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# Mechanical properties of nanohydroxyapatite reinforced poly(vinyl alcohol) gel composites as biomaterial

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**Abstract** Nanohydroxyapatite reinforced poly(vinyl alcohol) gel (nano-HA/PVA gel) composites has been proposed as a promising biomaterial, especially used as an articular cartilage repair biomaterial. In this paper, nano-HA/PVA gel composites were prepared from mixing nano-HA particles modified by silicon coupling agent, with physiological saline solution (PSS) of PVA by freezing-thawing method. The effects of various factors on the mechanical properties of nano-HA/PVA gel composites were evaluated. It was shown that the mechanical behavior of nano-HA/PVA gel composites was similar to that of natural articular cartilage, which held special viscoelastic characteristics. The tensile strength and tensile modulus of the composites improved correspondingly with the increase of freezing-thawing times and concentration of PVA solution. The more concentration of PVA solution, the higher influence degree of concentration on the tensile strength of composites is. The tensile strength and tensile modulus of nano-HA/PVA hydrogel composites increased first and then decreased with the rising nano-HA content of the composites. The tensile modulus of the composites improved remarkably with the increase of elongation ratio.

## Introduction

Poly (vinyl alcohol) (PVA) hydrogel is an excellent artificial articular cartilage repair material due to its biocompatibility and biotribological properties [1–4]. It possesses high porous structure and high content of free water, similar to that of natural articular cartilage. PVA hydrogel has increasingly attracted interest in application as an articular repairing material [5, 6]. However, it has limited durability and does not adhere well to tissue. For example, for articular cartilage applications PVA may require the use of a fixation method to achieve better adhesion. Furthermore, it is a pendent question to improve the interfacial bonding strength between the implant material and natural tissue [7].

Nano-HA has been applied widely in medical field as a bone repair material because of its excellent bioactive properties [8, 9]. Nanosized hydroxylapatite particles reinforced PVA gel composites prepared by incorporating nano-HA with PVA endows composites bioactive properties as well as the improving interfacial bonding strength between nano-HA/PVA composites and natural tissue, because of the implanted material inducing the osteoblast adhesion on and growing into the repair material and thus formed bioactive bonding at the interface. It can also improve interfacial bonding strength and mechanical compatibility between the implanted material and natural tissue. This is the effective method to improve the adhesion properties [6, 10].

In this paper, considered the equilibrium of osmotic pressure between implanted material and natural tissue, nano-HA/PVA gel composites were prepared by mixing nano-HA particles modified by silicon coupling agent, with physiological saline solution (PSS) of PVA while adopting freezing-thawing method. The influences of various factors and the content of nano-HA particles on the mechanical behavior were both investigated.

## Material and methods

### Materials

PVA was purchased from Shanghai Chemical Co., Ltd, with the degree of saponification of 99% and number-

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average degree of polymerization of 1,750 ± 50. For the synthesis of hydroxyapatite, $Ca(OH)_2$ and $H_3PO_4$ were obtained from Siopharm chemical reagent Co., Ltd., China. All the chemical reagents used here were analytical grade and without any further purification.

### Synthesis of nanohydroxyapatite and preparation of Nano-HA/PVA gel composites

First, hydroxyapatite particles were synthesized by wet chemical method. The synthesis procedure involved the drop by drop introduction of the $H_3PO_4$ solution (100 ml, 0.6 M) into an aqueous suspension of $Ca(OH)_2$ (125 ml, 0.8 M) while stirring vigorously for about 4 h at 80 °C. Ammonia solution was added to maintain the pH at 10–11. The obtained white precipitate was washed with de-ionized water and was dried in vacuum oven at 80 °C for 24 h.

The mixed solution of nano-HA and PVA was prepared by blending various weight ratios of nano-HA particles, which were modified by silicon coupling agents, with PSS of PVA. The nano-HA and PVA mixing solution was stirred continuously at 90 °C for 6 h and a homogeneous solution of polymer in physiological saline was then obtained. Subsequently, for degassing of the air trapped in solution during the stirring process, the viscous nano-HA and PVA mixed solution was stored at 60 °C for 30 min. Then, the mixture was poured into stainless steel container. Finally, the stainless steel container with nano-HA and PVA solution was subjected to various cycles of freezing at –20 °C for 14 h and thawing at room temperature for 4 h. According to this process, the different freezing-thawing cycles times (N) of nano-HA/PVA gel composite was prepared.

### Mechanical properties testing

The tensile strength measurements were performed on mechanical test equipment (Model: INSTRON 3367). In the strength test process, the nano-HA/PVA gel would easily slide from the clamps due to its smooth surface if strong clamping force is not given. Furthermore, the pressure distribution in the sample would be inappropriate due to the deformation of the tightening part place, and it may influence the test results with merely a flat board-shaped test specimen. So, dumbbell shape specimen was prepared and the mechanical test equipment was adapted for the measurement of nano-HA/PVA gel composites sample by sticking sandpaper (grid No. 240) to the geometry, which can improve the friction force between the sample and clamps. The test strain rate of the sample is 10 mm per minute.

The tensile modulus of the composites at different strain regions was determined by the finite difference method and expressed as the following equation.

$$E_\varepsilon = \frac{\sigma_{\varepsilon+\Delta\varepsilon} - \sigma_{\varepsilon-\Delta\varepsilon}}{2\Delta\varepsilon} \quad (1)$$

Where $E_\varepsilon$ is the tensile modulus of the composites as the strain achieves the value of $\varepsilon$. The value of $\Delta\varepsilon$ is 2%.

In mechanical test experiments, for a fair assessment of the contribution of the HAp nanoparticles to the mechanical properties, the weight ratio between PSS and PVA of all the nano-HA/PVA gel composites was kept constant (at 5.67).

### Transmission electron microscopy (TEM)

The microstructure of synthesized hydroxyapatite was examined and photographed in a JEM 2100 transmission electron microscope at 200 kV.

### Scanning electron microscopy (SEM)

The morphology of the nano-HA/PVA gel composites and PVA gel were observed by JSM-6380 LV scanning electron microscopy at 20 kV. All the samples were dried by vacuum oven at 70 °C for 24 h prior to SEM observation.

## Results and discussion

### Microstructure of nano-HA and composites

Figure 1 shows the morphology of synthesized HAp by TEM observation. It can be clearly seen that the synthesized HAp crystal in this study results nanometer in size. The morphology of HAp presents needle-like crystals with an average size of approximately 30–40 nm in width and 180–240 nm in length.

Figure 2 shows the SEM images of PVA gel and nano-HA/PVA gel composites after dried by vacuum oven at 70 °C for 24 h. Figure 2a shows that the microstructure of

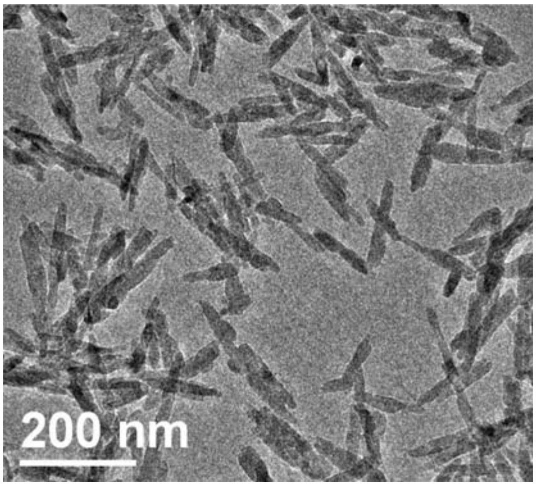
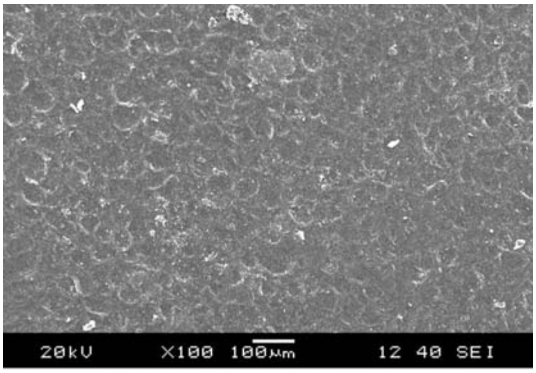
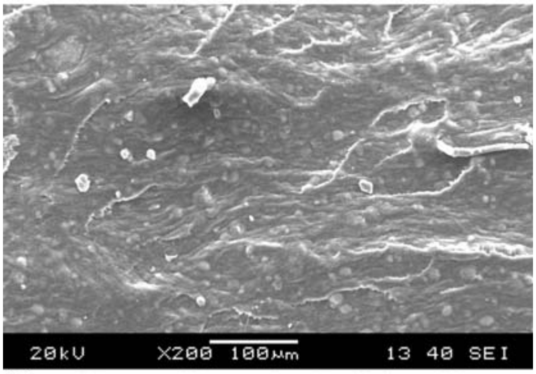


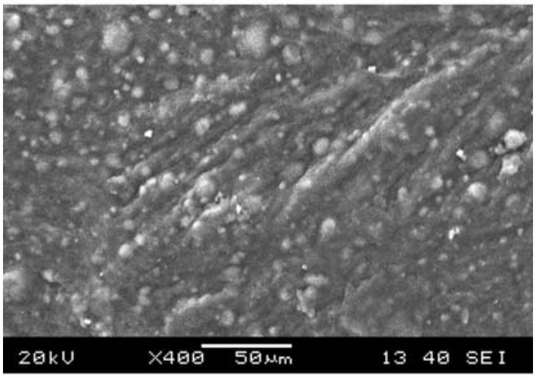
**Fig. 1** TEM micrograph of synthesized HA particles



**(a)** 15%PVA+85%PSS (by w/w), N=5



**(b)** 1.5%HA+14.8%PVA+83.7%PSS (by w/w), N=5



**(c)** 6%HA+14.1%PVA+79.9%PSS (by w/w), N=5

**Fig. 2** SEM micrograph of the composites with various weight ratio of HA particles. (**a**) 15%PVA + 85%PSS (by w/w), *N* = 5. (**b**) 1.5%HA + 14.8%PVA + 83.7%PSS (by w/w), *N* = 5. (**c**) 6%HA + 14.1%PVA + 79.9%PSS (by w/w), *N* = 5

pure PVA gel has many micropores on the surface of the specimen. For the nano-HA/PVA gel specimen (Fig. 2b, c), large number of HA particles were observed and distributed uniformly in the PVA matrix. It shows a tendency to agglomerate with an increase in nano-HA amount in PVA matrix (Fig. 2c).

## Stress-strain behavior of composites

Figure 3 shows the stress-strain characteristics of the composites with various weight ratios of nano-HA particles prepared by 5 freezing-thawing cycle times. It can be concluded from Fig. 3 that the stress-strain behaviors of all the composites present nonlinear relationship and the composites possess typical viscoelastic properties.

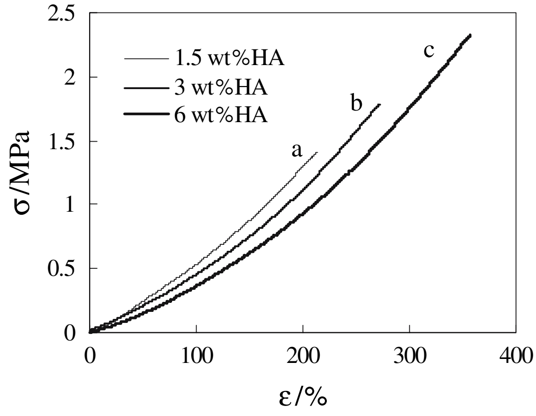


**Fig. 3** Stress-strain characteristics of the composites. (**a**) 1.5%HA + 14.8%PVA + 83.7%PSS, PSS:PVA = 5.67, *N* = 5; (**b**) 3%HA + 14.6%PVA + 82.4%PSS, PSS:PVA = 5.67, *N* = 5; (**c**) 6%HA + 14.1%PVA + 79.9%PSS, PSS:PVA = 5.67, *N* = 5

The unique mechanical behavior of nano-HA/PVA composites depends significantly on its special structure, which is composed of four parts such as amorphous region formed by PVA molecule, microcrystalline region by hydrogen bonding of intra- and inter-PVA molecular chains, nano-HA particles reinforcing phase and lots of free water among three-dimensional network structure of PVA gel. The elastic properties of the composites are attributed to the microcrystalline region of the composites and nano-HA particles. Both free water and amorphous region in the composites are beneficial to the viscous characteristics of the composites. It is indicated from Fig. 3 that the relationship between stress and strain is nonlinear and the strain ratio is much higher, which almost extends to 360%, than that of normal elastic material. Three-dimensional network structure in the composite holds lots of free spaces. These free spaces enable the polymer chains to response rapidly to the external force and polymer chains rearranged simultaneously, which ultimately results in the relatively high elongation ratio of the composites.

## Tensile strength

The effect of nano-HA content on the tensile strength of the composites prepared by 5 freezing-thawing cycle times is presented in Fig. 4, which shows that the tensile strength of the composites increased first and then slightly decreased with the increase of nano-HA content. The tensile strength of PVA gel increases from 1.43 to 2.34 MPa, increasing 64%, while the nano-HA content rises from 0 to 4.5 wt.%.

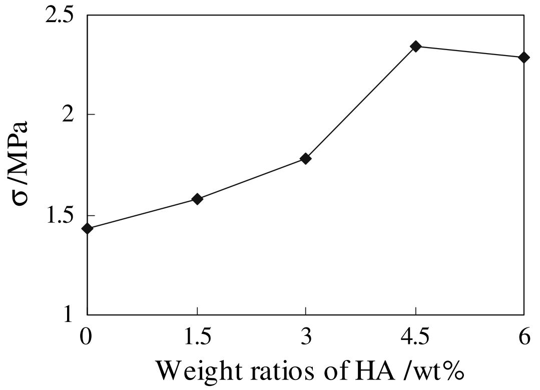


**Fig. 4** The influence of HA content of the composites on tensile strength (PSS:PVA = 5.67, *N* = 5)

As the content of nano-HA increases further, the tensile strength of the composites presents decreasing trend.

The mechanical properties of the polymer are expected to be improved effectively by adding inorganic nanoparticles into polymer matrix due to their high mechanical strength and surface energy [11]. Thus, the interfacial bonding strength between particle and polymer matrix was improved due to the high surface energy of nanoparticles. Contrarily, the nano-HA particles can easily agglomerate because of its high surface active energy, while the content of nano-HA exceeding a certain percent. The agglomeration of nano-HA particles cannot act as a reinforcement phase but becoming the original defective region, which deteriorates the tensile strength of the composites.

The synergistic effects of freezing-thawing cycle times and nano-HA percentage on the tensile strength of the composites shown in Fig. 5 is characterized by the increase of tensile strength of the composites with a rise in freezing-thawing cycle times as well as the increase of nano-HA content. Furthermore, the influence degree of freezing-thawing cycle times on the tensile strength of the composites slowly reduces with the increase of nano-HA content in the composites.

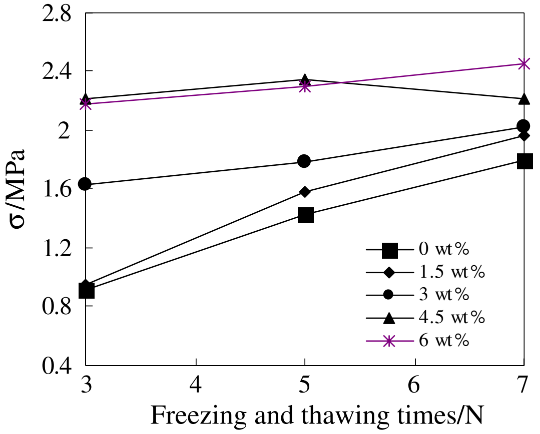


**Fig. 5** The influence of HA content and freezing-thawing times on tensile strength of composites (PSS:PVA = 5.67)

For example, while the nano-HA content in the composites is 0 and 1.5 wt.%, the tensile strengths of the composites increase from 0.91 and 0.94 MPa to 1.80 and 1.97 MPa, increasing 98% and 110%, respectively, as the freezing-thawing cycle times rising from third times to seventh times. While the nano-HA content is higher than 3 wt.%, the tensile strength of the composites increases hardly as the freezing-thawing cycle time rises.

PVA hydrogel is a semi-crystalline material where the microcrystalline and amorphous regions coexist. Both the entanglement force of hydrogen bonding formed among the intra- and inter-PVA polymer chains and the stability of the crystalline particles are enhanced with the increase of freezing-thawing cycle times. Furthermore, the interstitial space of the network structure and the size of micro pores both reduce due to its more compact three-dimensional network. These factors cause the tensile strength of the composites enhanced as the freezing-thawing cycle times rises [12, 13].

On the other hand, the interaction degree between the nano-HA and the hydroxyl group in PVA polymer chains, the ability of forming hydrogen bond between nano-HA and PVA polymer molecules, and the number of hydrogen bonding all improve with the increase of nano-HA content. Thus, the capability of forming hydrogen bond among PVA polymer molecules themselves decreased and the number of hydrogen bond almost saturated as the nano-HA content reached a certain percents [14]. Since the synergistic effects of these two influence factors, the tensile strength of the composites increased obviously with the freezing-thawing cycle times at low nano-HA content, and the freezing-thawing cycle times has little effects on the tensile strength while the content of the nano-HA particles rising further.

The effect of PVA concentration on the tensile strength of PVA gel was obtained as shown on Fig. 6. It is indicated from Fig. 6 that the tensile strength of PVA gel increased with an increase in the concentration of PVA solution, especially in the high concentration region of PVA solution. For example, the tensile strength of PVA gel only increased 42% as the concentration rising from 10 to 15 wt.%. It increased almost 1.7 times while the concentration of PVA solution increasing from 15 to 20 wt.%. The results are mainly ascribed to the increasing of the number of PVA molecules per volume in the hydrogel, the number of hydrogen bond and the fraction of crystallinity of PVA gel with a rise in PVA concentration. Furthermore, the relative content of free water in the PVA gel decreased gradually as the PVA concentration promoted. As a result,

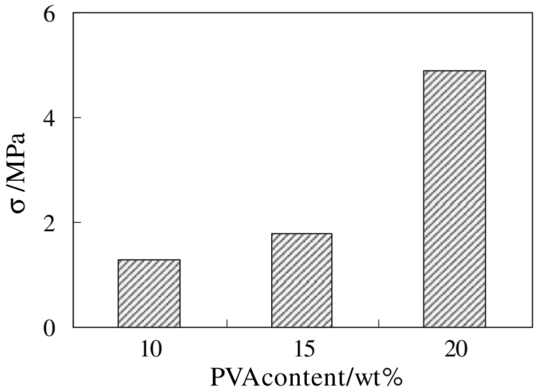


**Fig. 6** The effect of PVA concentration on tensile strength

the tensile strength of PVA gel increased with the rise of concentration of PVA solution.

## Tensile modulus

Figure 7 shows the relationship between mean tensile modulus and the content of nano-HA particle in the composites. The mean tensile modulus of nano-HA/PVA gel represents rising trend until the content of nano-HA particles reach to 1.5 wt.% and then decreases slightly while the nano-HA particles rise further.

The tensile modulus expresses the capability of the composites to resist the deformation under external force. The increase of nano-HA content in the composites could improve the rigidity and decrease the crystallinity degree of PVA matrix in the nano-HA/PVA gel composites simultaneously [14]. The improved rigidity increases the tensile modulus of the composites and the decreased crystallinity of PVA matrix is expected to contribute to the decrease of modulus of the composites due to the rising relative contents of the amorphous region in the composites. It can be deduced from Fig. 7 that the tensile modulus mainly depended on the rigidity of the composites and caused the mean tensile modulus of the nano-HA/PVA composites increased at low nano-HA content. While the content of nano-HA particles become higher and higher, the amorphous region in the composites takes predominant effect on the tensile modulus and offset the effect of the rigidity. These two contrary influences ultimately cause the mean tensile modulus almost invariable while the nano-HA rising further.

Figure 8 illustrates the effect of PVA concentration on the mean tensile modulus. The mean tensile modulus of the composites increased with the rising of PVA concentration. The higher concentration of PVA polymer, the larger degree of the influence on the mean tensile modulus is. The result is consistent with that of the effect of PVA content on the tensile strength. The tensile modulus increased 35% as the PVA concentration rising from 10 to 15 wt.% and it increased 68% while the PVA concentration increasing from 15 to 20 wt.%. The number of the PVA molecules in unit volume increases rapidly and the movement ability of the polymer molecule chain was restricted due to the rise of PVA concentration. These effects cause the number of hydrogen bonding of the intra- and inter-PVA molecules and the degree of the crystallinity increase. So the tensile modulus increased with an increase in the concentration of PVA.

The effect of elongation and freezing-thawing cycle times on the tensile modulus of the composites is shown in Fig. 9. It can be concluded from Fig. 9 that the tensile modulus of the composites increase with the rise of the freezing-thawing cycle times at different elongation ratios and it increased linearly with the rise of elongation ratio at different freezing-thawing cycle times. Furthermore, the influence degree of the elongation ratio on the tensile modulus is obviously larger than that of freezing-thawing cycle times. The tensile modulus increased 2–2.7 times at

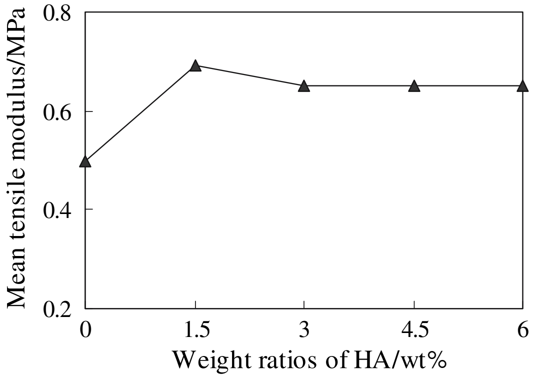


**Fig. 7** The variation of mean tensile modulus with the change of HA content (PSS:PVA = 5.67)

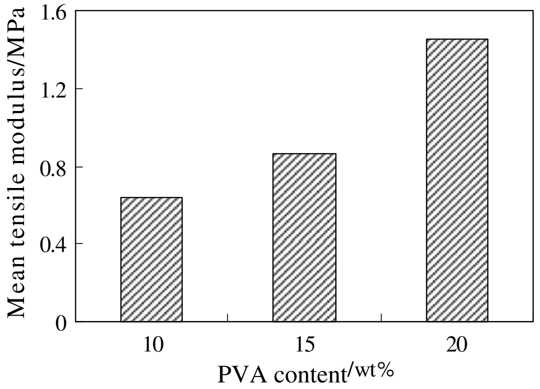


**Fig. 8** The effect of PVA content on the mean tensile modulus

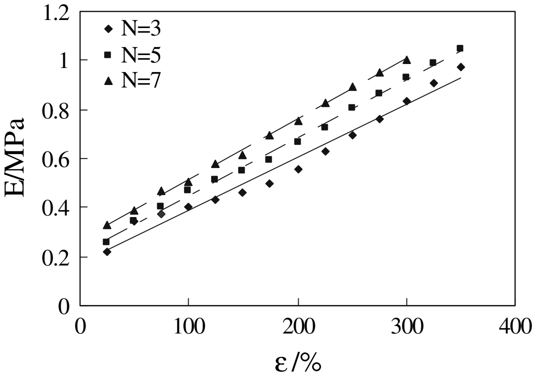


**Fig. 9** The effect of strain and freezing-thawing cycle times on tensile modulus of the composites (3%HA + 14.6%PVA + 82.4%PSS; PSS:PVA = 5.67)

different freezing-thawing cycle times while the elongation increased from 25% to 300%.

The mechanical behavior of the composites that the tensile modulus increases with the rising of the elongation is similar to that of the natural articular cartilage. This mechanical characteristic is very important for its application as an articular cartilage biomaterial. Low value of the tensile modulus of the composites at the small elongation endows the composites excellent deformation ability on low stress condition, whereas the composites have excellent resistance to external stress at high stress level due to its tensile modulus almost linear increasing with the increase of elongation. Nano-HA/PVA gel composite is an excellent multi-characteristics material that possesses the capability of easy deformation at low stress and excellent resistance to external force at high loading stress. The response to different level external stress of nano-HA/PVA gel composites is very similar to that of articular cartilage. Natural articular cartilage bears low stress at normal human activities. The stress can be uniformly distributed by enlarging the contact area of the articular cartilage due to its easy deformation at low stress level. The articular cartilage is expected to bear considerably high stress while it is in the running and jumping condition. The deformation of the articular cartilage has little increase and it presents excellent resistance to compressive stress at high loading force due to its increased tensile modulus. These mechanical properties can insure the cartilage against damage caused by deformation under relatively high loading force.

## Conclusions

1. The stress-strain characteristics of nano-HA/PVA gel composites represent nonlinear mechanical behavior and the composite is a viscoelastic material.
2. The tensile strength of the composites increased first and then decreased with the rise of nano-HA content, and it increased with the rise of PVA concentration and freezing-thawing cycle times.
3. The content of nano-HA particles and freezing-thawing cycle times have synergistic effects on the tensile strength of the composites. The tensile strength of the composites increased significantly with the freezing-thawing cycle times at low content of nano-HA particles. The influence degree of the freezing-thawing cycle times on the tensile strength decreased while nano-HA particles rise further.
4. The tensile modulus of the composites increased with the PVA concentration and freezing-thawing cycle times. It increased first and then decreased slightly with the rising of nano-HA content and it improved obviously as the elongation ratio rising.
5. The mechanical behavior of nano-HA/PVA composites is similar to that of natural articular cartilage. The composite is an excellent articular cartilage repair material.

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