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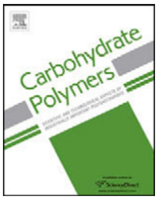

Synthesis, characterization and *in vitro* antimicrobial activities of boron/starch/polyvinyl alcohol hydrogels

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ABSTRACT

Starch/polyvinyl alcohol (PVA) hydrogel films (SF) and boron complexes of these hydrogels were synthesized with or without using glutaraldehyde as a cross-linking agent (SF-BA, SF-GA, SF-GA-BA) and characterized by using Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscope (SEM) and X-ray diffraction analysis (XRD) methods. In the preparation of the hydrogels; glutaraldehyde (GA) was used as cross-linking agent. Degree of swelling and tensile strength tests were performed for the synthesized hydrogel films. The antimicrobial activities of the films were assayed with *in vitro* conditions by the disc diffusion susceptibility tests for five different bacterial cultures and one fungus. Standard discs of amoxycillin/clavulanic acid (AMC), ofloxacin (OFX), netilmycin (NET), erythromycin (E) and amphotericin B (AFB) were individually used as positive controls during antimicrobial activity testes. As a result SF-GA-BA and SF-GA showed moderate antibacterial activity and antifungal activity against tested microorganisms. However, SF-BA had no antimicrobial activity against these microorganisms.

1. Introduction

Hydrophilic natured cross-linked polymer networks capable of absorbing and holding water within the interstitial space of the polymer are called hydrogels (Pal, Banthia, & Majumdar, 2007). Hydrogels have long been used as biomaterials in superficial burns, donor areas and in the treatment of chronic wounds containing light exudates (Piacquadio, 1994). Natural polymers such as starch are being recently used for the preparation of hydrogels because of their non-toxicity, biocompatibility, biodegradability and abundance in nature. However, in order to form stable hydrogels, water soluble starch needs to be mixed with a polymer capable of forming good films (Pal, Banthia, & Majumdar, 2006).

Starch/PVA has been studied as a potential biodegradable polymer and a stable support medium for starch films (Follain, Joly, Dole, & Bliard, 2005; Jayasekara, Harding, Bowater, Christie, & Lonergan, 2004; Xiao & Yang, 2006; Zhai, Yoshii, & Kume, 2003; Zhai, Yoshii, Kume, & Hashim, 2002). However, their wide applications are limited by the lack of water resistance and the poor mechanical property of starch/PVA films (Bikiaris et al., 1998). On the other hand, chemical cross-linking is a highly versatile method to modify polymers, where properties can be improved, such as mechanical, thermal and chemical stability. Cross-linking agents enhances not only the thermal properties but also the mechanical properties of starch/PVA hydrogels by reinforcing the intermolecular binding with the introduction of covalent bonds to supplement natural intermolecular hydrogen bonds (Sreedhar, Chattopadhyay, Karunakar, & Sastry, 2006). Starch was also cross-linked with PVA by boric acid and the film forming properties, and related physical properties were investigated (Yin, Li, Liu, & Li, 2005). It was found that these films had excellent mechanical properties.

Boron and its compounds are used for many different purposes in industry and are known to form complexes rapidly and reversibly in aqueous media with polyhydroxy compounds, monohydric alcohols, diols and aromatic o-hydroxymethylphenolic compounds due to the high affinity towards hydroxyl groups (Özay, Yurdakoç, Karakaplan, & Hosgoren, 2006; Tayman & Mehet, 2003).

In recent years, boron containing polymers and their derivatives have gained much attention amongst scientific and industrial community. The incorporation of boron in the backbone of polymers improves thermal stability, mechanical, electrical, antibacterial and antifungal properties, oxidative resistance, flexibility, flame retardancy than their virgin counterparts (Gao, Liu & Wang, 2001; Gao, Su & Xia, 2005; Martín, Hunt, Ebdon, Ronda & Cadiz, 2006; Martín, Ronda, & Cádiz, 2006; Uslu et al., 2007; Wang, Chang, & Chen, 2008).

In this work we attempted to prepare boron complexes of starch/PVA hydrogels and investigate their *in vitro* antimicrobial activities. In the preparation of the hydrogels; glutaraldehyde (GA)

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was used as cross-linking agent. Degree of swelling and tensile strength tests were performed for synthesized hydrogels. The characterization of the prepared complexes was realized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscope (SEM) and X-ray diffraction analysis (XRD) methods. Antimicrobial activities of the hydrogels were assayed by the disc diffusion susceptibility tests for five different bacterial cultures and one fungus.

2. Materials and methods

2.1. Materials

The potato starch (Fluka 85643), polyvinyl alcohol (Fluka 81384) of analytical reagent grade were used in this study and no further purification was made before use. Glutaraldehyde (Merck 8.20603) was used as a cross-linking agent and boric acid (BA)(Merck 1.00160) was used for the preparation of boron complexes. All other chemicals used were of analytical reagent grade. In all experiments, potato starch used in preparation of starch/PVA hydrogels and boron complexes was oven dried for 2 h at 105 °C.

Glutaraldehyde reagent was prepared by mixing 0.250 mL GA in a solution mixture of 5 mL ethanol (Riedel-de Haën 07102) and 0.025 mL hydrochloric acid (Riedel-de Haën 07102).

Definite pH solutions (pH 2.5–8.0) used in the investigation of swelling behaviors of the synthesized hydrogels were prepared by using citric acid (Merck 1.00242) and disodium hydrogen phosphate (Merck 1.06580) at constant ionic strength ($I = 0.01$).

A Denver 215 model pH meter, a Heildolp MR 3001 model magnetic shaker, Retsch PM 200 model grinder and a Polyscience 9006 model refrigerating-heating circulator were used during the experiments.

2.2. Synthesis of boron-starch/PVA hydrogel films

25 mL 10% (w/v) aqueous PVA solutions were blended with 25 mL 5% (w/v) aqueous gelatinized starch solutions at 70 °C for 1 h with constant stirring at 400 rpm to get homogeneous mixtures. To these mixtures; 5.275 mL GA, 0.0375 g boric acid or 0.0375 g boric acid-5.275 mL GA reagent blends were added. The flasks were stopper well and the contents were stirred and refluxed at the same temperature for 2 h at 1250 rpm. The solutions were cast into glass Petri dishes and dried at room temperature. The membranes so obtained were transparent and named as SF-GA, SF-BA and SF-GA-BA, respectively.

2.3. Characterization of the films

To characterize hydrogel films FTIR analysis were conducted with Perkin-Elmer Spectrum BX-II Model FTIR spectrophotometer. All samples were dried to a constant weight in an air oven at 50 °C for 24 h before use and KBr pellets were recorded in the range of 4000 and 400 cm^{-1}, at a resolution of 4 cm^{-1} as an average of 50 scans.

In order to investigate the thermal properties of starch, PVA, boric acid and synthesized hydrogels, TGA analysis of the samples were carried out with Perkin-Elmer Diamond TG/DTA Analyzer. The analyses were made in aluminum pans under a dynamic nitrogen atmosphere in temperature range of 25–600 °C at a heating rate of 5 °C/min.

The surface of the complexes was observed with an emission scanning electronic microscope. The samples were coated with a thin gold layer (two times, 40 mA, 60 s; approx. 30 nm) by a sputter coater unit (BALZER SCD 050 Sputter Coater, BAL-TEC) and surface topography was analyzed with a JEOL JSM 6300F Scanning Electron Microscope (SEM) operated at an acceleration voltage of 5 kV.

The X-ray diffraction patterns (XRD) of the hydrogels were recorded with oriented mounts, in a Philips X'Pert Pro X-ray diffractometer using Cu Kα radiation at 45 kV and 40 mA in the 2θ range of 0–60°.

The tensile strength (TS), elongation at break (E) and Young's modulus of the hydrogels were determined using a AG-IS 100 kN model Shimadzu Universal tensile testing device equipped with a 5 kN load cell at a cross head speed of 0.5 mm/min. Each result was taken from 3 (replicates, $n = 3$) "dog bone" shaped specimens, according to ASTM Standard Method (ASTM D638-02a) and the results were given as averages. The thicknesses of the films produced were between 0.10 and 0.40 mm depending on the blend composition.

2.4. pH dependent swelling behavior of the hydrogels

In order to investigate the swelling behavior of the hydrogels, the swelling equilibrium times at ultra pure water and citric acid-phosphate solutions of definite pH values (2.5, 4.5, 6.5 and 8.0) were studied initially. The dried samples were immersed in the solutions at room temperature and removed at intervals of 5 min, dried with filter paper to remove surface water, weighed and then returned to the same solutions until the equilibrium was reached.

The pH dependent swelling behavior of the membranes were determined by swelling up the dried membranes in water until equilibrium times and then immersing the same products in the citric acid-phosphate solutions of different pH values, respectively and standing up the membranes for maximum 2 h in each solution.

The swelling ratios were calculated on a dry basis using the following Eq. (2.1); where W_h is the weight of the product after hydration and W_d is the weight of the dried product. The experiments were conducted in triplicates and the results were given as averages.

$$\text{Swelling ratio} = \frac{W_h - W_d}{W_d} \times 100 \qquad (2.1)$$

2.5. In vitro antimicrobial activities of the hydrogels

Antimicrobial activity of hydrogels was assayed by the disc diffusion susceptibility test according to the recommendation of the National Committee for Clinical Laboratory Standards (NCCLS) (Clark, Jacobs, & Appelbaum, 1998). The disc diffusion tests were performed on Muller-Hinton agar plates for five different bacterial cultures; *Escherichia coli* [ATCC 25922], *Staphylococcus aureus* [ATCC 25923], *Streptecocus pyogenes* [ATCC 19615], *Pseudomonas aeruginosa* [ATCC 27853], *Bacillus subtilis* [ATCC 11774] and one fungus, *Candida albicans* [ATCC 10231]. Plates were dried at 35–36 °C for about 30 min in an incubator before inoculation. Three to five freshly grown colonies of bacterial strains were inoculated into 25 mL of Mullar–Hinton broth medium in a shaking water bath for 4–6 h until a turbidity of 0.5 McFarland (1×10^8 CFU/mL) was reached. Final inocula were adjusted to 5×10^5 CFU/mL. Three to five colonies of *C. albicans* were inoculated into 25 mL of Sabouraud dextrose broth in a shaking water bath for 8–10 h until a turbidity of 0.5 McFarland was reached. The final inocula were adjusted to 5×10^5 CFU/mL using a spectrophotometer (Kirkpatrick et al., 1998). The inoculum (50 mL) from the final inocula was applied to each agar plate and uniformly spread with a sterilized cotton spreader over the surface. Absorption of excess moisture was allowed to occur for 30 min before application of hydrogel discs (9 mm). Hydrogel discs were incubated at 37 °C for 24 h for bacteria and 48 h for fungi. Standard discs of amoxycillin/clavulanic acid (AMC, 30 μg/disc), ofloxacin (OFX, 5 μg/disc), netilmycin (NET, 30 μg/disc), erythromycin (E, 15 μg/disc) and amphotericin B (AFB, 30 μg/disc) were individually used as positive controls. Inhibition

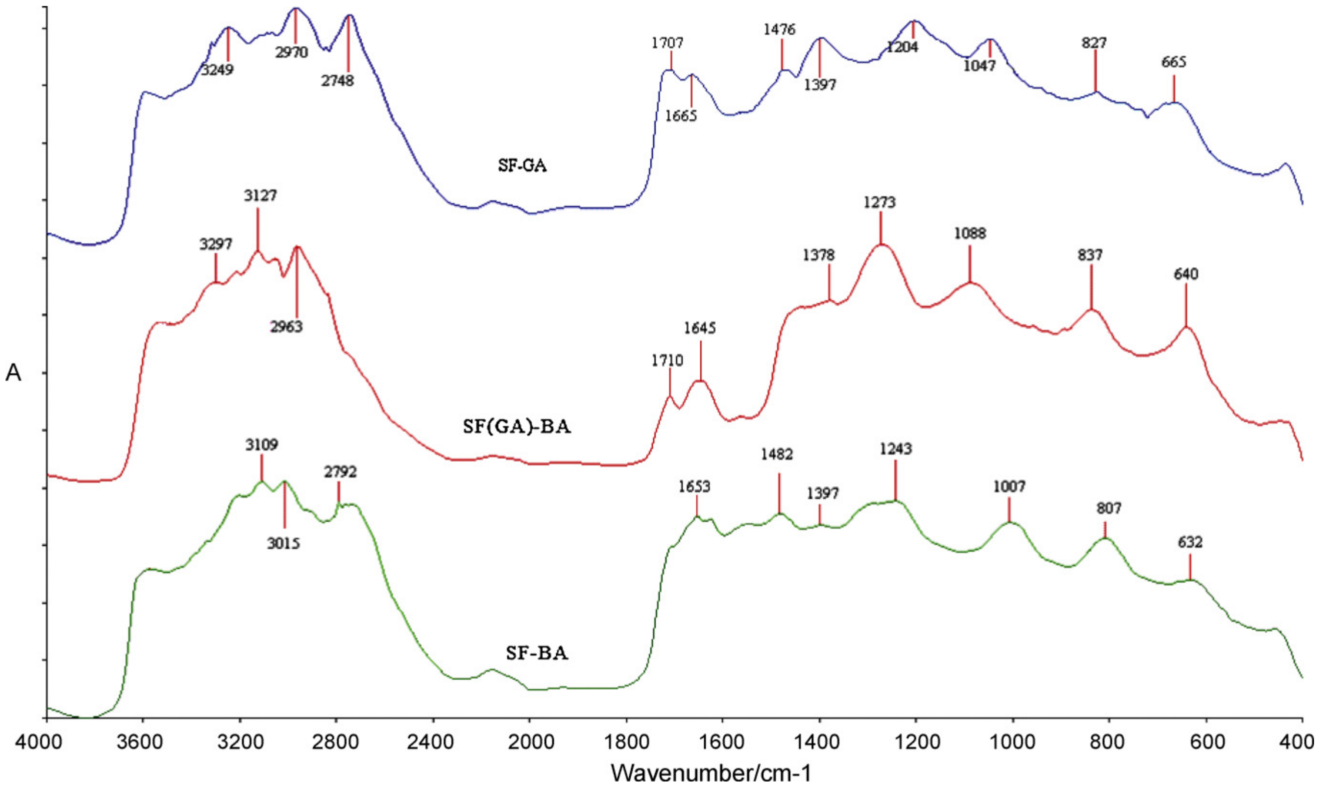

Fig. 1. The FTIR spectra of boron-starch/PVA hydrogel complexes.

zone diameter (mm) surrounding each sample was measured after 24 h incubation of Hydrogel discs (12 mg/9 mm) onto agar plates at 37 °C. The diameters of the inhibition zones were measured in millimeters using an inhibition zone ruler.

3. Results and discussion

3.1. FTIR analysis

The FTIR spectra of boron-starch/PVA hydrogels are given in Fig. 1. The spectrum of SF-GA showed bands between 3300 and 3000 cm^{-1} indicating the presence of intermolecular and intramolecular hydrogen bonded hydroxyl groups. This gives us the indication of the presence of free hydroxyl groups of both the raw materials in the hydrogel. In addition, the bands at 2970 and 1397 cm^{-1} were attributed to the presence of hydrocarbon chromophore. The bands between 1200 and 800 cm^{-1} were due to C–O stretching. Absence of the band in 1740–1720 cm^{-1} range indicated absence of aldehydic group. From this it can be inferred that all the aldehydic groups of the GA has been used for cross-linking and hence the chance of cytotoxicity is greatly reduced.

When boric acid was used with glutaraldehyde (SF-GA-BA) the infrared spectra of the new complex was slightly changed compared to spectra of SF-GA. Bands which were due to intermolecular and intramolecular hydrogen bonded hydroxyl groups were shifted to higher frequencies while the bands of hydrocarbon chromophore were shifted to lower frequencies. Also the shape of these bands were little bit changed. The intensity of the bands which were related to C–O stretching in general was increased and these bands were shifted to higher frequencies. When just boric acid was used, the bands at 2970 and 1397 cm^{-1} were nearly disappeared. In the spectra of SF-BA, the bands due to C–O stretching were shifted and the intensities of these bands were increased.

3.2. TGA analysis

The TGA/DTG data of all samples were given in Table 1. The thermogram of starch showed two-step decomposition while PVA and synthesized boron-starch/PVA hydrogels were exhibiting three-step thermal decomposition. The first step of weight loss could be attributed to evaporation of adsorbed water for all samples. The other decomposition stages were due to thermal decomposition stages of the products.

The shoulder in the starch degradation peak that was observed in the second step may have been due to the different degradation rates of amylose and amylopectin, the former probably being degraded first because of its linear structure.

Table 1
TGA/DTG data of Starch, PVA and boron-starch/PVA films.

Samples	First stage		Second stage		Third stage	
	DTG maxima (°C)	% Weight loss	DTG maxima (°C)	% Weight loss	DTG maxima (°C)	% Weight loss
Starch	55	7	299	76	–	–
PVA	25	4	267	67	418	22
SF-GA	112	9	313	61	419	22
SF(GA)-BA	111	7	341	59	423	22
SF-BA	114	8	308	62	420	17

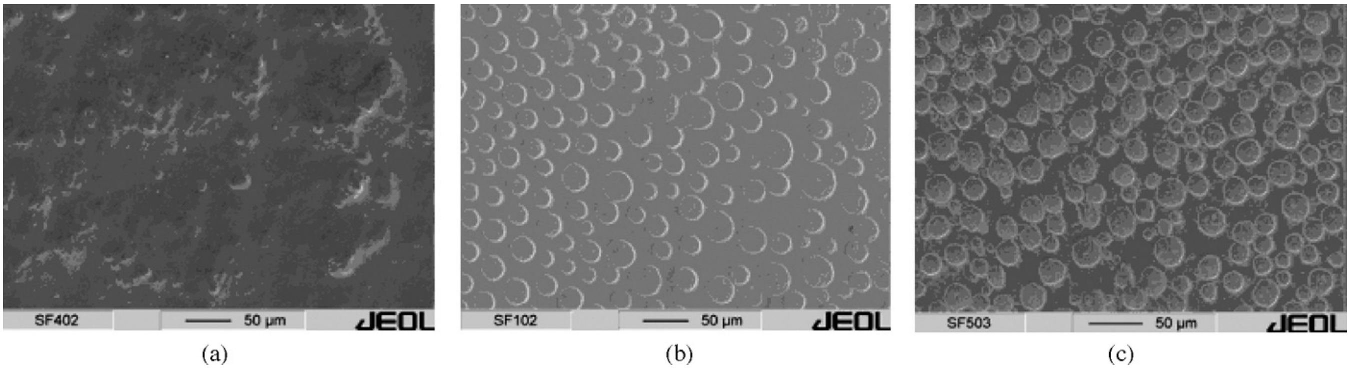

Fig. 2. SEM photographs of the surface of boric acid-starch/PVA hydrogel films: (a) SF-BA, (b) SF-GA and (c) SF-GA-BA.

The results showed that the thermal stability of starch increased for all hydrogel complexes after modification processes.

3.3. SEM analysis

SEM analysis has been applied to boric acid-starch/PVA hydrogel complexes. The photos of the surface of the complexes at 50 μm are shown in Fig. 2.

Surface morphology of boric acid-starch/PVA hydrogel complexes showed that regular shaped spheres could not be seen when only boric acid was used in the synthesis and the size of the spheres decreased a little bit when boric acid and glutaraldehyde was used together instead of glutaraldehyde.

3.4. XRD analysis

The X-ray diffraction patterns of synthesized hydrogels and summary of XRD results were shown in Fig. 3 and Table 2. In the diffractogram of starch only one strong diffraction peak was observed at $2\theta = 17.0^\circ$ which resembles to the characteristic of B-type crystalline structure (Cairns, Sun, Morris, & Ring, 1995). Starch is known to be semi-crystalline in nature due to the amylopectin fraction that exists in it and have typical crystalline peaks at 16.6° and 22.0° because of its close molecular packing and regular crystallization.

PVA had peaks at $2\theta = 18.9^\circ$ and 38.9° and the peak at 18.9° were most intense. The X-ray diffractograms of hydrogels revealed amorphous compounds, with intense peaks at approximately 20.0° indicating that the crystallinity of the membranes were mainly contributed by PVA (Pal, Banthia, & Majumdar, 2008).

The XRD analysis results showed that the morphology of starch was changed when starch was blended with PVA in the synthesized hydrogels. There appeared an increase in overall intensities of the XRD reflections after complexation and at the same time the crys-

Table 2
Summary of XRD results for the synthesized hydrogel films.

Samples	2θ (°)	d (Å)
Starch	16.6	5.337
	22.0	4.045
	34.0	2.636
PVA	18.9	4.695
	38.9	2.263
SF-BA	17.1	5.179
	19.7	4.507
SF-GA	19.6	4.530
SF-GA-BA	19.5	4.553

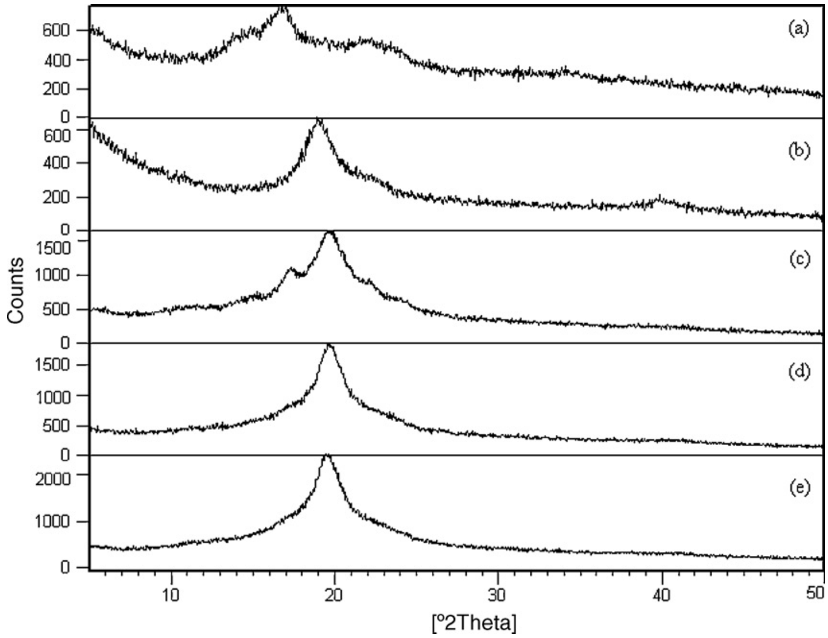

Fig. 3. The XRD patterns of (a) starch, (b) PVA, (c) SF-BA, (d) SF-GA and (e) SF-GA-BA.

Table 3
Mechanical properties of the starch/PVA hydrogel films.

Samples	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
SF-GA	43.62	1.54	3.85
SF-BA	47.39	1.70	4.95
SF(GA)-BA	50.15	1.81	5.94

talline peaks of starch and PVA at $2\theta = 34.0^\circ$ and 38.9° completely disappeared.

The fact that no boric acid peaks (as BA gives single crystal peaks) can be identified in the hydrogels suggests that few or no BA remained in a crystal state inside the microparticles of the hydrogel complexes (Li et al., 2009).

3.5. Mechanical properties of the hydrogels

The mechanical properties of starch/PVA hydrogel complexes were measured and the results were summarized in Table 3.

t-Test was performed to compare the experimental data and statistical significance was set at 0.05. According to statistical analysis, it was found that the difference was not statistically significant ($p > 0.05$) among the tensile strength, Young's modulus and elongation at breaks of the hydrogels.

The tensile strengths of SF-GA, SF-BA and SF-GA-BA were found 43.62, 47.39 and 50.15 MPa, respectively. The alteration of the breaking elongation and Young's modulus expressed a tendency similar to that of the tensile strength for the synthesized hydrogels. As a result because of their relatively good mechanical properties, the synthesized hydrogels showed potential for biomedical applications.

3.6. Swelling behaviors of the hydrogels

The results of equilibrium swelling times of the hydrogels at ultra pure water and citric acid-phosphate solutions of definite pH values were represented in Fig. 4. The equilibrium times were found to be approximately 3, 0.5 and 0.5 h at water, also 2, 0.5 and 0.5 h at each pH solution for SF-GA, SF-BA and SF-GA-BA, respectively. While investigating the pH dependent swelling behaviors, membranes were kept in water and in all of the solutions at this determined equilibrium times.

During the pH dependent swelling experiments the hydrogels were swollen approximately 250%, 350% and 90% at water for SF-GA, SF-BA and SF-GA-BA, respectively. When the same samples were immersed in the citric acid-phosphate solutions of different pH values and leaved in each solution for maximum 2 h no remarkable change was observed in the swelling ratio for all hydrogels. These results denoted that the swelling behavior of the membranes

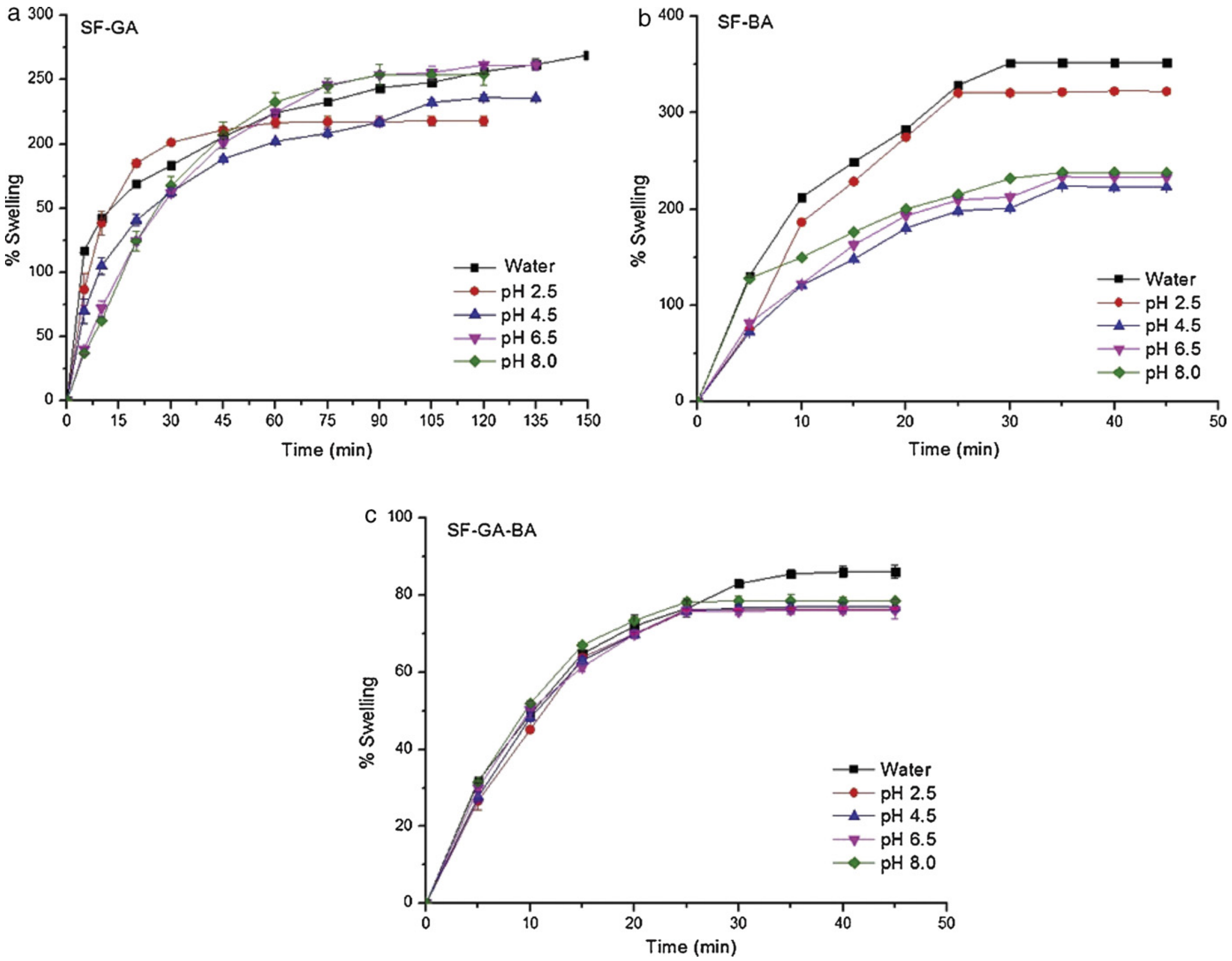

Fig. 4. The swelling equilibrium times for the hydrogel films: (a) SF-GA, (b) SF-BA and (c) SF-GA-BA.

Table 4
Antimicrobial activity of synthesized hydrogels and standard antibiotics.

Tested organisms	Zones of inhibition (mm)							
	Hydrogels[a]			Standard antibiotics[b]				
	SF-GA-BA	SF-BA	SF-GA	OFX 5	NET 30	E 15	AMC 30	AFB 30
Escherichia coli ATCC 25922	14	–	–	28	26	14	20	NT
Staphylococcus aureus ATCC 25923	13	–	–	20	18	18	>30	NT
Streptecocus pyogenes ATCC 19615	–	–	–	22	>30	>30	28	NT
*Pseudomonas aeruginosa*ATCC 27853	12	–	–	16	22	R	R	NT
Bacillus subtilis ATCC 11774	–	–	6	24	>30	>30	24	NT
Candida albicans ATCC 10231	14	–	6	NT	NT	NT	NT	13

OFX: ofloxacin; NET: netilmycin; E: erythromycin; AMC: amoxycillin/clavulanic acid; AFB: amphotericin B; NT: not tested; R: resistance; (–) not active.

[a] 12 mg/9 mm disc.

[b] μg/6 mm paper disc.

were essentially independent of pH and were based on water. As starch and PVA contained no ionizable functional groups, this result was compatible with the expected one.

3.7. Antimicrobial activity tests

Antimicrobial activities of prepared Starch/PVA based hydrogels were investigated. The results were given in Table 4. Inhibition zone formation confirms that SF-GA-BA and SF-GA hydrogels had antimicrobial activity. However, SF-BA had no antimicrobial activity against tested microorganisms.

The results denoted that SF-GA-BA and SF-GA showed moderate antibacterial activity and antifungal activity. SF-GA-BA indicated 14-mm inhibition zones against *E. coli* (ATCC 25922) so as this result is comparable with standard antibiotic erythromycin and 13-mm zones against *Staphylococcus aureus* (ATCC 25923), 12-mm zones against *P. aeruginosa* (ATCC 27853) and 14-mm zones against *C. albicans* (ATCC 10231). Also, SF-GA indicated 6-mm inhibition zones against *B. subtilis* (ATCC 11774) and 6-mm zones against *C. albicans* (ATCC 10231). Thus, it can be seen from Table 4, standard antibiotics showed different zones against tested organisms.

From the results obtained, it appears that the antibacterial action of the SF-GA-BA is more pronounced on Gram-negative than on Gram-positive bacteria. The reason of different sensitivity between Gram-positive and Gram-negative bacteria could be ascribed to the morphological differences between these microorganisms.

4. Conclusions

Starch/polyvinyl alcohol (PVA) hydrogel films and boron complexes of these hydrogels were synthesized with or without using glutaraldehyde as a cross-linking agent and their *in vitro* antimicrobial activities were investigated.

There were no bands in the FTIR spectrum of the hydrogels that highly differ from the bands corresponding to their individual components. So this reveals the functional groups in the structure of starch and PVA did not almost change with cross-linking and complex formation.

TGA thermograms and DTG curves showed that the thermal stability of starch increased in the boron-starch/PVA hydrogels as a result of modification processes.

The X-ray diffractograms of hydrogels revealed amorphous compounds, with intense peaks at approximately $2\theta = 20.0^\circ$ suggesting that the crystallinity imparted in the hydrogels were mainly due to crystallinity of PVA.

The swelling behaviors of the hydrogels were found to be independent of pH. Since starch and PVA contained no ionizable functional groups, this was compatible with the expected results.

The hydrogels displayed relatively good mechanical properties, so they showed potential for biomedical applications. When the antimicrobial activities of the hydrogels were investigated inhibition zone formation, it confirmed that SF-GA-BA and SF-GA hydrogels had moderate antimicrobial activity. However, SF-BA had no antimicrobial activity against tested microorganisms. SF-GA-BA indicated 14-mm inhibition zones against *E. coli* (ATCC 25922) so as this result was comparable with standard antibiotic erythromycin. The results denoted that SF-GA-BA has better antibacterial and antifungal activity than other hydrogels.

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