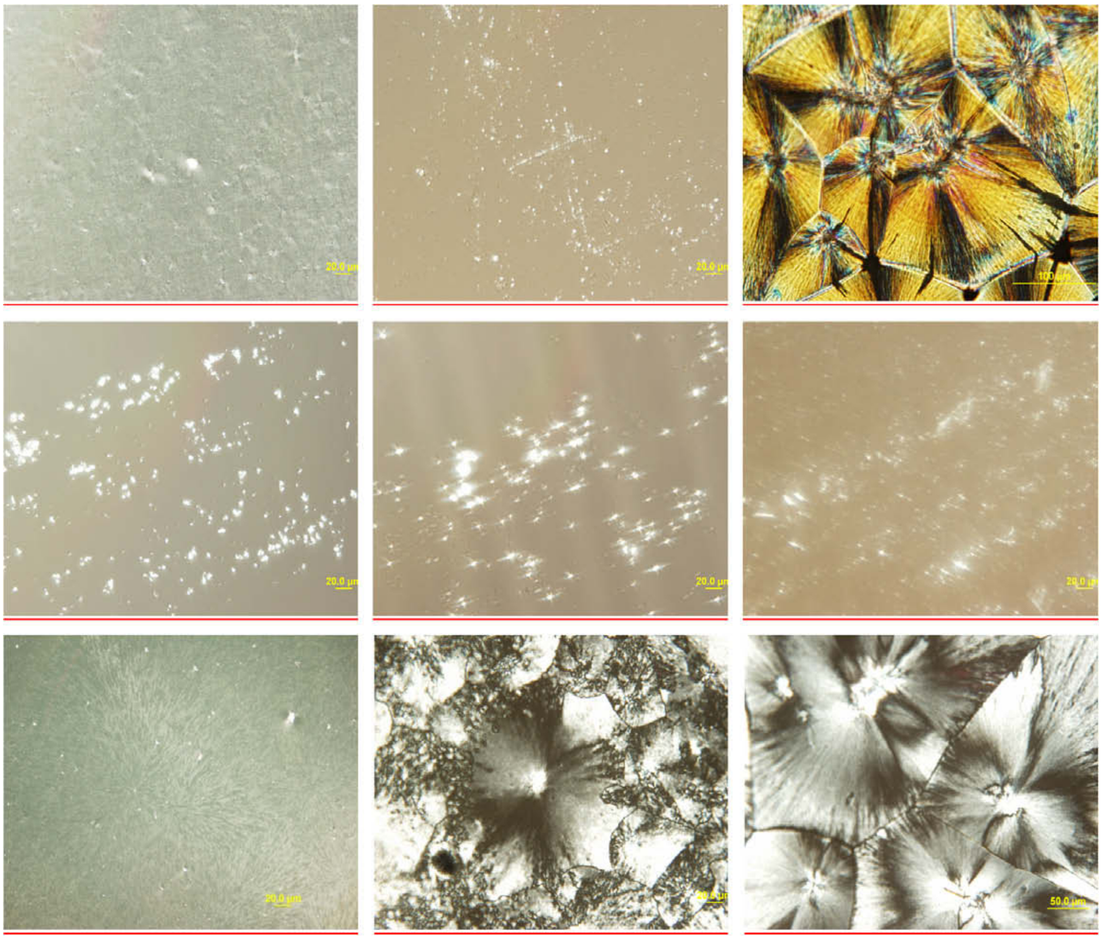

Fig. 1. Polarized micrographs of chitosan, PVP and PEO films (top), chitosan/PVP films with ratios of 75/25, 50/50, 25/75 (middle), and chitosan/PEO films with ratios of 75/25, 50/50, 25/75 (bottom) within 24 h after casting.

films. Since both chitosan and PVP are only partially crystalline polymers (Sakurai et al., 2000), the extent of crystallization of their films is much lower compared to crystallization of chitosan/PEO films. PEO has high potential for crystallization and its crystals appeared as monoclinic unit cells of crystals with four radially oriented PEO chains. With increasing PEO content, PEO crystals became larger and tightly packed inside the films causing their opacity (Fig. 1).

3.3. Water vapor permeability

Table 1 shows the WVP values of chitosan, PVP, PEO and their composite films. The hydrophilic nature of PVP polymer contributed to higher water vapor permeability of the blend films. Replacement of 75% of chitosan with PVP in the films resulted in almost doubled value for WVP, from 3.53 to 6.36 [g mm/m^2 h kPa]. Interestingly, PEO although itself a hydrophilic polymer, had tendency to decrease the water vapor permeability of the blend films. Such behavior of chitosan/PEO films may be explained by two factors: first, the strong intermolecular interactions between chitosan and PEO molecules result in shorter intermolecular distances forming more compact films, and second, crystallinity of PEO chains can cause the percolation of water molecules around the insoluble crystals and thus impede the diffusivity of water molecule through the film matrix (Zivanovic et al., 2007).

Hydrocolloid-based films generally have high water vapor permeability (Krochta and De Mulder-Johnson, 1997; Mali, Grossmann, Garcia, Martino, & Zaritzky, 2002). Comparing to the WVP values of other natural polymers, our chitosan, chitosan/PVP and chitosan/PEO films behaved similarly to 140-μm thick wheat gluten films with WVP of 4.52 g mm/m^2 h kPa (Aydt, Weller, & Testin, 1991), whey protein isolate films with WVP of 5.06 g mm/m^2 h kPa (Perez-Gago, Nadaud, & Krochta, 1999) and highly carboxymethylated starch films with WVP of 7.56 g mm/m^2 h kPa (Kim, Ko, & Park, 2002). Having in mind these WVP values, relatively small differences in WVP values caused by addition of PVP (3.53–8.06 g mm/m^2 h kPa) and PEO (1.81–3.82 g mm/m^2 h kPa) may not be practically significant, and addition of these two polymers (PVP or PEO) should not be considered from the sole application of altering films' water vapor permeability.

3.4. Mechanical characteristics

The puncture strength (PS), tensile strength (TS) and elasticity of chitosan, chitosan/PVP and chitosan/PEO films with different ratios are shown in Fig. 2. The PS of the films decreased significantly as the chitosan fraction decreased – from 520.69 ± 25.13 N/mm for pure chitosan films to 144.58 ± 5.90 N/mm for PVP films and 66.78 ± 28.69 N/mm for PEO films (Fig. 2a). Addition of either PVP or PEO made the films easier to puncture, with PEO being more efficient in reducing the PS of the films.

Similarly to the PS, PEO contributed to significant decrease of tensile strength of the films (Fig. 2b). Thus, TS values changed from 87.68 ± 8.86 MPa to only 9.89 ± 1.05 MPa for pure chitosan and PEO films, respectively. However, addition of 25% and 50% of PVP did not significantly affect TS of the films although the values were lower compared to pure chitosan films. Pure PVP films had the tensile strength of 59.13 ± 3.31 MPa while the chitosan/PVP films with the blend ratio of 75/25 to 25/75 had the TS values between 64.77 ± 4.04 and 60.78 ± 6.03 MPa. Compared to the TS values of other biopolymer films, such as whey protein isolate films with the TS value of 13.9 MPa (McHugh & Krochta 1994), zein films with 6.81 MPa (Lai & Padua 1997), and widely used plastic films, such as LDPE and HDPE with the values of 8.6–17.3 and 17.3–34.6 MPa (Brinston 1988), respectively, our chitosan/PVP and chitosan/PEO had much higher tensile strength.

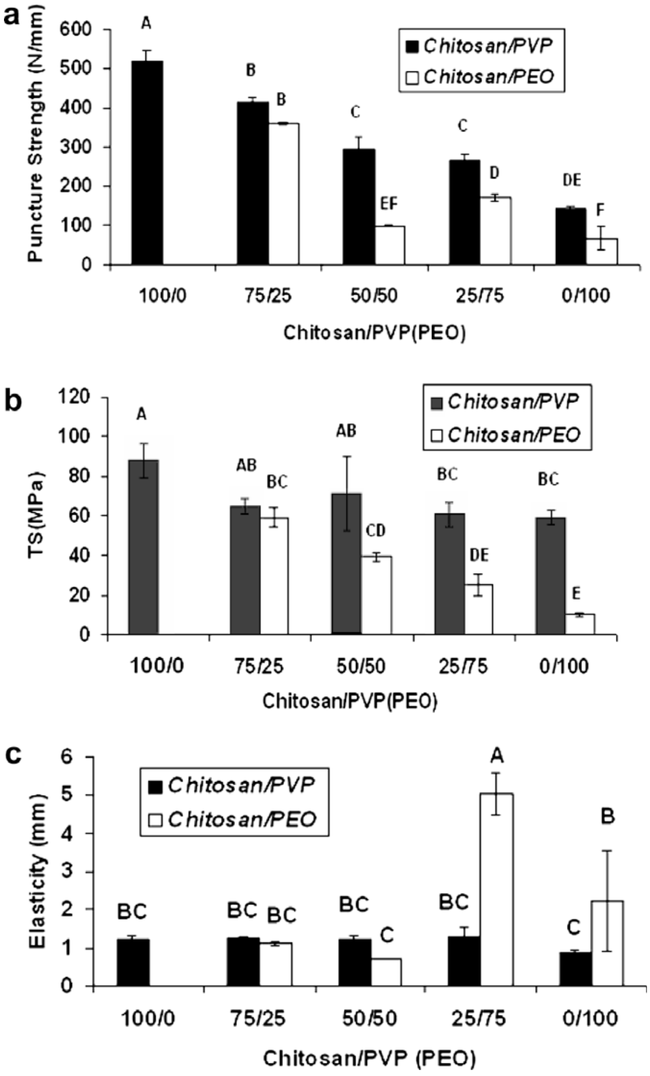

Fig. 2. Comparison of puncture strength (a), tensile strength (b) and elasticity (c) of chitosan/PVP and chitosan/PEO films with blend ratio from 100/0 to 0/100. Error bars represent standard deviation ($n = 3$). Letters indicate significant difference at $p < 0.05$.

One disadvantage of pure chitosan films is the lack of flexibility. Unfortunately, the increase of PVP content in the blends did not improve elasticity of the films, and the elasticity stayed in the range of 1.20 ± 0.11 to 1.29 ± 0.24 mm (Fig. 2c). On the other hand, since PEO chains are flexible, incorporation of PEO is expected to increase flexibility of the blend films. However, although the addition of 25% and 50% of PEO did not have significant effect, 75% PEO significantly increased elasticity of the films – from 1.22 ± 0.11 to 5.04 ± 0.56 mm. Pure PEO films did not show further increase in elasticity but the values had high standard deviation probably due to extreme crystallization of PEO in the films.

3.5. Film metal-binding capacity

Prior to testing for metal-binding, all the films were treated in methanol to remove residual acetic acid that can cause dissolution of the films when in contact with water. After the methanol treatment, chitosan, chitosan/PVP and chitosan/PEO films maintained good shape and structure but pure PVP or PEO films completely dissolved in chromium solutions.

All the films showed excellent ability to remove chromium ions from aqueous solutions (Fig. 3). Even the films with chitosan

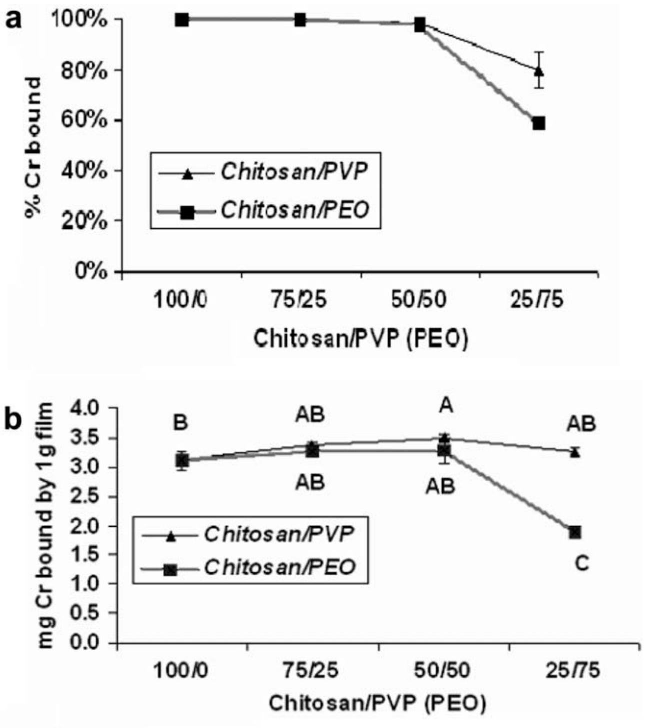

Fig. 3. Chromium binding by chitosan-based films; (a): percentage of Cr (VI) bound by chitosan/PVP and chitosan/PEO films with blending ratio from 100/0 to 25/75 in 25 mL 10 mg/L chromium solution, and (b): weight of Cr (VI) (mg) bound by 1 g of chitosan/PVP and chitosan/PEO films with blending ratio from 100/0 to 25/75 in 25 mL 10 mg/L chromium solution. Error bars represent standard deviation ($n = 3$). Letters indicate significant difference at $p < 0.05$.

content of only 50% removed 98% of chromium ions from 25 mL of 10 mg/L solutions (Fig. 3a) and bound similar amounts of chromium per 1 g of film compared to pure chitosan films (Fig. 3b). Chitosan/PVP films even showed strong binding at 25/75 blend ratio by removing 80% chromium ions from solution. Addition of 75% of PEO in the films resulted in binding of 60% Cr(VI) from solution what translates to 1.8 mg Cr/g film. These results suggest that incorporation of PVP or PEO in chitosan films does not significantly reduce metal-binding property of chitosan. It appears that number of chitosan molecules and, more importantly, their protonated amino groups on the surface of the films play crucial role in metal-binding and their amount was sufficient for effective binding even with addition of PVP or PEO up to 50%.

3.6. Antibacterial efficiency

Our previous study has shown that chitosan/PEO films with blend ratio 100/0 to 50/50 could reduce the number of *E. coli* K-12 by approximately 3 log CFU/mL (Zivanovic et al., 2007). The current study further proved that chitosan/PEO films with the ratio of even 25/75 still had ability to reduce 2.93 log CFU/mL of *E. coli* cells (Table 2). As seen in Table 2, chitosan/PVP films also had satisfactory antibacterial effect. Only the films with 75% PVP showed significantly lower cell reduction, 2.15 CFU/mL compared to 3.32 CFU/mL for pure chitosan films. In addition, chitosan/PVP films in general, showed lower antibacterial efficiency compared to chitosan/PEO films.

Table 2
Inhibitory effects of chitosan/PVP and chitosan /PEO blend films toward *Escherichia coli* K-12 inoculated in sterile phosphate buffer (0.05 M, pH 7.08) and stored for 6 h at 25 °C[*].

Film composition	*E.coli* K-12 reduction (Log_{10} CFU[**]/ml)
Chitosan (Chi)	3.32 ± 0.26^{ab}
Chi/PVP (75/25)	2.82 ± 0.38^{bc}
Chi/PVP (50/50)	2.48 ± 0.08^{cd}
Chi/PVP (25/75)	2.15 ± 0.15^{d}
Chi/PEO (75/25)	3.42 ± 0.10^{ab}
Chi/PEO (50/50)	3.75 ± 0.20^{a}
Chi/PEO (25/75)	2.93 ± 0.48^{bc}

[*] Means of three replicates ± standard deviation. Superscript letters indicate significant difference at $p < 0.05$ by Tukey–Kramer HSD test (JMP 007).
[**] CFU = colony-forming unit.

Chitosan has been widely studied as antimicrobial material and the possible mechanism of its antibacterial activity is attributed to the cationic amino groups that can interact with negatively charged bacterial surface and change cell wall and membrane permeability, causing the interruption in cell metabolism, leakage of intracellular components, and finally death of the cells (Tsai & Su, 1999). The possible reason for lower antibacterial activity of chitosan films with PVP compared to the films prepared with PEO is that unlike the linear structure of PEO molecules, the pyrrolidone rings in PVP may obstruct the interaction of chitosan with microbial cells and thus delay or reduce interaction between chitosan and bacterial cells.

4. Conclusions

Films formed from blends of chitosan and PVP or PEO had altered physical properties compared to films formed by single polymer. Films with either of two polymers had less yellowish discoloration compared to pure chitosan films. All chitosan films with 25–75% w/w PVP appeared transparent but the films prepared with PEO were clear only with 25% PEO. Addition of higher levels of PEO caused whitish, opaque appearance due to the formation of large PEO crystals in the films. Incorporation of PVP or PEO into the films made them easier to puncture and tear, with PEO having more pronounced effect. The flexibility of the films did not significantly change with PVP at any tested level, but addition of 75% PEO enhanced elasticity over three times compared to pure chitosan films. Although all chitosan/PEO films had lower water vapor permeability values than films with any of the chitosan/PVP ratio, blending of chitosan with hydrophilic polymers does not appear to be an effective way to improve the WVP on practical levels. Our study showed that incorporation of 25–50% of PVP or PEO in chitosan films did not significantly decrease the metal-binding and antibacterial properties of chitosan. Since synthetic polymers are available at a lower price than biopolymer chitosan, substitution of chitosan by these synthetic polymers could reduce the price of chitosan-based films with no effect on their functionality. Based on our results, chitosan/PVP and chitosan/PEO blend films have the potential to be used in the food industry as active packaging materials to inhibit food borne pathogens and as absorbent to bind heavy metal from various environmental sources.

Acknowledgments

This research was funded by U.S. EPA Science To Achieve Results (STAR) program Grant No. GR832372 and Hatch fund from the Tennessee Experiment Station TEN264.

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