ELSEVIER

Contents lists available at ScienceDirect

Carbohydrate Polymers

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



Synthesis and characterization of pectin/poly (sodium acrylate) hydrogels

Xiaoye Ma^a, Ruili Wei^{a,*}, Jinwei Cheng^a, Jiping Cai^a, Juan Zhou^{b,**}

- a Department of Ophthalmology, Changzheng Hospital, Second Military Medical University, 415 Fengyang Road, Shanghai 200003, People's Republic of China
- ^b National Engineering Research Center for Nanotechnology, Shanghai 200241, People's Republic of China

ARTICLE INFO

Article history: Received 19 January 2011 Received in revised form 31 March 2011 Accepted 23 April 2011 Available online 18 May 2011

Keywords: Hydrogel Volume expansion ratio Orbital implant Pectin Poly (sodium acrylate)

ABSTRACT

The aim of the research was to develop a hydrogel tissue expander for orbital implant. To this end, a new superabsorbent hydrogel composed of pectin (PEC) and poly (sodium acrylate) (PAAS) has been fabricated by the free radical copolymerization of acrylic acid (AA) in the pectin aqueous solution. The effects of crosslinker content, initiator content and the weight ratio of PEC to AA on the volume expansion ratios of the PAAS–PEC hydrogels were investigated. In addition, the mechanical properties of the PAAS–PEC hydrogels swollen in PBS were evaluated. Furthermore, the morphologies and structures of the PAAS–PEC hydrogels were characterized by SEM, FTIR and TG. The results revealed that the introduction of pectin contributed to the increase of the volume expansion ratio and the decrease of the mechanical properties for the PAAS–PEC hydrogels. These new PAAS–PEC hydrogels could be promising in orbital implant or other biomedical applications.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Hydrogels have attracted extensive attention in the fields of drug-delivery systems, cell encapsulation and tissue engineering scaffolds because of its excellent hydrophilicity and biocompatibility (Deligkaris, Tadele, Olthuis, & van den Berg, 2010; Kopecek, 2007). Furthermore, the inflatable hydrogel as orbital implant has been proved to be necessary to stimulate the growth of the bony orbit in order to prevent or reduce midface asymmetry, which is meaningful to the rehabilitation of the congenitally anophthalmic or microphthalmic (Mazzoli, Raymond, Ainbinder, & Hansen, 2004; Schittkowski, Katowitz, Gundlach, & Guthoff, 2006). Schittkowski et al. have fabricated self-inflating hydrogel expanders by using the copolymer on the basis of methylmethacrylate and vinyl pyrrolidone, which showed potential application as orbital implant (Schittkowski et al., 2006). We aim to explore new available hydrogel tissue expanders used as orbital implant or other biomedical materials. Poly (sodium acrylate), as superabsorbent hydrogels with high swelling ratio, have been widely used in agriculture and diapers. Recently, PAA-based superabsorbent hydrogels have been investigated in the field of drug delivery, and showed great potential application as a kind of biomedical material (Chang, Duan, Cai, & Zhang, 2010; Changez, Burugapalli, Koul, & Choudhary, 2003; Changez, Koul, & Dinda, 2005).

Pectin, as a kind of polysaccharide originated from skeletal tissues of plants, has shown to be promising in targeted gene delivery and tissue engineering due to its good biocompatibility and hydrophilicity (Coimbra et al., 2011; Katav et al., 2008; Liu et al., 2004; Mohnen, 2008). With high molecular weight and a polyanionic nature, pectin is sensitive to the environments with a reversible transformation from dense gels to dilute solutions. These properties endow pectin polymers with functions of carrying signal molecules and supporting various biologically active substances and great potential to be used as a new biomedical material. Therefore, the introduction of pectin into the PAA-based hydrogels is able to facilitate its application as biomedical materials. The fabrication of PAA-based hydrogels with chitosan or gelatin has been reported (Burugapalli, Bhatia, Koul, & Choudhary, 2001; de la Torre, Torrado, & Torrado, 2003). Compared with other natural polymers such as chitosan and gelatin, pectin is advantageous of its low cost and general availability. To the best of our knowledge, studies on the hydrogels prepared from PAA and pectin have never been published.

In the present study, we reported the synthesis and characteristic of pectin/poly (sodium acrylate) (PAAS-PEC) composite hydrogel via a free radical polymerization. Generally, the network formation of the polymer hydrogels is significantly influenced by the polymerization conditions, such as the monomer concentration, cross linker content and initiator content. In this study, we focus on investigating how these factors control the volume expansion ratio during the PAAS-PEC network formation. Mechanical properties of the hydrogels were also investigated to elucidate their feasibility of application in the ocular implant or other biomedical materials. In addition, the morphology and structure of the

^{*} Corresponding author. Tel.: +86 21 81885921.

^{**} Corresponding author. Tel.: +86 21 34291286; fax: +86 21 34291125.

E-mail addresses: ruiliwei@gmail.com (R. Wei), xmcjuan@gmail.com (J. Zhou).

PAAS-PEC hydrogels were also investigated to elucidate their expansion mechanism.

2. Materials and methods

2.1. Materials

Acrylic acid (AA), potassium persulfate (PPS, used as received) and N,N'-methylenebisacrylamide (MBA, used as received) were supplied by Shanghai Reagent Corp. (Shanghai, China) of analytical grade. 0.1 M PPS and 0.1 M MBA solutions were prepared with distilled water and filtered to be used. Acrylic acid (AA) was purified through reduced pressure, and the purified AA was kept in dark at 4 °C before using. Pectin was purchased from Sigma (NO. P9135).

2.2. Preparation of the PAAS hydrogels

Poly (sodium acrylate) (PAAS) hydrogel was synthesized by radical polymerization, with the PPS as the initiator and MBA as the crosslinker. Firstly, AA (20, 25, 30, 35, and 40 wt%) was neutralized by NaOH (mole ratio of NaOH to AA was 70%) in the three-neck flask by magnetic stirring at room temperature, and the mixed solution was purged with nitrogen gas continuously for 10 min. Secondly, MBA (0.5–1 wt% of AA) and PPS (0.05–0.5 wt% of AA) solutions were dropwise added into the mixed solution and stirred for further 10 min. Then the mixed solutions were immediately injected into the model and the reactions were carried out at 65 °C for 3 h. After gelation, gels were demoulded and further dried at 65 °C for 24 h. The dried gels were then immersed in a large amount of distilled water for 3 days, and water was changed twice every day to remove the residual chemicals. Then, by heating at 60 °C for 24 h, the dried hydrogels were obtained.

2.3. Preparation of the PAAS-PEC hydrogels

With the same procedure as above, the PAAS-PEC hydrogels were prepared by mixing different amounts of pectin (0 wt%, 5 wt%, 10 wt%, 15 wt% and 20 wt% of AA) and AA before polymerization. The PAAS-PEC hydrogels were coded as PAAS-PEC5, PAAS-PEC10, PAAS-PEC15 and PAAS-PEC20, respectively, based on the PEC content

The reaction scheme is shown in Fig. 1. Before polymerization, pectin was homodispersed in the AA aqueous solution. Then the polymerization was initiated at a temperature of 65 °C. In the presence of the crosslinker, crosslinking reaction occurred and finally a three dimensional (3D) polymer network of PAAS–PEC was formed. The pectin chains interdiffused and got entangled within this PAAS 3D network.

2.4. Volume expansion ratio measurements

The equilibrium volume expansion ratios of the hydrogels were investigated in distilled water, physiological saline water (PSW, 0.9 wt% NaCl aqueous solution) and phosphate buffer saline (PBS, 0.1 M, pH = 7.4). The hydrogels swelling in water or other salt solutions with no volume change were considered as reaching an equilibrium state. As observed, the hydrogels swelled rapidly in water or other salt solutions, and attained equilibrium completely within 24 h. The volume expansion ratio was calculated as: volume expansion ratio = V_s/V_d , where V_s was the volume of the wet hydrogel at swelling equilibrium at 37 °C, V_d was the volume of the hydrogel in the dry state. The cylinder shaped hydrogels were obtained depending on the mould used. Therefore, the volume of the hydrogels was calculated by the formula: $V = \pi D^2 H/4$, where D_s and D_s respectively. In order to simplify the calculation procedure, we evaluated

the volume expansion ratio and height expansion ratio of the PAAS and the PAAS–PEC hydrogels, which were of similar value. The data was not shown here. The result indicated that their expansion is wholly isotropic, that is, expansion occurs identically in all directions. Therefore, the calculation formula of the volume expansion ratio was simplified as: volume expansion ratio = $V_s/V_d = (D_s/D_d)^3$, where D_s and D_d represent the diameter of the wet hydrogel at swelling equilibrium at 37 °C and the hydrogel in the dry state, respectively. The diameter and height of the hydrogels were measured by a slide caliper. Each value was averaged over at least three parallel measurements. Statistical analysis was performed using one-way ANOVA way in ORIGIN 8.0. All quantitative data are presented as means \pm standard deviation. Differences between groups of $p \le 0.05$ were considered statistically significant.

2.5. Mechanical properties

The mechanical properties of the hydrogels were also characterized by compressive stress–strain measurements which were performed on swollen hydrogels in PBS using an HY-0230 compression testing machine. The cylindrical gel samples were cut into testing samples with thickness of 8 mm, while the diameter was kept original. Then they were put on the lower plate and compressed by the upper plate, which was connected to a load cell, at a rate of 5 mm/min. The elastic modulus was determined by the average slope of the stress–strain curve over the strain range 0–20%. The fracture stress and fracture strain were also reported. Four parallel samples per measurement were performed, and the obtained values were presented as means \pm standard deviation.

2.6. Morphology and structure characterization

To investigate the morphology and structure characterization of the hydrogels, the PAAS and PAAS–PEC hydrogels were swollen to equilibrium in distilled water at $37\,^{\circ}\text{C}$ for 24 h, and then freeze dried for 48 h. The PEC samples were fabricated by freeze-drying the 10% PEC aqueous solution for 48 h.

Scanning electron microscope (SEM) images were taken with a Hitachi S-4800 microscope. The freeze dried samples were frozen in liquid nitrogen and snapped immediately. The fracture surface (cross-section) of the samples was sputtered with gold, and then observed.

Fourier transform infrared spectra (FTIR, Nicolet 6700) were measured with an attenuated total reflectance accessory (ATR). Each spectrum was acquired in transmittance mode on a diamond substrate by the accumulation of 16 scans with a resolution of $4\,\mathrm{cm}^{-1}$ and a spectral range of $4000-600\,\mathrm{cm}^{-1}$.

Thermal stability of the hydrogels was studied on a Linseis STA PT1600, with a temperature range of 25–550 °C at a heating rate of $10\,^\circ\text{C}\,\text{min}^{-1}$. A sample size of $10\pm5\,\text{mg}$ was used in all the experiments

3. Results and discussion

3.1. The volume expansion ratio of the PAAS hydrogel

Many previous reports focused on the effects of external factors, such as initiator, crosslinker and monomer concentration on the swelling ratio of the hydrogel (Burugapalli et al., 2001; Chen & Zhao, 2000; Zhang, Wang, & Wang, 2007; Zhou et al., 2009). Generally, the swelling ratio was expressed as the percentage of the hydrogel weight gain in water or other salt solution. The density of the hydrogels, calculated by the weight per unit volume, is different with water, which resulted in the difference between the swelling ratio and the volume expansion ratio. No information about the effects of these factors on the volume expansion ratio was reported,

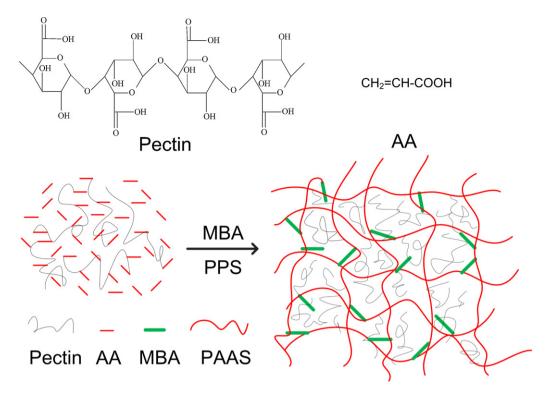


Fig. 1. Schematic representation of formation of PAAS-PEC hydrogels.

to the best of our knowledge, which supplied the information of the volume change. As a new orbital implant with expansibility, the volume expansion ratio was an important parameter, which could help to evaluate the implanted volume required for the surgeons. Therefore, the effects of AA, MBA and PPS content on the volume expansion ratio of the PAAS hydrogel in water and PSW were investigated, and the results are shown in Fig. 3. It could be seen from Fig. 3(a) that the volume expansion ratio of the PAAS hydrogel in water and PSW decreased continuously with the increase of AA content. As the AA content increased to more than 30%, the volume expansion ratio of the PAAS hydrogel in water or PSW showed less difference. The ability of the PAAS hydrogel swelling extensively was facilitated by the carboxylic acid groups on the polymer chain, which strongly associated with water molecules. The PAAS hydrogel was a kind of polyelectrolyte with Na⁺ and carboxylic acid, and the osmotic pressure difference between the hydrogels and external solution decreased when there was an increase of Na+ concentration in the solution, such as PSW. Therefore, the volume expansion ratio of the PAAS hydrogel in PSW was significant lower than that in water.

As shown in Fig. 3(b), the volume expansion ratio of the PAAS hydrogel in water and PSW increased first and then decreased with increasing MBA content. At a higher MBA content, the crosslinking density of the composites increased, which led to the decrease of the volume expansion ratio. However, at a lower MBA content, the PAAS formed no ideal polymer network, which resulted in the lower volume expansion ratio. Similar variation tendency of the volume expansion ratio is also observed in Fig. 3(c), with increasing PPS content. Initiator has an important effect on the molecular weight of polymers and rate of the polymerization. At lower PPS content, the molecular weight of PAAS was higher and the rate of the polymerization was slow, so the formation of ideal polymer network could not occur easily and the volume expansion ratio decreased. However, at higher PPS content, the molecular weight of PAAS was lower, the rate of polymerization was rapid and crosslinking density increased, which also resulted in the decrease of volume

expansion ratio. We could infer that at lower MBA content and PPS content, the formation of polymer network played a dominating role in the volume expansion ratio, whereas at higher MBA content and PPS content, the crosslinking density played a main role.

The results of the swelling experiments demonstrated that the monomer concentration, MBA and PPS content during the polymerization significantly affected the formation of polymer network and crosslink density, which further influenced the equilibrium volume expansion ratio of the PAAS hydrogels.

3.2. The volume expansion ratio of the PAAS hydrogel

On the basis of the above research, we further studied the synthesis of the PAAS–PEC hydrogels by directly introducing the pectin aqueous solution into the AA aqueous solution. The representative graphs of the PAAS–PEC15 hydrogels at different swollen state are shown in Fig. 2. It could be obviously observed that the hydrogels had a significant different dimension change after swelling in water



Fig. 2. Typical appearance of different PAAS–PEC15 hydrogels after removing from moulds. (a) Dried hydrogel; (b) swollen hydrogel after swelling in water for 3 days; (c) swollen hydrogel after swelling in PSW for 3 days; (d) swollen hydrogel after swelling in PBS for 3 days.

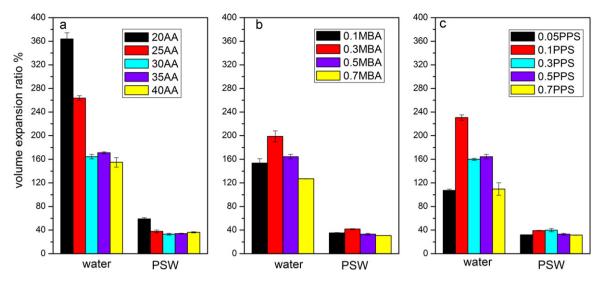


Fig. 3. Volume swelling ratio of the PAAS hydrogels in water and PSW; (a) with different AA contents, while the other parameters were kept constant: the MBA content was 0.5%, PPS content was 0.5%; (b) with different MBA contents, while the other parameters were kept constant: the AA content was 30%, and PPS content was 0.5%; (c) with different PPS contents, while the other parameters were kept constant: the AA content was 30%, and MBA content was 0.5%.

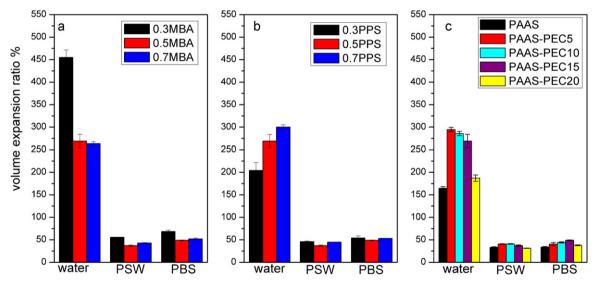


Fig. 4. Volume expansion ratios of the PAAS–PEC hydrogels in water, PSW and PBS; (a) with different MBA contents, while the other parameters were kept constant: the AA content was 30%, PPS content was 0.5%, and PEC/AA was 15%; (b) with different PPS contents, while the other parameters were kept constant: the AA content was 30%, MBA content was 0.5%, and PEC/AA was 15%; (c) with different weight ratios of PEC to AA, while the other parameters were kept constant: the AA content was 30%, PPS content was 0.5% and MBA content was 0.5% and MBA content was 0.5%

with other simulated biological solution, and the PAAS-PEC15 hydrogels showed similar dimension in PSW and PBS. Meanwhile, the effect of MBA content, PPS content and weight ratio of PEC to AA on the volume expansion ratio of the PAAS-PEC hydrogels in water and other simulated biological solution, including PSW and PBS, were evaluated.

In order to investigate the effect of crosslinker and initiator on the synthesis of the PAAS-PEC hydrogels, the same range of MBA content from 0.1% to 0.7% and PPS content from 0.05% to 0.7% as the

Table 1Compression properties of the hydrogels in PBS at room temperature.

Samples	Modulus [kPa]	Fracture stress [kPa]	Fracture strain [%]
PAAS	64.28 ± 14.34	289.24 ± 25.99	81.62 ± 14.34
PAAS-PEC5	41.94 ± 4.69	161.31 ± 43.20	75.44 ± 7.06
PAAS-PEC10	39.15 ± 10.46	208.49 ± 26.41	75.48 ± 3.37
PAAS-PEC15	41.33 ± 3.43	175.13 ± 83.20	73.05 ± 1.97
PAAS-PEC20	40.03 ± 8.37	189.67 ± 28.70	79.14 ± 1.95

above study was investigated. Interestingly, we could not obtain any hydrogel when 0.1% MBA was used. In addition, no hydrogel was successfully obtained in the presence of 0.05% and 0.1% PPS. It could be speculated that the introduction of PEC interrupted the formation of the hydrogel due to the contact obstacles of AA, MBA and PPS. Therefore, the volume expansion ratios of the available hydrogels are shown here. As observed in Figs. 3 and 4, all of the hydrogels with PEC had a higher volume expansion ratio in water than the PAAS hydrogel without PEC. This indicated that the introduction of PEC improved the volume expansion ratio of the PAAS-PEC hydrogel because of the good hydrophilicity of PEC. As shown in Fig. 4(a), the PAAS-PEC hydrogel had a volume expansion ratio in water of 454.8 \pm 16.7%, 269.1 \pm 14.7% and 263.4 \pm 4.3% when 0.3%, 0.5% and 0.7% MBA were used, respectively. This result further verified the volume expansion ratio decreased with increasing MBA content, which led to the increase of crosslinking density. As observed in Fig. 4(b), the volume expansion ratio in water of the PAAS-PEC hydrogel increased from $204.3 \pm 17.5\%$ to $300.2 \pm 4.9\%$

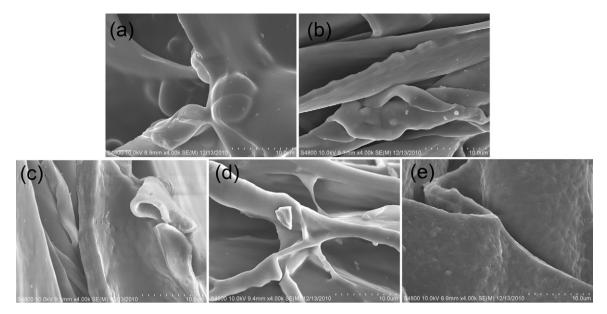


Fig. 5. SEM micrographs of the PAAS-PEC hydrogels with different PEC concentrations. (a) PAAS; (b) PAAS-PEC5; (c) PAAS-PEC10; (d) PAAS-PEC15; (e) PAAS-PEC20.

with the increase of PPS content from 0.3% to 0.7%. This tendency was consistent with the PAAS hydrogels, which was due to the formation of ideal polymer network with increasing PPS content.

As shown in Fig. 4, the volume expansion ratios of the PAAS–PEC hydrogels were appreciably reduced in simulated biological solution (PSW and PBS) when compared to the values measured in water. This was due to the existence of large amount of Na $^+$, which resulted in the decrease of osmotic pressure. Different with the PAAS hydrogel, the volume expansion ratio of the PAAS–PEC hydrogels in PSW and PBS exhibited a minimum when 0.5% MBA and 0.5% PPS was used, which was $37.1\pm1.6\%$ and $48.8\pm1.0\%$, respectively. Furthermore, the volume expansion ratio trend of the PAAS–PEC hydrogels in PSW and PBS is different with that in water. This suggested that both the salt concentration and the presence of PEC influenced the volume expansion ratio of the PAAS–PEC hydrogel. However, more experiments were still needed to elucidate their relationship.

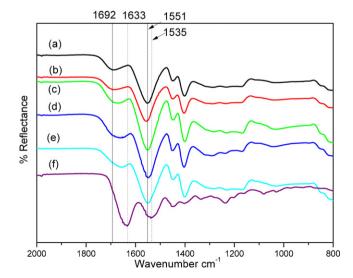


Fig. 6. FTIR of the PAAS, PEC and PAAS–PEC hydrogels with different PEC concentrations. (a) PAAS; (b) PAAS–PEC5; (c) PAAS–PEC10; (d) PAAS–PEC15; (e) PAAS–PEC20; (f) PEC.

The effect of weight ratio of PEC to AA ranged from 5% to 20% on the volume expansion ratios of the PAAS-PEC hydrogels was investigated and the results are shown in Fig. 4(c). It was observed that all of the hydrogels with PEC showed higher volume expansion ratio than PAAS probably due to the hydrophilicity of the PEC. The PAAS-PEC5 hydrogel showed a maximum expansion ratio in water of 294.6 \pm 4.7% compared to 164.5 \pm 3.8% in case of PAAS hydrogels. Interestingly, the volume expansion ratio of the PAAS-PEC5 hydrogel (30% AA was used) was just between that of PAAS with 20% AA and 25% AA, which further indicated PEC improved the volume expansion ratio of PAAS because of the interruption of polymer network in the presence of PEC. However, the volume expansion ratio in water of the PAAS-PEC hydrogels decreased with increasing PEC content, which indicated the formation of hydrogen bond between the PAAS and PEC. At higher PEC content, the PAAS-PEC hydrogel network was strengthened by hydrogen bonds, thereby hindered mobility and relaxation of the polymer chains, which in turn increased the resistance of water absorption. After swelling in PSW, the PAAS-PEC hydrogels showed an increase tendency with the increase of PEC content when PEC content was less than 5%, which showed values between $31.1 \pm 0.4\%$ and $40.6 \pm 0.8\%$. Further increasing PEC content to 20% resulted in a gentle decrease of the volume expansion ratio. Nonetheless, the volume expansion ratios in PBS of the PAAS-PEC hydrogels showed an increase until PEC content increased to 15%. After that, they showed a decrease, which were between 37.8 \pm 1.0% and 48.8 \pm 1.0%. The different ionic strengths of PSW and PBS may result in the difference of the volume expansion ratio of the PAAS-PEC hydrogels.

3.3. Effects of weight ratio of PEC to AA on the mechanical properties of the PAAS–PEC hydrogels

The tissue expander hydrogels designed for orbital implant need to have considerable mechanical strength at physiological conditions to resist in vivo stresses. All mechanical tests were carried out with fully hydrated hydrogel samples in PBS. The elastic modulus, fracture stress and fracture strain of the hydrogels are summarized in Table 1. The PAAS hydrogel has an elastic modulus of 64.28 ± 14.34 kPa, an ultimate compressive stress of about 289.24 ± 25.99 kPa and an ultimate strain of about 81.62 ± 14.34 %. The addition of pectin into the hydrogel decreased the elastic modulus and the ultimate compressive stress. The effect may be

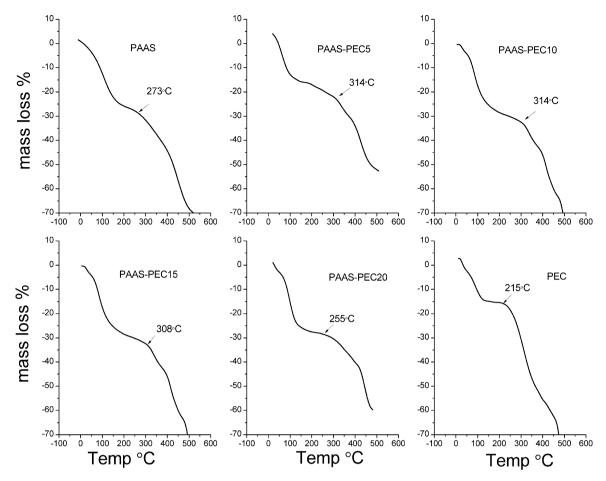


Fig. 7. TG of the PAAS, PEC and PAAS-PEC hydrogels with different PEC concentrations.

explained on the basis of formation of looser networks, due to the polyanionic nature of pectin, which resulted in the higher volume expansion ratio. With increasing the pectin content, the elastic modulus and ultimate strain of the PAAS-PEC hydrogels did not change a lot. Compared with the other hydrogels, such as the cellulose-based hydrogels (Chang, Duan, & Zhang, 2009), the cationic starch-based hydrogels (Li, Xu, Wang, Chen, & Feng, 2009), the superporous hydrogels of poly (acrylamide-co-acrylic acid)/polyethylenimine (Kim & Park, 2004) and the hydrogels based on dextran and gelatin (Liu & Chan-Park, 2009), the PAAS-PEC hydrogels have higher compressive strength. They also have similar compressive strength with the silk fibroin/polyacrylamide semiinterpenetrating network hydrogels (Mandal, Kapoor, & Kundu, 2009), which was fabricated for potential tissue engineering and biomedical applications. Therefore, the excellent mechanical properties of the PAAS-PEC hydrogels exhibited with high water absorption would facilitate its application for orbital implant or other biomedical materials.

3.4. The SEM of the PAAS-PEC hydrogels

SEM micrographs of the cross-section of the PAAS and the PAAS-PEC hydrogels with various compositions are observed and shown in Fig. 5. As observed, PAAS showed a smooth surface, whereas the PAAS-PEC hydrogels showed a relatively rough surface. However, we could not infer from the surface micro-morphology change that the introduction of PEC may influence the penetration of water into the polymeric network. Therefore, the structure of the hydrogels was further studied.

3.5. The FTIR of the PAAS-PEC hydrogels

As observed in Fig. 4(c), the introduction of PEC resulted in the increase of the volume expansion ratio of the PAAS-PEC hydrogel. This was probably due to the formation of new structure between PAAS and PEC, since we could hardly speculate the reason from SEM results. To investigate the complex formation between PAAS and PEC, FTIR were conducted. Fig. 6 shows the FTIR spectra of PAAS, PEC and the PAAS-PEC hydrogels with different PEC contents. The FTIR spectra of PEC showed the typical peak at 1633 cm⁻¹, which was assigned to the vibration of C=O of the carboxyl (Fellah, Anjukandi, Waterland, & Williams, 2009; Synytsya, Copikova, Matejka, & Machovic, 2003). The FTIR spectra of the PAAS-PEC hydrogels were similar to those of PAAS. For the PAAS-PEC hydrogels, the intensity of the characteristic peak at 1692 cm⁻¹, which could be observed clearly in PAAS, decreased gradually, and new absorption bands were observed between 1690 cm⁻¹ and 1655 cm⁻¹. This indicated that new intermolecular hydrogen bond interaction in the hydrogel was formed, which was in evidence that hydrogen bond interactions of the PAAS hydrogel were replaced by hydrogen bond interactions between PAAS and PEC. According to the above investigation, -OH on the surface of PEC reacted with acrylic acid, which could improve the polymeric network, and then enhance the volume expansion ratio.

3.6. The TG of the PAAS-PEC hydrogels

The TG of PAAS, PEC, and the PAAS–PEC hydrogels is shown in Fig. 7. It was observed that PEC had lower thermal stability than PAAS. The weight loss around 273 °C of PAAS was attributed to its

decomposition, whereas PEC showed decomposition at 215 °C. It was interesting to note that $T_{\rm d}$ (decomposition temperature) of the PAAS–PEC hydrogels was higher than that of pure PAAS or PEC, which indicated that the hydrogen bond between PAAS and PEC could stabilize the composites. However, with the increase of PEC content, the $T_{\rm d}$ of the hydrogel decreased because of the lower stability of PEC. In the case of the PAAS–PEC hydrogels, since the chains were more closely entangled together, the volume expansion ratio in water decreased with increasing PEC content.

4. Conclusion

This study has demonstrated the successful fabrication and the volume expansion ratios of the synthetic PAAS-PEC hydrogels for applying in the orbital implant. From these studies it could be concluded that the volume expansion ratios of the PAAS-PEC hydrogels were dependent upon the composition as well as the MBA and PPS content. The PAAS-PEC hydrogels exhibited higher volume expansion ratios in water, PSW and PBS than the PAAS hydrogels. By adjusting the MBA content, PPS content and the weight ratio of AA to PEC, the volume expansion ratio of the PAAS-PEC hydrogels in PSW and PBS can be manipulated in the range of 31-68%. In addition, this hydrogels possess relatively high compressive strength making it desirable for orbital implant or other biomedical materials. The results of IR and TG indicated that hydrogen bond formed between PAAS and PEC, which led to the decrease of the volume expansion ratio in water with increasing PEC content. This study could not only give valuable information about the volume expansion ratio and mechanical properties of the PAAS-PEC hydrogels, but also provide a research foundation for the synthesis of other acrylate-based polymers. For orbital implant applications, biocompatibility of the hydrogels is also important consideration, which is currently in progress and will be reported soon.

Acknowledgements

This research work was supported by the army medical technology "12th Five-Year Plan" scientific research projects of China (Surface Project).

References

- Burugapalli, K., Bhatia, D., Koul, V., & Choudhary, V. (2001). Interpenetrating polymer networks based on poly(acrylic acid) and gelatin. I: Swelling and thermal behavior. John Wiley & Sons, Inc., pp. 217–227.
- Chang, C., Duan, B., Cai, J., & Zhang, L. (2010). Superabsorbent hydrogels based on cellulose for smart swelling and controllable delivery. *European Polymer Journal*, 46(1), 92–100.
- Chang, C., Duan, B., & Zhang, L. (2009). Fabrication and characterization of novel macroporous cellulose-alginate hydrogels. *Polymer*, 50(23), 5467–5473.

- Changez, M., Burugapalli, K., Koul, V., & Choudhary, V. (2003). The effect of composition of poly(acrylic acid)-gelatin hydrogel on gentamicin sulphate release: In vitro. *Biomaterials*, 24(4), 527–536.
- Changez, M., Koul, V., & Dinda, A. K. (2005). Efficacy of antibiotics-loaded interpenetrating network (IPNs) hydrogel based on poly(acrylic acid) and gelatin for treatment of experimental osteomyelitis: In vivo study. *Biomaterials*, 26(14), 2095–2104.
- Chen, J., & Zhao, Y. (2000). Relationship between water absorbency and reaction conditions in aqueous solution polymerization of polyacrylate superabsorbents. John Wiley & Sons, Inc., pp. 808–814.
- Coimbra, P., Ferreira, P., de Sousa, H. C., Batista, P., Rodrigues, M. A., Correia, I. J., et al. (2011). Preparation and chemical and biological characterization of a pectin/chitosan polyelectrolyte complex scaffold for possible bone tissue engineering applications. *International Journal of Biological Macromolecules*, 48(1), 112–118.
- de la Torre, P. M., Torrado, S., & Torrado, S. (2003). Interpolymer complexes of poly(acrylic acid) and chitosan: Influence of the ionic hydrogel-forming medium. *Biomaterials*, 24(8), 1459–1468.
- Deligkaris, K., Tadele, T. S., Olthuis, W., & van den Berg, A. (2010). Hydrogel-based devices for biomedical applications. Sensors and Actuators B-Chemical, 147(2), 765–774.
- Fellah, A, Anjukandi, P., Waterland, M. R., & Williams, M. A. K. (2009). Determining the degree of methylesterification of pectin by ATR/FT-IR: Methodology optimisation and comparison with theoretical calculations. *Carbohydrate Polymers*, 78(4), 847–853.
- Katav, T., Liu, L., Traitel, T., Goldbart, R., Wolfson, M., & Kost, J. (2008). Modified pectin-based carrier for gene delivery: Cellular barriers in gene delivery course. *Journal of Controlled Release*, 130(2), 183–191.
- Kim, D., & Park, K. (2004). Swelling and mechanical properties of superporous hydrogels of poly(acrylamide-co-acrylic acid)/polyethylenimine interpenetrating polymer networks. *Polymer*, 45(1), 189–196.
- Kopecek, J. (2007). Hydrogel biomaterials: A smart future? Biomaterials, 28(34), 5185–5192.
- Li, X., Xu, S., Wang, J., Chen, X., & Feng, S. (2009). Structure and characterization of amphoteric semi-IPN hydrogel based on cationic starch. *Carbohydrate Polymers*, 75(4), 688–693.
- Liu, Y., & Chan-Park, M. B. (2009). Hydrogel based on interpenetrating polymer networks of dextran and gelatin for vascular tissue engineering. *Biomaterials*, 30(2), 196–207.
- Liu, L., Won, Y. J., Cooke, P. H., Coffin, D. R., Fishman, M. L., Hicks, K. B., et al. (2004). Pectin/poly(lactide-co-glycolide) composite matrices for biomedical applications. *Biomaterials*, 25(16), 3201–3210.
- Mandal, B. B., Kapoor, S., & Kundu, S. C. (2009). Silk fibroin/polyacrylamide semiinterpenetrating network hydrogels for controlled drug release. *Biomaterials*, 30(14), 2826–2836.
- Mazzoli, R. A., Raymond, W. R. I., Ainbinder, D. J., & Hansen, E. A. (2004). Use of self-expanding, hydrophilic osmotic expanders (hydrogel) in the reconstruction of congenital clinical anophthalmos. *Current Opinion in Ophthalmology*, 15(5), 426–431.
- Mohnen, D. (2008). Pectin structure and biosynthesis. Current Opinion in Plant Biology, 11(3), 266–277.
- Schittkowski, M. P., Katowitz, J. A., Gundlach, K. K. H., & Guthoff, R. F. (2006). Self-inflating hydrogel expanders for the treatment of congenital anophthalmos. In *Oculoplastics and orbit*. Berlin, Heidelberg: Springer., pp. 205–221.
- Synytsya, A, Copikova, J., Matejka, P., & Machovic, V. (2003). Fourier transform Raman and infrared spectroscopy of pectins. *Carbohydrate Polymers*, 54(1), 97–106.
- Zhang, J., Wang, Q., & Wang, A. (2007). Synthesis and characterization of chitosan-g-poly(acrylic acid)/attapulgite superabsorbent composites. *Carbohy-drate Polymers*, 68(2), 367–374.
- Zhou, W., Zhang, Y., Jin, K., Qiu, X., Ren, X., Hu, S., et al. (2009). Synthesis and characterization of functionalized acrylic-acrylamide-based superabsorbent gels. Wiley Subscription Services, Inc., A Wiley Company., pp. 2828– 2836.