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Study on compressive mechanical properties of nanohydroxyapatite reinforced poly(vinyl alcohol) gel composites as biomaterial

Yusong Pan · Dangsheng Xiong

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Abstract Nanohydroxyapatite reinforced poly(vinyl alcohol) (nano-HA/PVA) gel composites has been proposed as a promising biomaterial to replace diseased or damaged articular cartilage. In this paper, nano-HA/PVA gel composites were prepared by in situ synthesis nano-HA particles in PVA solution and accompanied with freeze/thaw method. The influence of nano-HA content, PVA concentration and freeze/thaw cycle times on the compressive mechanical behavior of nano-HA/PVA gel composites were evaluated using mechanical test equipment. The results showed that the compressive mechanical behavior of nano-HA/PVA gel composites was similar to that of natural articular cartilage, which held special viscoelastic characteristics. Both the compressive strength and modulus of the composites improved correspondingly with the rise of freeze/thaw cycle times and PVA concentration. The compressive strength and modulus of nano-HA/PVA gel composites firstly increased and then presented decreasing trend with the rise of nano-HA content. Furthermore, the compressive modulus of the composites improved exponentially with the rise of compressive strain ratio.

Y. Pan (✉)
Department of Material Science & Engineering,
Anhui University of Science and Technology,
Huainan 232001, People's Republic of China
e-mail: yusongpan@163.com

D. Xiong
Department of Material Science & Engineering,
Nanjing University of Science and Technology,
Nanjing 210094, People's Republic of China

1 Introduction

Poly (vinyl alcohol) (PVA) hydrogel is an excellent articular cartilage repair biomaterial due to its favorable biocompatibility and bio-tribological properties [1–4]. It possesses high porous structure and high content of free water, which is similar to that of natural articular cartilage. PVA hydrogel has increasingly attracted interest in application as biomaterials to replace diseased or damaged articular cartilage because of its well physicochemical properties, especially of its excellent bio-tribological properties [5–7]. However, the major challenge of PVA hydrogel used in clinical application is its fixation method with the nature tissue. Since PVA hydrogel itself does not adhere to tissue due to its non-bioactivity, long-term fixation of PVA hydrogel implant by suture is difficult.

Nano-HA has been applied widely in medical field as a bone repair material because of its excellent bioactive properties [8, 9]. Therefore, composition of nano-HA and PVA to prepare nano-HA/PVA gel composites not only improves the mechanical properties of the composites but also endows its excellent bioactivities. It can form bone-bonding with natural tissue through osteo-conduction mechanism [10]. This is the effective method to improve adhesion properties between implanted material and nature tissue. Our previous study results showed that the tensile mechanical properties of nano-HA/PVA gel composite were similar to those of articular cartilage [11]. However, it is more important to investigate the compressive mechanical properties of the composites since it always endures compressive stress while used as an articular cartilage repair material. There has been little assessment on the compressive mechanical properties of nano-HA/PVA gel biocomposites.

In this paper, nano-HA/PVA gel composites were prepared by in situ synthesis of nano-HA particles in PVA solution combining with freeze/thaw method. The influences of various factors and the content of nano-HA particles on the compressive properties were both investigated.

2 Material and methods

2.1 Materials

PVA was purchased from Shanghai Chemical Co., Ltd, with the saponification degree of 99% and number-average polymerization degree of 1750 ± 50. For the synthesis of hydroxyapatite, $Ca(OH)_2$ (analytical reagent, with purity of 95 wt%) and H_3PO_4 (analytical reagent, with purity more than 85 wt%) were supplied by Siopharm Chemical Reagent Co., Ltd. All chemicals were used without any further purification.

2.2 Preparation of nano-HA/PVA gel composites

First, 9.3 g $Ca(OH)_2$ was added into the 220 ml distilled water to prepare calcium hydroxide suspension. Second, 77.6 g PVA was introduced into the calcium hydroxide suspension. Third, The blending solution of $Ca(OH)_2$ and PVA was stirred continuously at 90°C for 1 h. Fourth, H_3PO_4 solution (90 ml, 0.8 M) was added drop-by-drop to the blending solution of $Ca(OH)_2$ and PVA. The solution was maintained thoroughly stirring at 90°C during the course of the reaction. The quantities of the reactants were selected to provide a Ca/P molar ratio, R, of 1.67.

After the reaction, the solution was maintained stirring at 90°C for another 14 h. Subsequently, the solution was stored at 60°C for 30 min to eliminate air bubbles. Then, the mixture was poured into stainless steel mould. Finally, Nano-HA/PVA gel composites were obtained by subjecting the mixed solution to several repeated freeze/thaw cycles. In each cycle, the sample was frozen at about −20°C for 12 h, and then thawed at room temperature for 6 h. According to this process, the different freeze/thaw cycles of nano-HA/PVA gel composite was prepared.

2.3 Mechanical properties testing

The compressive strength measurements were performed on mechanical test equipment (Model: INSTRON 3367). During the compressive strength test, it is very difficult to crush the samples due to their high deformation capacities. Taking this into consideration, all the samples were compressed to 40% of its original height and the compressive strength of each sample was evaluated on this compressive strain ratio. The test strain rate of the sample was 10 mm/min.

The compressive modulus of the composites at different compression strain levels were determined by the finite difference method and expressed as the following equation [11].

$$E_{\varepsilon} = \frac{\sigma_{\varepsilon+\Delta\varepsilon} - \sigma_{\varepsilon-\Delta\varepsilon}}{2\Delta\varepsilon} \tag{1}$$

where E_{ε} is the compressive modulus of the composites at the compression strain ratio value of ε. The value of Δε is 1%.

In mechanical test experiments, for a fair assessment of the contribution of the nano-HA particles to the mechanical properties, the weight ratio between water and PVA for all the nano-HA/PVA gel composites was kept constant (at 4).

2.4 Scanning electron microscopy (SEM)

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

3 Results and discussion

3.1 Stress–strain behavior of the composites

The effects of freeze/thaw cycle times and nano-HA content on the compressive stress–strain characteristics of the gel composites were described in Figs. 1 and 2, respectively. It can be concluded from the figures that the stress–strain behaviors of all the gel composites present exponential relationship and the composites possess typical viscoelastic properties. Furthermore, at the same strain level, the compressive stress of the composites increases with the rise of nano-HA contents and freeze/thaw cycles. This effect is more distinct with the rise of strain ratio.

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 particle reinforcing phase and lots of free water among three-dimensional network structure of PVA gel [12, 13].

Figure 3 shows the schematic diagram of hydrogen bond between PVA molecules or among PVA molecule. 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 Figs. 1 and 2 that the

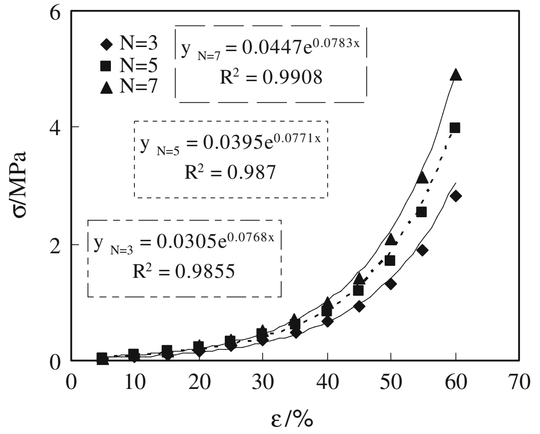


Fig. 1 Stress–strain characteristic of the composites prepared by different freeze/thaw cycles (nano-HA content: 6%; PVA concentration: 20%)

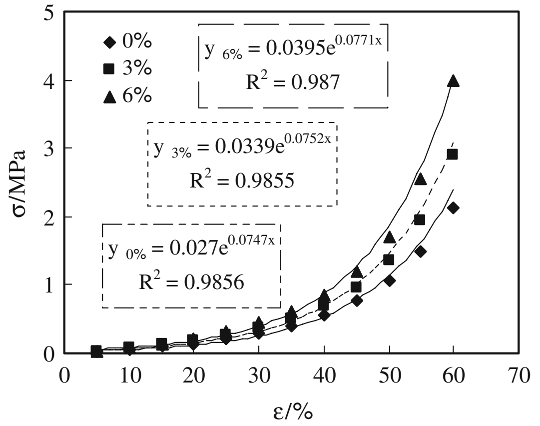
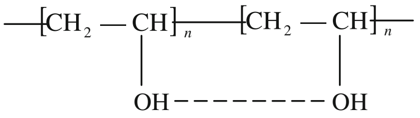


Fig. 2 Stress–strain characteristic of the composites with various weight ratios of nano-HA particles prepared by 5 freeze/thaw cycles (PVA concentration: 20%)

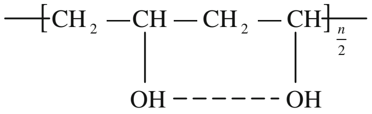
relationship between stress and strain is nonlinear and the strain ratio is much higher, which can reach to 60%, than that of normal elastic material. Three-dimensional network structure in the composite holds lots of free spaces. These free spaces enable the polymer chains to respond rapidly to the external force and polymer chains rearranged simultaneously, which ultimately results in the relatively high compressive strain ratio of the composites.

3.2 Compressive strength

The effect of nano-HA content on the compressive strength of the composites prepared by different freeze/thaw cycles is presented in Fig. 4, which shows that the compressive strength of the composites increases firstly and then decreases with the rise of nano-HA content. For example, at fifth freeze/thaw cycle, the compressive strength of nano-HA/PVA gel composites increases from 2.13 to 3.99 MPa, increasing 87%, while the nano-HA content rises from 0% to 6%. As the content of nano-HA increases further, the compressive strength of the composites presents a decreasing trend.



(a) Hydrogen bond between PVA molecules



(b) Hydrogen bond intra- PVA molecule

Fig. 3 The schematic diagram of hydrogen bond between PVA molecules or intra-PVA molecule

The mechanical properties of the polymer are expected to be improved effectively by adding inorganic nanoparticles into polymer matrix as their high mechanical strength and surface energy [14, 15]. Thus, the interfacial bonding strength between particle and polymer matrix was improved due to the high surface energy of nanoparticles. On the other hand, while the content of nano-HA exceeding a certain percent, the nano-HA particles can also be easily agglomerated because of its high surface active energy. Ultimately, the agglomerated nano-HA particles deteriorate the mechanical properties of the composites. Figure 5 shows the morphology of the composites with different nano-HA content. It can be noted that the nano-HA particles distribute uniformly in the PVA matrix while nano-HA content is

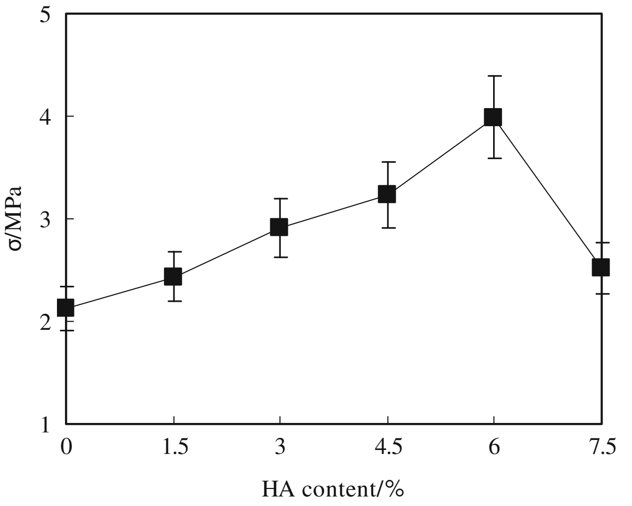


Fig. 4 The effect of HA content on the compressive strength of the composites (Freeze/thaw cycles: $N = 5$; PVA concentration: 20%; compression ratio: $\varepsilon = 60\%$)

suitable low (Fig. 5a–c). Contrarily, while the content of nano-HA exceeding a certain percent, it can be found that nano-HA particles in the PVA matrix represent agglomeration trend (Fig. 5d).

The effect of freeze/thaw cycles and PVA concentration on the compressive strength of the composites is shown in Fig. 6. It can be concluded from Fig. 6 that the compressive strength of the composites increases with the rise of freeze/thaw cycles as well as the PVA concentration. Furthermore, the influence degree of freeze/thaw cycles on the compressive strength of the composites slowly reduces with the increase of freeze/thaw cycles. For example, while the freeze/thaw cycle rises from 3 to 5, the compressive strength of the composites with 20% PVA concentration increases from 1.99 to 2.91 MPa, almost increasing 46%. While the freeze/thaw cycle increasing from 5 to 7, the compressive strength of the composites with 20% PVA concentration only increases 21%.

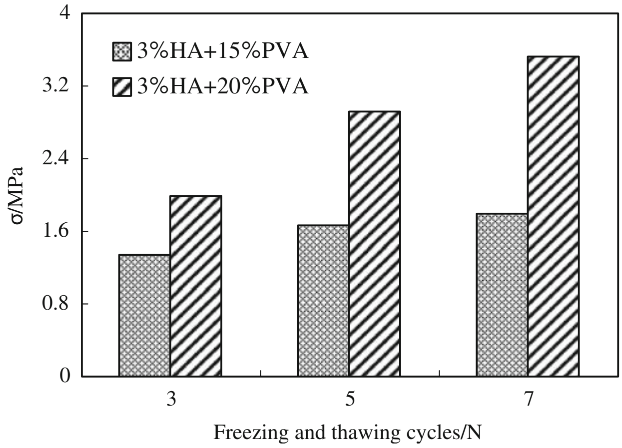
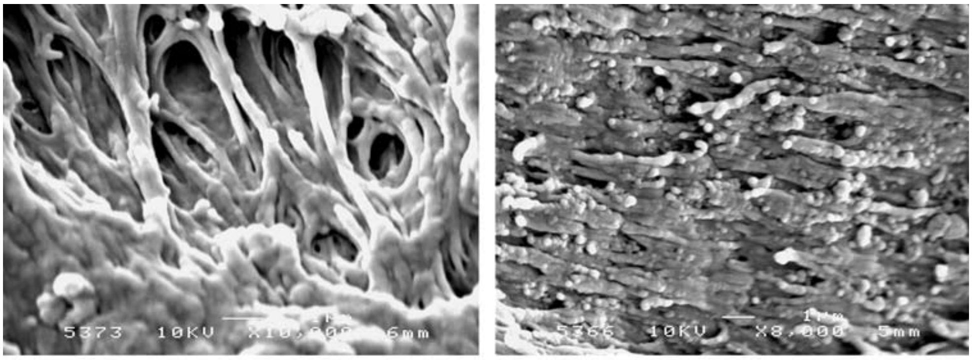


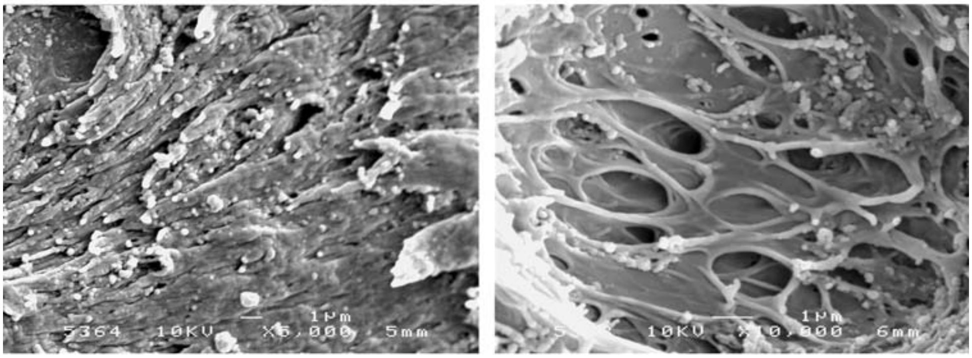
Fig. 6 The effect of freeze/thaw cycle times and PVA concentration on the compressive strength

In the nano-HA/PVA gel composites, the matrix of PVA hydrogel is a semi-crystalline material where the micro-crystalline and amorphous regions coexist. Both the bonding force of hydrogen bonding formed among the intra- and inter-PVA polymer chains and the stability of the crystalline particles are enhanced with the rise of freeze/thaw 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 as the freeze/thaw cycle times rises. These factors cause the compressive strength of the composites enhanced as the freeze/thaw cycles rises [16, 17]. On the other hand, while the freeze/thaw cycle rise to a certain times, the number of hydrogen bond between PVA molecules or among intra-PVA molecules tends to saturation and caused the influence degree of freeze/thaw cycles on the compressive strength slowly reducing while the freeze/thaw cycles increasing further.

Fig. 5 Section micro-morphology of the composites with various nano-HA content (PVA concentration: 20%)



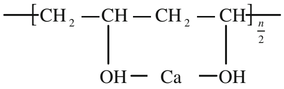
(a) HA content: 0 wt% **(b)** HA content: 3 wt%



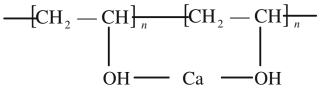
(c) HA content: 6 wt% **(d)** HA content: 7.5%

It can be also seen from Fig. 6 that the compressive strength of the composites also increases with the rise of PVA concentration. At the fifth freeze/thaw cycle, the strength of the composites improved from 1.66 to 2.91 MPa, almost increasing 75%, while the PVA concentration rise from 15% to 20%.

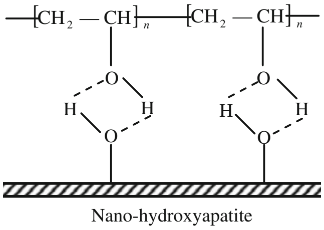
The results are mainly ascribed to the increasing number of PVA molecules per volume in the hydrogel, the number of hydrogen bond and the fraction of crystallinity of PVA gel with the rise of PVA concentration. Furthermore, the relative content of free water in the PVA gel decreases gradually as the PVA concentration promoted. The results of Xu [18] showed that two binding mode between hydroxyapatite and PVA molecules exited in the composites: (1), The Ca^{2+} cation in the hydroxyapatite and inter-PVA molecules or intra-PVA molecule forms bond bridge band, and this can improve the rigidity of the network in the composites. (2), The hydroxyl group of hydroxyapatite and the free hydroxyl group in PVA molecules linked by the forms of hydrogen bond, and this can improve the interfacial bonding strength between hydroxyapatite and PVA polymer. Figure 7 shows the schematic diagrams of the interaction between hydroxyapatite and PVA polymers.



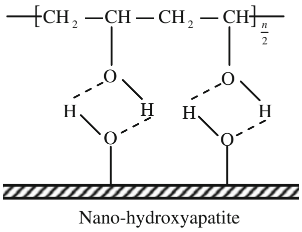
(a) The interaction between Ca^{2+} cation and intra-PVA molecule



(b) The interaction between Ca^{2+} cation and inter-PVA molecules



(c) The hydrogen bond between nano-hydroxyapatite and inter-PVA molecules



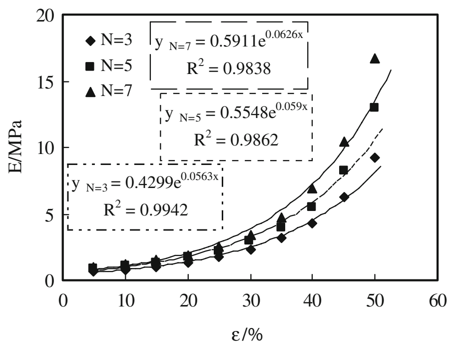
(d) The hydrogen bond between nano-hydroxyapatite and intra-PVA molecules

Fig. 7 The interaction between hydroxyapatite and PVA molecules

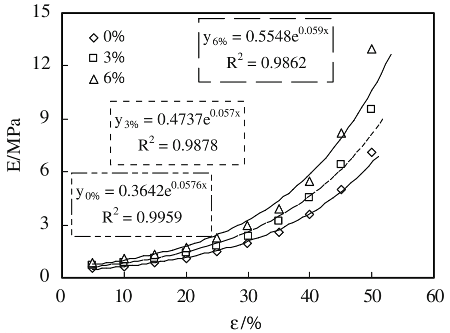
It can be concluded that PVA polymer can provide a lot of free hydroxyl group to act with hydroxyl group on the surface of hydroxyapatite while the PVA concentration increases. As a result, the compressive strength of PVA gel increased with the rise of concentration of PVA solution.

3.3 Compressive modulus

The effects of compression ratio, freeze/thaw cycles and nano-HA content on the compressive modulus of the composites are shown in Fig. 8, and some results can be concluded from Fig. 8. Firstly, the compressive modulus of the composites increases exponentially with the rise of compression ratio. This indicates that the compressive modulus depends significantly on the compression ratio. For example, the compressive modulus of the composites (6% HA + 20% PVA) prepared by 7 freeze/thaw cycles increases from 0.96 MPa to 16.74 MPa, increasing 16.4 times, while the compression ratio rising from 5% to 50% (Fig. 8a). Secondly, at every compressive strain level, the compressive modulus of the composites both increases with the freeze/thaw cycles and nano-HA content, and this change behavior presents more evidently at high compression strain ratios.



(a) The relationship between compressive modulus and compression ratio at different freeze/thaw cycles (Nano-HA content: 6%; PVA concentration: 20%)



(b) The relationship between compressive modulus and compression ratio at different HA content (Freeze/thaw cycle times: N=5; PVA concentration: 20%)

Fig. 8 The change behavior of compressive modulus with compression ratios

For example, while the compression ratio is 25%, the compressive modulus of the composites prepared by 3, 5, 7 freeze/thaw cycles are 1.76 MPa, 2.22 MPa and 2.53 MPa, respectively. The compressive modulus increases 27% and 12%, respectively, as the freeze/thaw cycles rising from 3 to 5 and from 5 to 7. While the compression ratio rises to 50%, the compressive modulus of the composites prepared by 3, 5, 7 freeze/thaw cycles are 9.25, 12.97 and 16.74 MPa, respectively. The compressive modulus increases 32% and 28%, respectively, as the freeze/thaw cycles rising from 3 to 5 and from 5 to 7. Thirdly, the higher the freeze/thaw cycle and nano-HA content, the higher increasing rate of compressive modulus is.

The compressive modulus expresses the capability of the composites to resist the deformation under external force. Under the same external force, the higher compressive modulus of the composites, the higher capability of the composites to resist deformation. The mechanical behavior of the composites that the compressive modulus increases with the rise of the compression ratio is similar to that of the natural articular cartilage. Such mechanical characteristic is very important for its application as an articular cartilage biomaterial.

In the human activities, articular cartilage always bears compressive stress. Low compressive stress that the articular cartilage endured generally corresponds to the normal human activities such as walking and cantering, whereas the high compressive stress which articular cartilage endured always corresponds to the running and jumping activities. In walking and running activities, the articular cartilage bears low and considerably high compressive stress, respectively. In low compressive stress conditions (walking and cantering), the compressive stress can be uniformly distributed by enlarging the contact area of the articular cartilage due to its easy deformation at low stress level. While it is in the running and jumping condition, natural articular cartilage is expected to bear considerably high stress. The deformation of the articular cartilage has little increase and it presents excellent resistance to compressive stress under high loading force due to its increased compressive modulus. Such mechanical properties can insure the cartilage against damage caused by deformation under relatively high loading force.

While nano-HA/PVA gel composites are used as an articular cartilage repair material, low value of the compressive modulus of the composites at the low compression ratio endows the composites excellent deformation ability on the low stress condition, whereas the composites have excellent resistance to external stress at high stress level due to its modulus increasing exponentially with the rise of compression ratio. 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.

4 Conclusions

The compressive mechanical properties of nano-HA/PVA gel composites prepared by in situ synthesis nano-HA particles in PVA solution and accompanied with freeze/thaw method have been investigated. The following points can be summarized for the present investigation.

1. The stress–strain characteristics of nano-HA/PVA gel composites represent nonlinear mechanical behavior and the composite is a viscoelastic material. The change behavior of the compressive stress with the compression ratio is in accordance with the exponential function.
2. The compressive strength of the composites increases firstly and then decreases with the rise of nano-HA content. Their maximum values are obtained while nano-HA content is 6% in the composites. It increases with the rise of PVA concentration and freeze/thaw cycle times.
3. The compressive modulus of the composites increases with the nano-HA content and freeze/thaw cycle times. The compressive modulus of the composites increases exponentially with the rise of compression ratio.
4. The compressive 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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