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Stress Relaxation Behaviour and Model of Multi-Layered Nano-Hydroxyapatite Reinforced PVA Gel Biocomposites†

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Stress relaxation characteristics of multi-layered graded nano-hydroxyapatite/PVA gel biomaterial under different effect factors were studied. The results showed that the stress relaxation behaviour of the biocomposites is similar to that of natural articular cartilage and it can be described by logarithmic model. The stress relaxation rate declined with the rise of relaxation time, but it increases with the rise of compressive strain level and freeze-thaw cycle times under the whole relaxation time. Moreover, the normalized equilibrium relaxation modulus of the composites decreases with the rise of strain and freeze-thaw cycle times.

Key Words: Multi-layered graded nano-hydroxyapatite/PVA gel composites, Stress relaxation, Relaxation model, Normalized equilibrium modulus.

INTRODUCTION

Nano-hydroxyapatite/PVA gel composite is an excellent articular cartilage repair biomaterial due to its favourable bioactivity and mechanical properties, similar to that of natural articular cartilage. The composites has increasingly attracted interest in application as biomaterials to replace diseased or damaged articular cartilage because of its well physico-chemical properties, especially of its excellent bio-tribological properties[1-3]. However, while the content of nano-hydroxyapatite particles in PVA gel matrix exceeding a certain per cent, the nano-hydroxyapatite particles can be easily agglomerated and caused the mechanical properties, as well as the lubrication function of the composites deteriorated rapidly[3]. On the other hand, the higher the nano-hydroxyapatite content in the composites, the higher the osteoconductive and the earlier the bio-resorption. Thus, there is contradiction between mechanical and bioactive properties of the composites.

In order to simultaneously optimize the mechanical and bioactive properties, as well as frictional properties of the implant material, functional graded materials provided new concept for artificial articular cartilage design with graded component and graded structure where one face of the material is high free water content thereby providing excellent lubrication function and the opposite face of the material is high nano-hydroxyapatite content, thereby improving the bioactivity of the material and stimulating cell growth. Here, we selected nano-hydroxyapatite as the bioactive component, PVA hydrogel as matrix to prepare one novel multi-layered graded nano-hydroxyapatite/PVA gel biocomposites comprising of the lowest nano-hydroxyapatite content to form surface layer and acting as lubrication function, the middle content nano-hydroxyapatite content to form middle layer and providing stress transfer function, the highest nano-hydroxyapatite content to form bottom layer and acting as bioactive layer. According to this design, in the condition that controlling of the total content of nano-hydroxy-apatite in a certain range, every layer plays to different functional roles. Various properties of the material such as mechanical, bioactivity and bio-tribology can simultaneously optimize by regulating the nano-hydroxyapatite content of every layer. The functional graded materials idea may help for improvement of not only mechanical and bioactive properties, but also frictional property.

In this study, multi-layered nano-hydroxyapatite/PVA gel composites were prepared through layer-by-layer casting method combining with freeze-thaw cycle technology. The influences of various factors on the stress relaxation behaviour were investigated.

EXPERIMENTAL

The multi-layered graded nano-hydroxyapatite/PVA hydrogel composites were prepared through layer-by-layer

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casting method and incorporation with freeze-thaw cycle technology. The stress relaxation measurements were performed on mechanical test equipment. In order to expediently discuss the stress relaxation properties of the composites at the different stress relaxation states, the normalized relaxation modulus ($G_{(t)}$) was proposed as an evaluation criteria. The normalized relaxation modulus was expressed as the following equation:

$$G(t) = \frac{E(t)}{E(0)} = \frac{\sigma(t)/\varepsilon_0}{\sigma_0/\varepsilon_0} = \frac{\sigma(t)}{\sigma_0} \quad (1)$$

where E(t) and σ(t) are the relaxation modulus and relaxation stress, respectively, as functions of time. E(0) and σ(0) are the initial relaxation modulus and initial relaxation stress. ε_0 is the constant strain ratio.

RESULTS AND DISCUSSION

Stress relaxation characteristics of the biocomposites: Fig. 1 shows the stress relaxation behaviour of multi-layered nano-hydroxyapatite/PVA gel biocomposites with the relaxation time under different freeze-thaw cycle times and compressive strain levels, respectively. It is concluded from the figure that the normalized relaxation modulus of the composites decreases rapidly in the initial relaxation stage. With the relaxation time prolonged, the declining rate of the normalized modulus was decreased. Ultimately, it reached to relaxation equilibrium stage. Moreover, some results can be concluded from the figure. Firstly, the relaxation rate of the composites increases with the rise of strain level. For example, while the compressive strains increase from 30 to 60 %, the normalized relaxation modulus of the composites reduce from 1 to 0.84 and 0.68 at 300 s, decreasing 16 % and 32 %, respectively. Secondly, the relaxation rate of the composites decreases with the rise of relaxation time under all the strain levels and freeze-thaw cycle times. Thirdly, the normalized equilibrium relaxation modulus of the composites decreases with the rise of strain and freeze-thaw cycle times. For example, while the freeze-thaw cycle times increases from 1 to 7, the normalized equilibrium relaxation modulus of the composites declined from 0.663 to 0.563.

The relationship between initial relaxation stress (σ_0) and normalized equilibrium relaxation modulus (G_e) under different compressive strain levels and freeze-thaw cycle times are shown in the insert graphs of Fig. 1(a-b), respectively. It can be concluded that the initial relaxation stress increases with the rise of strain level and freeze-thaw cycle times. However, the normalized equilibrium relaxation modulus decreases with the rise of strain level and freeze-thaw cycle times. Thus, the normalized equilibrium relaxation modulus is inverse proportion to the initial relaxation stress.

Relaxation model: Many researchers showed that the stress relaxation behaviour of natural articular cartilage can be described by Logarithmic stress relaxation model[4,5]. Multi-layered nano-hydroxyapatite/PVA gel composites prepared by the authors are mainly used as an artificial articular cartilage. Thus, logarithmic stress relaxation model was used to describe the stress relaxation behaviour of the biocomposites. The model can be expressed as following:

$$G(t) = \begin{cases} 1 & t=0 \\ c\ln t + d & t>0 \end{cases} \quad (2)$$

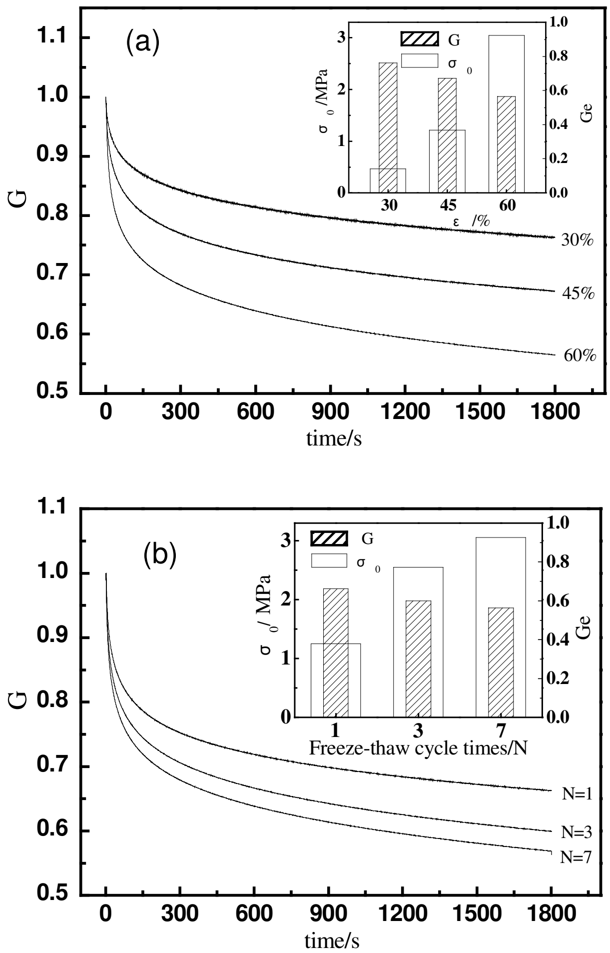

Fig. 1. Stress relaxation change behaviour of multi-layered biocomposites with the relaxation time (a) under different compressive strain level (1.5/4.5/7.5) % hydroxyapatite, PVA content: 20 %; (1.5/4.5/7.5) % hydroxyapatite represents that the multi-layered composites is comprised by three layers. Nano-hydroxyapatite content in the surface layer is 1.5 wt %, nano-hydroxyapatite content in the middle layer is 4.5 wt % and that in the bottom layer is 7.5 wt %. (b) under different freeze-thaw cycle times (3/9) % hydroxyapatite, PVA content: 20 %

where c and d are undetermined constants and they can be calculated by least square method:

$$\varphi(c,d) = \sum_{i=1}^{n} [G(t) - G_{EXP}]_i^2 \quad (3)$$

$$\frac{\partial\varphi}{\partial c} = 0 \quad \frac{\partial\varphi}{\partial d} = 0 \quad (4)$$

$$\text{That is, } \begin{cases} c\sum_{i=1}^{n}(\ln t)^2 + d\sum_{i=1}^{n}\ln t = \sum_{i=1}^{n} G_{EXP}\ln t \\ c\sum_{i=1}^{n}\ln t + \sum_{i=1}^{n} d = \sum_{i=1}^{n} G_{EXP} \end{cases} \quad (5)$$

In eqn. 3, G_{EXP} represents the experimental value of the normalized relaxation modulus at t relaxation time.

The experimental and theoretical values of normalized relaxation modulus of multi-layered nano-hydroxyapatite/PVA gel composites under different relaxation times are shown in Table-1. The theoretical value and experimental value are nearly same and their difference is less than 1 %. It can be

TABLE-1
COMPARISON OF NORMALIZED RELAXATION MODULUS BETWEEN EXPERIMENTAL VALUE AND THEORETICAL VALUE CALCULATED BY LOGARITHMIC MODEL (3/9) % HYDROXYAPATITE + 20 % PVA)

Relaxation time (s)	5	10	80	120	500	700	900	1200	1500	1800
G_{EXP}	0.9343	0.8894	0.7610	0.7327	0.6507	0.6295	0.6127	0.5934	0.5780	0.5652
G_{TH}	0.9357	0.8925	0.7628	0.7375	0.6485	0.6275	0.6118	0.5939	0.5800	0.5686
Error (%)	0.150	0.349	0.237	0.655	0.338	0.318	0.147	0.084	0.346	0.602

concluded that the logarithmic stress relaxation model can accurately describe the stress relaxation behaviour of multi-layered nano-hydroxyapatite/PVA gel bio-composites. This result shows that the stress relaxation behaviour of multi-layered nano-hydroxyapatite/PVA gel bio-composites is in good agreement to that of natural articular cartilage and both possess the same type of relaxation function.

Conclusion

The stress relaxation behaviour of multi-layered graded nano-hydroxyapatite/PVA gel composites is similar to that of natural articular cartilage and its variation with relaxation time can describe by logarithmic stress relaxation model. The stress relaxation rate declined with the rise of relaxation time. However, the stress relaxation rate increases with the rise of compressive strain level and freeze-thaw cycle times. The normalized equilibrium relaxation modulus of the composites decreases with the rise of strain and freeze-thaw cycle times.

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REFERENCES

1. S.A. Poursamar, F. Orang, S. Bonakdar and M.K. Savar, *Int. J. Nanomanufac.*, **5**, 330 (2010).
2. Y.S. Pan and D.S. Xiong, *J. Mater. Sci. Mater. Med.*, **20**, 1291 (2009).
3. Y.S. Pan and D.S. Xiong, *Wear*, **266**, 699 (2009).
4. G.W. Meng, J.P. Cheng and H.S. Ma, *J. Med. Biomechanics*, **18**, 239 (2003).
5. X.S. Weng, J.G. Zhang, J. Zhang and G.X. Qiu, *Acta Acad. Med. Sin.*, **21**, 53 (1999).