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Original Article

Swelling property of PVA hydrogels with different concentration and specifications and its influencing factors

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Abstract: Aim: This study aimed to prepare polyvinyl alcohol (PVA) hydrogel with the physical cross linking and then explore the water-swelling property of PVA hydrogels with different concentration and specifications. Methods: The cryodesiccated PVA hydrogels were swelled again using simulated body fluid (SBF) to observe the time-varying swelling law of PVA hydrogels with different concentration. Besides, PVA xerogel with different specifications were soaked in SBF to compare the effects of their size and shape on the water absorption rate of PVA hydrogels. Results: The volume of PVA gels was significantly different at the time of pre-drying, post-drying and reswelling. The swelling degree of PVA hydrogels with different concentration was also different. 25% PVA hydrogel swelled the fasted at the beginning of swelling, while 15% PVA hydrogel had a significantly high swelling rate than the other two types at last. All the PVA hydrogels soaked in 37°C SBF swelled fast that the volume swelling rate of them could be up to 5 times within 10 days. In addition, the lamelliform PVA hydrogel had the largest water absorption rate, indicating that the bigger specific surface area and smaller size of PVA hydrogels matched with faster equilibrium rate. Conclusion: in the study, the maximum volume swelling rates of PVA hydrogels in SBF were all larger than 5, indicating that they could use for the increment of oral soft tissues.

Keywords: Polyvinyl alcohol, hydrogel, swelling

Introduction

Implant restoration is a procedure that the implant is first surgically implanted into the jaw or under the periosteum and then the denture restoration is completed at the abutment which crosses the alveolar ridge mucosa [1-3]. With the loss of teeth, there will be different degrees of damage in both soft tissues and hard tissues. As a result, the early healing and long-term effects of implant, as well as the beauty, will be affected because of no ideal implanting site and soft tissue morphology [4, 5]. Furthermore, merely increased bone mass with insufficient soft tissue may lead to the implantation failure.

Currently, augmentation methods of soft tissues surrounded the implant are mainly as follows: Pedicled Mucosal Flap Transfer Operation, Subepithelial Connective Tissue Implantation and Free Gingival Autograft Operation [6]. However, all these methods could only increase limited soft tissue and are easy to induce bone dehiscence and infection of the operating field. In addition, the Spontaneous in Situ Gingival Augmentation reported by Langer can only applied for the teeth with residual root [7, 8]. Therefore, a simple, quick and safe method for the expansion of soft tissue in situ is urgently needed.

Polyvinyl alcohol (PVA) is a type of novel functional polymer materials. Its aqueous solution can be prepared into polyvinyl alcohol hydrogel via physical crosslinking, which is characterized by very small size after drying [9, 10]. PVA hydro-

Table 1. The component of SBF and body fluid

Lon	Concentration (mmol/mL)	
	SBF	Body fluid
Na^+	142.0	142.0
K^+	5.0	5.0
Mg^{2+}	1.5	1.5
Ca^{2+}	2.5	2.5
Cl^-	147.8	103.0
HCO^{3-}	4.2	27.0
HPO_4^{2-}	1.0	1.0
SO_4^{2-}	0.5	0.5

gel is regarded as a promising biomedical materials owing to such advantages as easy implantation into the body, favorable swelling property, super biocompatibility and stable structure especially [11, 12]. At present, PVA has been used in the synthesis of tissue materials such as artificial cornea, artificial pancreas, artificial nucleus and artificial articular cartilage [13, 14]. Besides, PVA can also be applied as the stent of slow-released drugs and used as test specimens. In view of good properties and remarkable medical achievements of PVA hydrogel, we attempted to implant it into oral mucosal tissue as an expanding material.

In this study, polyvinyl alcohol hydrogel was prepared via physical crosslinking with an attempt to provide experimental basis for its application to soft tissue augmentation in dental implant.

Materials and methods

Materials

Polyvinyl alcohol (polymerization degree: 1750 ± 50, alcoholysis degree > 99%) was obtained from Alfa Aesar (USA). The simulated body fluid (FBF) was provided by M&C GENE TECHNOLOGY (BEIJING) LTD. The lysozyme was purchased from Amres Co. (USA). Dehydrated alcohol was a kind gift of Shantou Dahao Fine Chemical Co. Phosphate buffered saline (PBS) was obtained from Fuzhou Maixin Biotech. Co. Finally, the deionized water was made in our laboratory.

Preparation of polyvinyl alcohol hydrogel

Moderate PVA was mixed with deionized water in a flask with two mouths and the mixture was fully stirred to dissolve at the indoor temperature for 30 minutes; and then the flask was moved into an oil bath pan with magnetic stirring to slowly heat up to 85°C. The mixture was stirred for 5 h at constant temperature. After that, the temperature of the flask was elevated to 90°C and then maintains for 30 min. Totally dissolved PVA solution was transferred into a homemade glass mould. Physical crosslinking was performed at -20°C for 20 hours and then unfreezing was conducted at 25°C for 4 hours. Gel-like PVA was made after repeating several times and soaked in deionized water until use.

Superficial syndrome of polyvinyl alcohol hydrogel

The two types of PVA hydrogels (15% PVA gel and 25% PVA gel) with high molecular weight were cut into sections with a size of 20 mm × 5 mm × 5 mm after freeze crosslinking. Several sections were randomly selected from the same gel before and after drying and at the secondary swelling, respectively. The change of hydrogels in surface morphology and volume was first recorded by a digital camera, and then the hydrogels were gilded and observed under a scanning electron microscope (resolution ratio: 22.0 mm; largest acceleration voltage: 18.0 kv).

Swelling rate study on PVA hydrogels of different concentration in simulated body fluid

The PVA with high molecular weight was selected and suffered freeze crosslinking for 5 times to prepare PVA hydrogels with the concentration of 15%, 20% and 25%, respectively. Three samples of each kind of hydrogen were prepared. The fully dried gels were soaked in simulated body fluid (SBF, **Table 1**) and their quality and volume were measured at regular intervals until PVA hydrogel got swelling equilibrium again (mass change within 24 hours < 2%).

The mass swelling rate computational formula of PVA hydrogel.

$$Sm = M_t/M_0 \times 100\% \quad \text{(Formula 1)}$$

M_0: initial dried hydrogels mass; M_t: hydrogels mass at t hour.

The volume swelling rate computational formula of PVA hydrogel.

$$Sv = V_t/V_0 \times 100\% \quad \text{(Formula 2)}$$

Figure 1. The PVA hydrogel in physical crosslinking.

Figure 2. The PVA hydrogel in drying.

V_0: initial dried hydrogels volume; V_t: hydrogels mass at t hour.

The effects of hydrogel in size and shape on water absorption rate

The high molecular weight PVA hydrogel with a concentration of 15% was made into sections with 4 different sizes after 5 times of physically crosslinking: cuboid of 20 mm × 6 mm × 6 mm, cube of 20 mm × 20 mm × 20 mm, cylinder with 5 mm radius and 10 mm height and slice with 0.5 mm thickness, 20 mm length and 20 mm width. Each specification of hydrogel was identified 3 samples.

We measured the mass of PVA hydrogel M_0 and volume V_0 after dried and then soaked them into SBF at 37°C. PVA hydrogel was took out to dry the surface moisture every 24 hours and measured M_t and V_t. A 10-day of continuous measurement was conducted to calculate the swelling rate of various specification of PVA hydrogel.

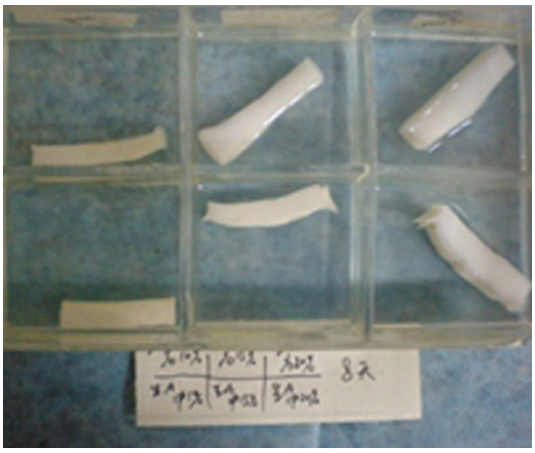

Figure 3. The reswelling PVA hydrogel.

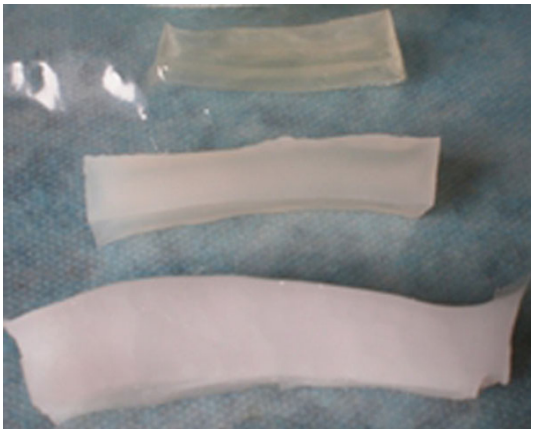

Figure 4. The comparison after and before drying.

Results

Surficial syndrome of polyvinyl alcohol hydrogel

The PVA hydrogel formed by physically freezing-unfreezing crosslinking showed a well film-forming property and intensity on the surface (**Figure 1**). **Figure 2** indicated a significant decrease of volume and change of shape in part of the gel during the cryodesiccation. With the increase of water absorption, the volume of the reswelling-PVA hydrogel significantly increased (**Figure 3**). **Figure 4** revealed the obvious difference of PVA gel in volume and shape before and after dying as well as during reswelling.

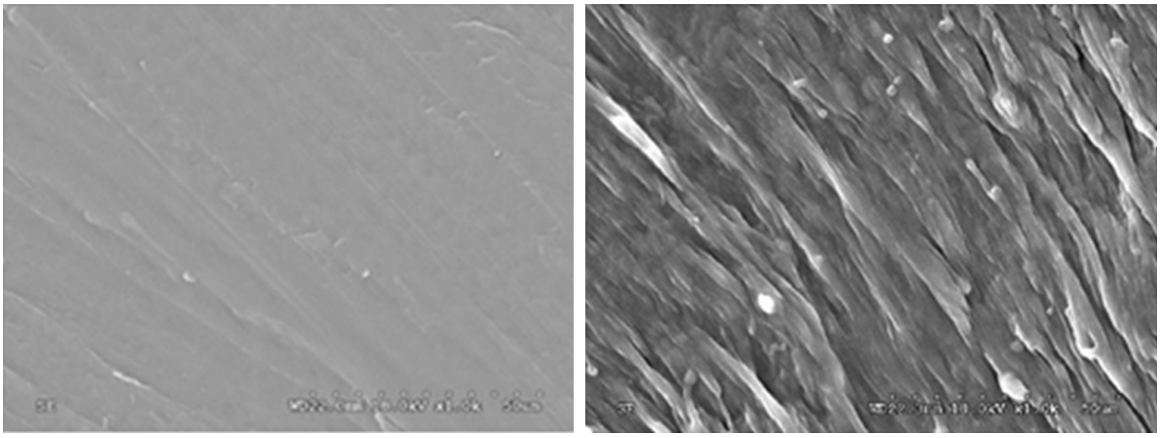

Figure 5. The configuration of PVA hydrogel experienced once and 5 times of refrigeration cycle (SEM × 900).

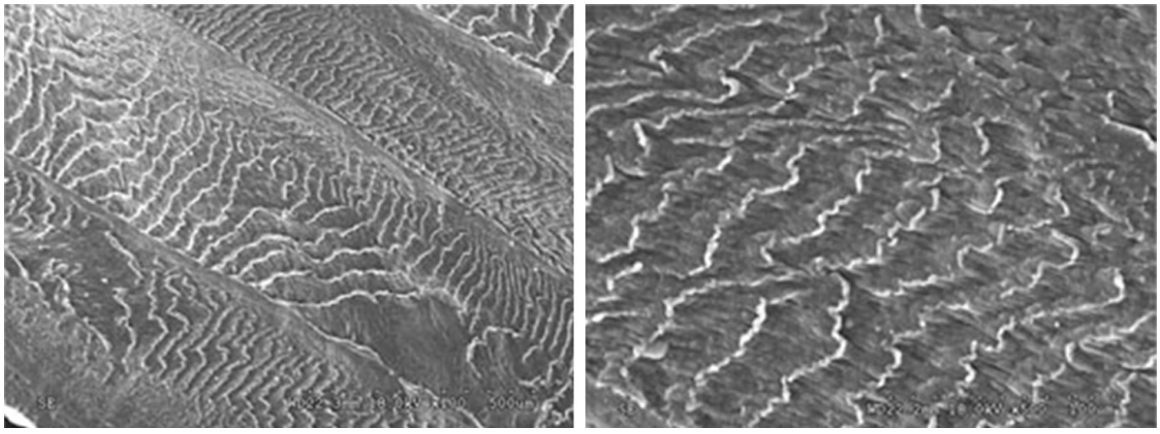

Figure 6. The surface configuration of the 25% PVA hydrogel after drying (SEM × 500).

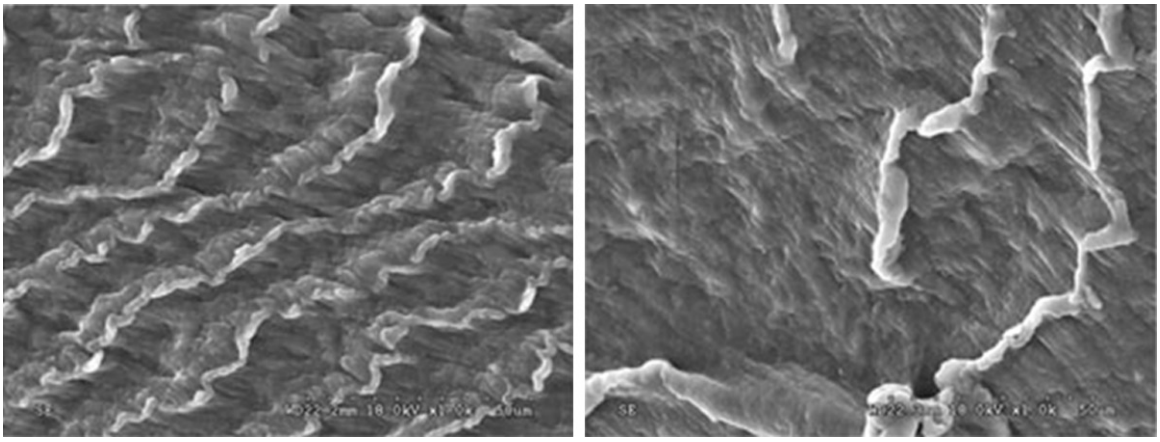

Figure 7. Configuration of surface of the 15% PVA hydrogel after drying (SEM × 1.0 k).

PVA hydrogel experienced once and 5 times of refrigeration cycle presented with an even and compact net structure on the surface; however, the former could see no obvious mesh (**Figure 5**). **Figure 6** was the surface configuration of PVA hydrogel with a concentration of 25% after

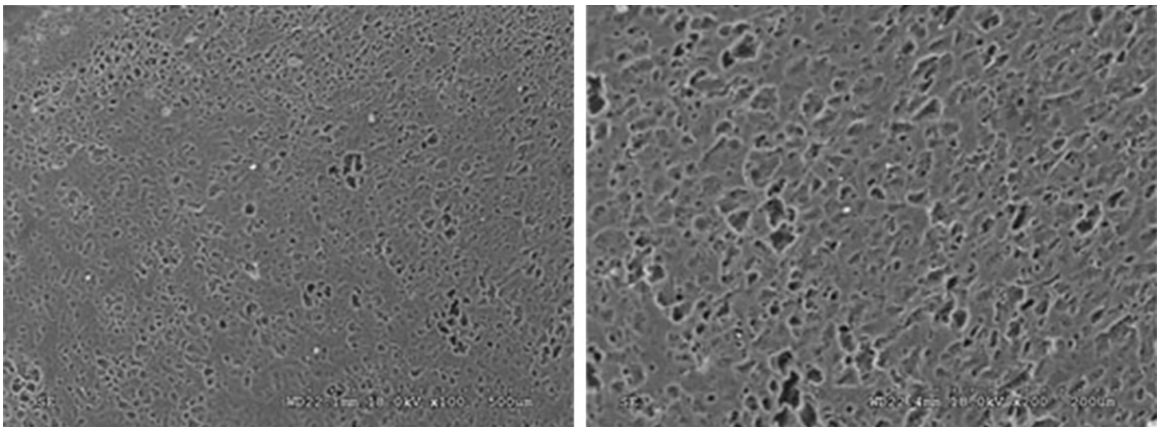

Figure 8. The surface configuration of the 25% PVA hydrogel after being soaked in water for a month (SEM × 200).

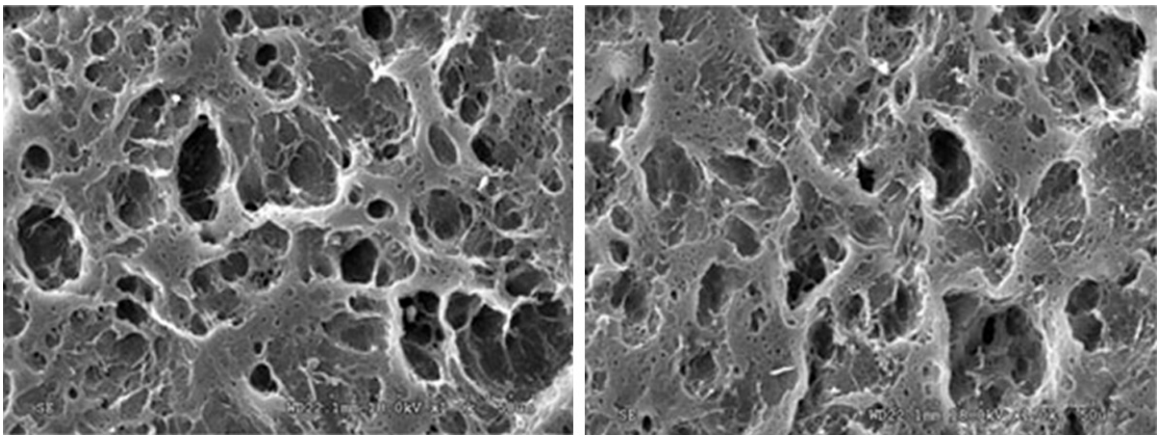

Figure 9. The surface configuration of the 15% PVA hydrogel after being soaked in water for a month (SEM × 1.0 k).

drying and **Figure 7** was the surface configuration of PVA hydrogel with a concentration of 15%. The surface of the two kinds of PVA hydrogel was uneven and regularly cord-like. The low concentration revealed a more significant change in surface shape and a more compact net structure, without obvious mesh structure.

After being soaked in the water for 30 days, the surface network structure of PVA hydrogel became lose with cavity among and within the network (**Figures 8**, **9**). It could be concluded from the figures that the network structure of 25% gel was more compact than that of 15% gel, with smaller gridding, indicating that increasing the concentration could still improve the density of the network to a certain extent.

Swelling degree of PVA gel of different concentration in simulated body fluid (SBF)

As shown in **Figure 10A**, the swelling trend of PVA gel of different concentration in 37°C simulated body fluid was as follows: 1) at the beginning of the swelling, the speed of 25% PVA hydrogel was higher than that of the rest two groups; and at the third day, the swelling degree reached 3.49, which was almost 84% of the maximum swelling degree (4.15). 2) Hydrogel samples with various concentrations showed different volume swelling speed, and within 72 hours, volume of PVA gel in groups with different concentration all exceeded 3 times the original volume.

As shown in **Figure 10B**, although the initial swelling speed of 15% PVA gel was relatively slow, its volume was increasing all the time, which tended to be stable on the 10th to the 12th day and was 5.3 times the initial volume. The swelling speed of 15% PVA hydrogel is the largest among the three kinds of PVA gel with the peak (5.33) higher than those of the others significantly.

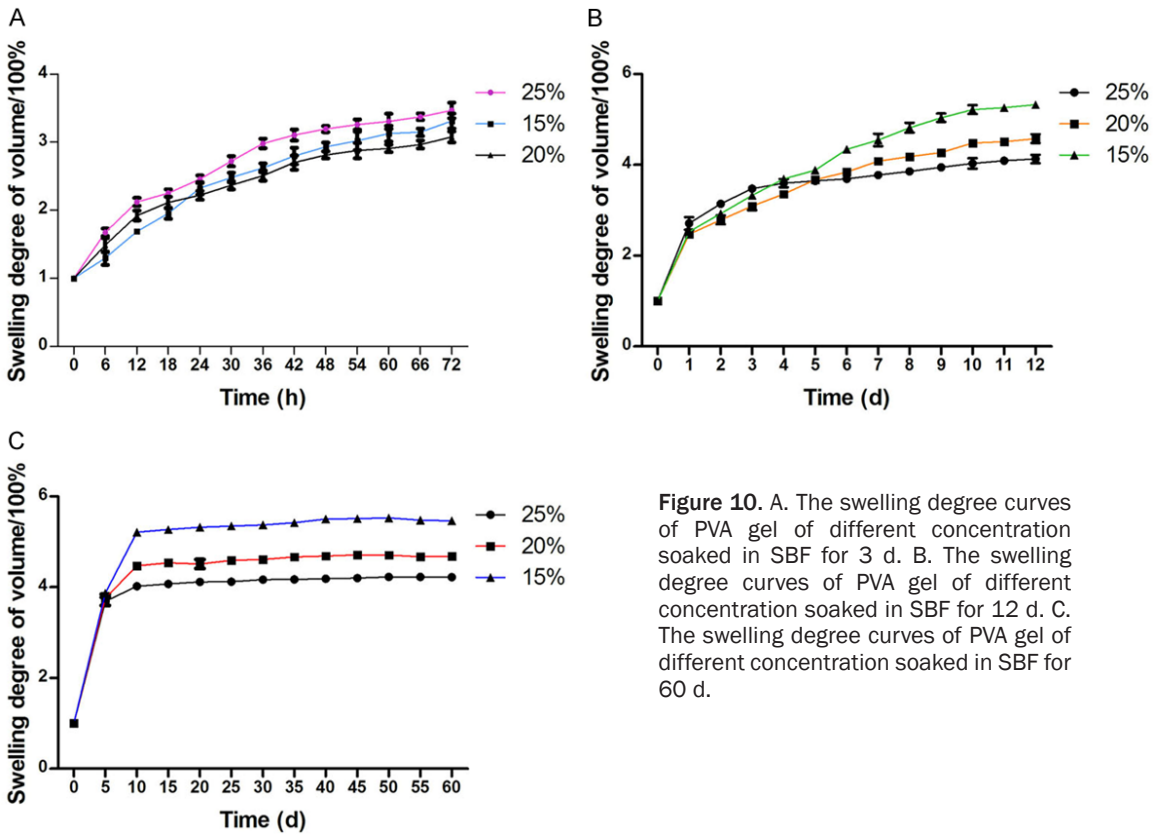

Figure 10. A. The swelling degree curves of PVA gel of different concentration soaked in SBF for 3 d. B. The swelling degree curves of PVA gel of different concentration soaked in SBF for 12 d. C. The swelling degree curves of PVA gel of different concentration soaked in SBF for 60 d.

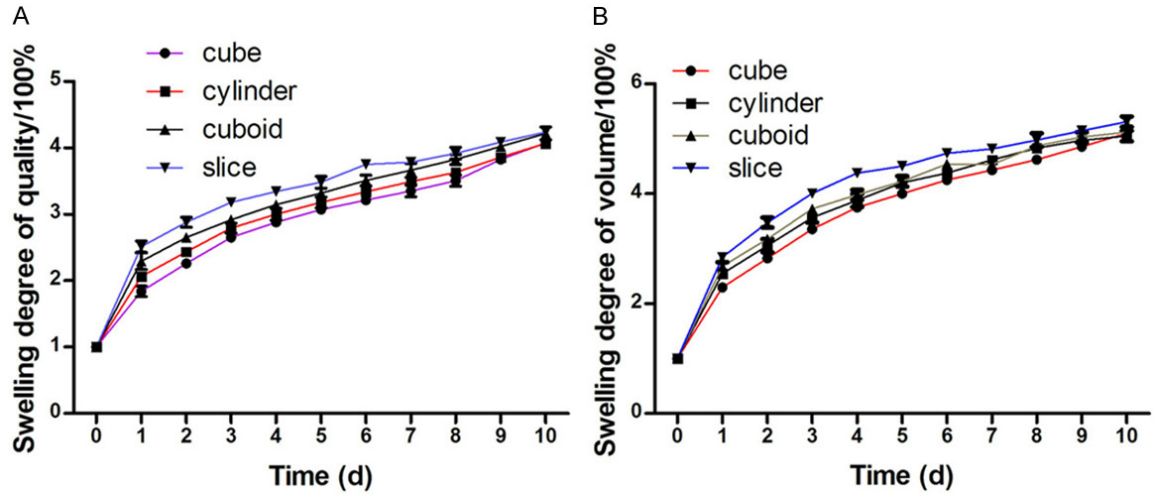

Figure 11. A. The quality swelling degree curves of PVA gel with different size soaked in SBF for 10 d. B. The volume swelling degree curves of PVA gel with different size soaked in SBF for 10 d.

Figure 10C showed the volume swelling degree of PVA gel samples of different concentration soaked for 60 d. The sample volume in each group all increased rapidly in the beginning, and came to a peak after a period of time. Then it turned to be stable, and finally became smaller at a low speed after a period of time. PVA gels of different concentration showed different volume swelling speed, different swelling peak spot, different period and degree of diminution. The volume of 25% PVA hydrogel was still stable on the 60th day of immersion with

no trend of diminution, while that of 15% PVA gel started to decrease on the 50th day with the trend of diminution.

The influence of size and shape on the bibulous rate of PVA gel

Figure 11A showed the quality change curves of different PVA gel with the mass concentration of 15% soaked in SBE under 37°C. As shown in the figure, lamelliform PVA gel absorbed a lot of water in a few days with the highest water absorption rate, while others showed relatively low rate, especially the square type with the lowest rate. Although the swelling degree of different samples was different, there was little difference. It demonstrated that PVA gel of the same concentration and different shape and size showed different equilibrium rate and equilibrium point when being soaked. With smaller size and larger surface area, the speed of reaching balance of PVA being soaked is higher. **Figure 11B** showed the change result of gel volume in this group. The change trend of each specimen in volume and mass was the same, but the swelling degree of volume was significantly higher than that of quality at the corresponding time.

Discussion

After drying, the volume of the PVA hydrogel is less than 20% of the initial volume in the present study, which can greatly facilitate surgical implants, decrease the wound and reduce pain in patients [15]. Implanting the dried PVA hydrogel into body is followed by a re-swelling process, so it is necessary to study the re-swelling performance of PVA hydrogel.

When the dry gel is put into the water, the water molecules would firstly combine with the polar hydrophilic group or hydroxyl groups which can form hydrogen bond, forming the primary combined water. Then the macromolecular chain begin to stretch and hydrophobic groups start to form a layer of secondary combined water around themselves by hydrophobic interaction [16, 17]. When the short-range interaction of these water molecules with the groups of the macromolecules is completed, the network continues to absorb water. Due to osmotic pressure, the gap of the network and big holes are filled with water molecules until getting the swelling equilibrium of the gels [18, 19].

Due to interconnection of the molecular chains of PVA hydrogel, swelling is not only a collaborative diffusion, but also a relaxation process. The components constituting the network, namely part of the polymer chains (such as part of the chains between the junction points), do not move independently but move in coordination with other part of the chains. Hence, the spread of part of the chains is not free, but the synergy diffusion. The synergy diffusion speed is much slower than the free diffusion of the solvent itself. So when the PVA hydrogel is soaked in the water, due to the osmotic pressure inside and outside of the gel, at first there would be a lot of water molecules spreading into the gel, which leads to the swelling state in gel water absorption, with the quality and volume increased. This is a slow process, in which PVA physical crosslinking network is in the state of adjustment and change and molecular chains between junction points extend gradually, as well as PVA macromolecules not involved in crosslinked state move out of the gel. When the osmotic pressure inside and outside of the gel reaches balance, its quality and volume will become stable gradually [20].

The greater the concentration of PVA hydrogel is, the more the microcrystalline area and the physical junction joints are during the thawing process. This will shorten the distance between the physical junction joints, decrease the size of the holes, increase the junction degree, and thus improve the water absorption capacity of the network [21]. So after the maximum of water absorption, the higher the concentration of PVA hydrogel is, the slower the water loss speed is, and the longer the time for reaching balance is.

The volume change rate of PVA hydrogel with different concentration in SFB is basically the same with that in water, but is always smaller than that in water. It may be due to that, when soaked in SBF, the osmotic pressure inside and outside of the gel is lower, resulting in the water absorption rate is smaller. When soaked in water, because of the osmotic pressure inside and outside of the gel, a large number of water molecules spread into the gels and therefore the quality and volumes are both increased. In the process, PVA physical crosslinking network is also adjusted and changed. Those PVA macromolecules that do not involve in crosslinking also move out of the gels, which is a slow pro-

cess. Despite the same trend of swelling degree and volume change of PVA hydrogel in SBF and water, the ions existed in SBF significantly affect the final structure of the crosslinking network. The swelling degree and volume change rate of PVA hydrogel with different concentration are basically the same in SBF and water.

This study illustrated that when soaked in the 37°C SBF, the lamelliform 15% PVA gel absorbed a lot of water in a few days, with the highest water absorption rate, while gels with other shapes showed relatively low rate, especially the square type. Thereby, we could conclude that when soaked in the same solution, gels with the same concentration, different shape and size had different equilibrium rates and points. In general, the smaller the size and the larger the specific surface area are, the faster the PVA gels reach equilibrium in the soak solution. Volume change trend of each sample is the same with quality change trend, while the corresponding volume swelling degree is significantly bigger than the quality swelling degree. Relatively speaking, volume change curve is more valuable because of the considerable factors affecting the quality change.

With the PVA gels dried at common temperature and freeze drying, the re-swelling rate of the former was slower than the latter, and the swelling degree and volume change rate of re-swelling were both smaller than the first swelling. This may be due to the short distant and hydrophobic interaction of hydrogels suffered natural air-dry and re-swelling and the existence of mesh structure in gels dried via cryodesiccation.

Disclosure of conflict of interest

None.

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