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Stress relaxation behavior of nano-hydroxyapatite reinforced poly(vinyl alcohol) gel composites as biomaterial

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Abstract Nano-hydroxyapatite 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, the stress relaxation mechanism of nano-HA/PVA gel composites was investigated. The various influence factors on the stress relaxation behavior of the composites were also evaluated. The results showed that the relaxation mechanism of the composites was mainly determined by the synergistic effect of two stress relaxation mechanisms analogous to those of the natural articular cartilage and the polymer. The relaxation rate of the composites increased with the rise of strain ratio, but it declined with the relaxation time. Under the given strain ratio, the relaxation rate of the composite presented a trend of rising first and then falling with the increasing amount of nano-HA content. Contrarily, the normalized equilibrium relaxation modulus of the composites decreased first and then presented increasing trend with the rise of nano-HA content. Furthermore, the normalized equilibrium relaxation modulus of the composites decreased with the rise of strain.

Introduction

Hydrogel based materials such as poly(vinyl alcohol) (PVA), collagen, poly(lactic acid), and chitosan exhibit excellent biocompatibility as well as degradability. They are widely used as bone tissue scaffold materials or substitutes for articular cartilage [1–3]. However, the hydrogels alone always do not provide adequate mechanical properties as well as absence of bioactivity for various biomedical applications including scaffold tasks. For example, PVA hydrogel has increasingly attracted interest in application as biomaterials to replace diseased or damaged articular cartilage due to its well physicochemical properties, especially of its excellent bio-tribological properties [4–6]. However, the major challenge of PVA hydrogel used in clinical application is its fixation method with the natural tissue due to its non-bioactivity [7]. Furthermore, while it is used as substitutes for articular cartilage, its mechanical properties are expected to be further improved due to its high load bearing.

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 can provide not only improved mechanical properties but also excellent bioactivities. It can form bone-bonding with natural tissue through osteo-conduction mechanism. This is the effective method to improve adhesion properties between implanted material and nature tissue.

Stress relaxation is the gradual decrease of stress when the material is held at constant strain. While the articular cartilage bearing external stress, it can alleviate the influence of the external load through the process of stress relaxation. Many research results demonstrated that the stress relaxation characteristics of the prosthesis implanted material had obvious influences on the micro-circulation system of the tissue adjacent to the prosthesis, the stress shielding rate of the bone, fracture healing of bone and morphology of tissue [10–12]. An example is that the bone

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plate with stress relaxation properties can effectively improve the micro-circulation system of the tissue adjacent to the prosthesis, avoiding bone resorption and mechanical strength deterioration [13]. Therefore, it has great significance to investigate the stress relaxation behavior of nano-HA/PVA gel composites before it is used as prosthesis implanted biomaterial. Our previous study results showed that the tensile, compressive, and viscoelastic mechanical properties of nano-HA/PVA gel composite were similar to those of articular cartilage [14–16]. However, there is almost no report on the stress relaxation properties of nano-HA/PVA gel composites.

In this study, nano-HA/PVA gel composites were prepared through the combination of in situ synthesis of nano-HA particles in PVA solution with freeze/thaw method. Stress relaxation characteristics and relaxation mechanism of the nano-HA/PVA gel composites were investigated. The influences of compressive strain ratio and nano-HA particles content on the compressive stress relaxation behavior of the composites were studied. The knowledge of the mechanical characteristics of the composites will be useful for their clinical application.

Materials and methods

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. Nano-hydroxyapatite reinforced poly(vinyl alcohol) (nano-HA/PVA) gel composites were prepared by in situ synthesis nano-HA particles in PVA solution and accompanied with freeze/thaw method, as previously reported [17].

Stress relaxation properties testing

The stress relaxation measurements were performed on mechanical test equipment (MODEL: AG-10TND, Japan). In this experiment, the stress relaxation measurements were divided into two parts:

1. Tensile stress relaxation: the test loading rate of the sample was 30 mm/min. The tensile stress of the composite would reach to 1.53 MPa while the peak load was achieved. Then, the tensile strain value of the composites was kept constant for 2400 s. The composite was restricted to the stress relaxation status while its strain value was maintained constant.
2. Compressive stress relaxation: in order to research the effect of compressive strain ratio on the stress relaxation behavior of the composites, the stress relaxation was performed by applying 30, 40, and 50% compression strains on the composite specimens and monitoring the diminishing load for 2400 s, respectively. The loading rate of the sample was 30 mm/min. On the other hand, in order to evaluate the effect of nano-HA content on the stress relaxation of the composites, the stress relaxation was performed on the gel composites with different nano-HA content. In these experiments, the strain ratio was kept at 60% and the relaxation time was 2400 s.

In order to expediently discuss and compare 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 in the following equation:

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

where $E(t)$ is the relaxation modulus at t time and $E(0)$ is the initial relaxation modulus. σ_0 is the initial relaxation stress and $\sigma(t)$ represents the relaxation stress value at the t relaxation time. ε_0 is the constant value of strain ratio.

Results and discussion

Stress relaxation behavior of the composites

The change behaviors of the relaxation stress and normalized modulus of the composites with the relaxation time are described in Figs. 1 and 2, respectively. It can be concluded from the figures that the whole stress relaxation process of the composites are distinctly divided into two stages, whose characteristics are described by rapid and slow relaxation stages, respectively. The relaxation stress and normalized modulus of the composites both decrease rapidly while the relaxation time starts from initial time to 500 s. Then, the declining rate of the relaxation stress and normalized modulus were both decreased with the relaxation time prolonged. Ultimately, both reach the state of relaxation equilibrium.

According to the stress relaxation findings on the natural articular cartilage of Weng et al. [18]. It is considered that the equilibrium point would reach when the decrease value of the relaxation stress in 10 min is less than 2% of its original stress. It can be calculated that the decrease value

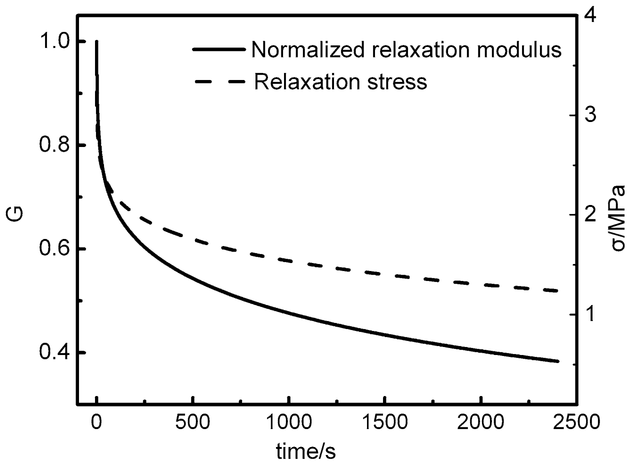

Fig. 1 Curves of compressive relaxation stress and normalized relaxation modulus

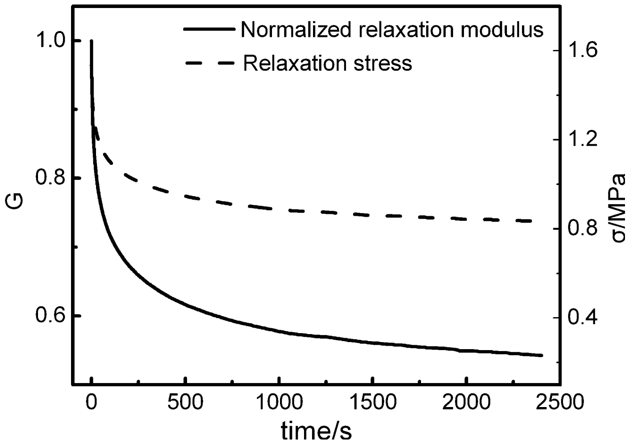

Fig. 2 Curves of tensile relaxation stress and normalized relaxation modulus

of the tensile and compressive relaxation stress of nano-HA/PVA gel composites is 0.9% and 1.8% of its original relaxation stress, respectively, while the relaxation time begins from 1800 to 2400 s. Thus, based on the criterion of Weng et al., it can be believed that both the tensile and compressive relaxation stress of the composites reach up to their equilibrium state after 2400 s of relaxation and the normalized equilibrium tensile and compressive relaxation moduli are 0.543 and 0.383, respectively. In comparison with the initial normalized relaxation modulus, they decreased 45.7% and 61.7%, respectively. Within the initial 500 s relaxation, the normalized equilibrium tensile and compressive relaxation modulus declined from 1 to 0.616 and 0.544, decreasing 38.4% and 45.6%, respectively, taking up 84% and 73.9% of the total decrease amplitude, the remaining 16% and 26% completed in 1900 s. It can be concluded that the former belongs to rapid relaxation stage and the latter belongs to slow relaxation stage.

Figure 3 shows the change behavior of the decline rate of the normalized relaxation modulus with the relaxation time. It can be concluded from Fig. 3 that the decline rate of the normalized relaxation modulus presents exponential decrease trend with the relaxation time, which indicates the rapid reduction of the decline rate in a short time. For example, the tensile and compressive relaxation modulus reduces 77% and 66.7% of total modulus in the initial 300 s. As the relaxation time increases further, the decline rate of the relaxation modulus also reduces quickly.

It should be noted that the findings on the stress relaxation of the natural articular cartilage is also characterized by the rapid and slow relaxation stages [19, 20]. The results of the Mow et al. [21, 22] showed that the solubility of the proteoglycan in the articular cartilage decreased due to the extrusion deformation on the external stress loading process. This resulted in the local pressure difference which was larger than intrinsic swelling pressure and thus the liquid in the articular cartilage was squeezed out. Therefore, the high relaxation rate on the initial relaxation stage is mainly caused by the rapid squeezing out speed of the free water in the cartilage. With the liquid in the cartilage being continuously squeezing out, the difference between

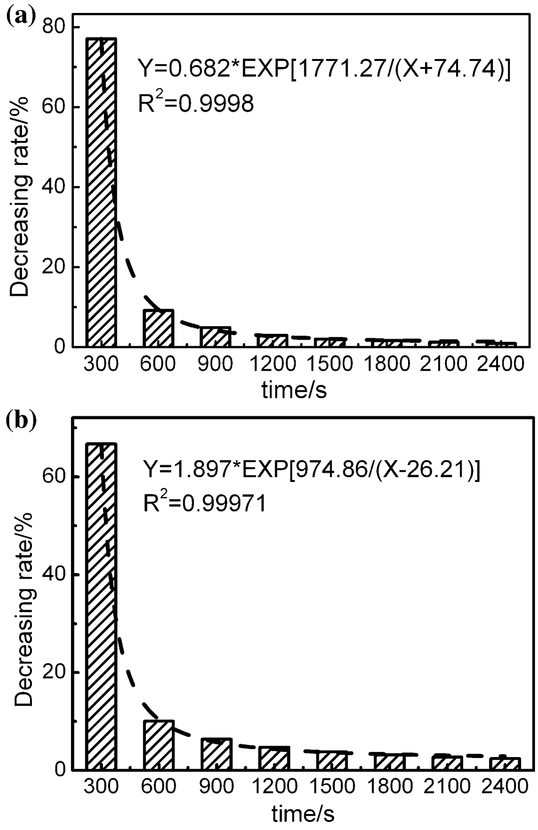

Fig. 3 Change behavior of the decline rate of the normalized relaxation modulus with the relaxation time. **a** Tensile normalized relaxation modulus. **b** Compressive normalized relaxation modulus

the intrinsic pressure and local pressure decreased. The relaxation rate thus becomes slow with prolonged relaxation, and the relaxation of the composites turned into slow relaxation stage. Our result of the relaxation equilibrium time of nano-HA/PVA gel composites is in accordance to the results of Mow et al. The result indicates that the stress relaxation characteristics of nano-HA/PVA gel are similar to that of natural articular cartilage.

Stress relaxation mechanism

The unique stress relaxation 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 [23–25].

Polymer stress relaxation process is mainly dominated by the movement and rearrangement of the polymer chain segment, as well as the change of the bond angle which is caused by the external force. The movement speed of the polymer chain segment directly restricts the stress relaxation rate [26]. In the stress relaxation experiment, the deformation of the sample caused by the initial rapid loading consists of two parts: one is regular elastic deformation caused by the variation of bond length and bond angle and the other is high-elastic deformation produced by the movement of the polymer chain segment. Furthermore, the initial deformation of the sample is mainly dominated by the regular elastic deformation whose modulus is relatively high. Therefore, the initial stress that maintains the strain is also comparative high. Simultaneously, a spontaneous rebound internal stress produces, whose value is equal to and its direction is opposite to the loading stress. On the influence of the spontaneous rebound internal stress, the polymer chain segments gradually changed from curling molecular conformation to extension molecular conformation with the extension of relaxation time. Thus the high elastic deformation occurred and the regular elastic deformation simultaneously stopped. The results of this process resulted in the internal stress that keeps the same constant strain decreasing and thus the stress relaxation occurs in that the high elastic modulus is much lower than that of regular elastic modulus. Since the high elastic deformation replaced the regular elastic deformation, the phenomenon that the stress decreases with the rise of the relaxation time can be observed [27].

In terms of nano-HA/PVA gel composites, while the sample bears an external force suddenly, the free water in the network of the composites is squeezed out quickly under the external force. With the relaxation time prolonged, the free water of the composites experience redistribution in the network until it reaches a new equilibrium state. Meanwhile, the stress relaxation of the polymer constituents in the composites would take place according to the relaxation mechanism of the polymer. Since the articular cartilage also contains lots of free water and this constituent in articular cartilage is the same to that of nano-HA/PVA gel composites, it can be concluded that the stress relaxation behavior of the nano-HA/PVA gel composites are mainly determined by the synergistic effect of two mechanisms analogous to those of the natural articular cartilage and the polymer.

Effect of strain

Figure 4 shows the compressive stress relaxation properties of the composites in three strain levels. It can be concluded from Fig. 4 that: first, the relaxation rate of the nano-HA/PVA gel composites increases with the rise of compressive strain level. For example, while the compressive strains are kept at 30, 40, and 50%, the normalized relaxation modulus of the composites reduced from 1 to 0.801, 0.746, and 0.712 after initial 100 s relaxation, decreasing 19.9%, 25.4%, and 28.8%, respectively. Second, under all the strain levels, the relaxation rate of the composites declines with the rise of relaxation time. Finally, the normalized equilibrium relaxation modulus of the composites decreases with the rise of strain. For example, while the compressive strain increases from 30% to 50%, the normalized equilibrium relaxation modulus of the composites decreases from 0.629 to 0.511.

In order to investigate the effect of strain on the relaxation behavior of the composites, Fig. 5 shows the relationship between initial relaxation stress and normalized equilibrium relaxation modulus under different compressive strain

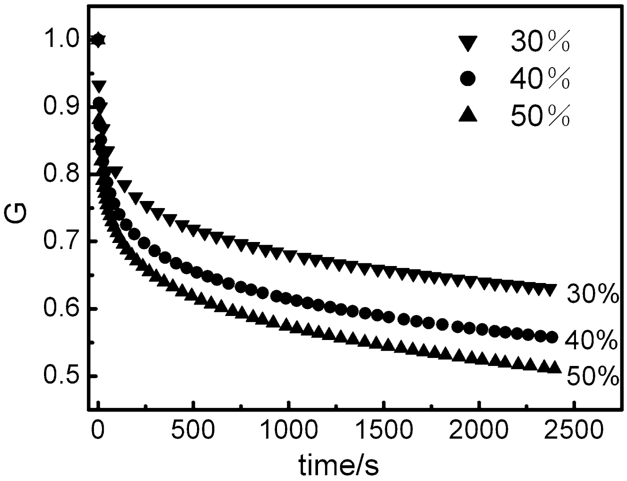

Fig. 4 Effect of compressive strain on the normalized relaxation modulus

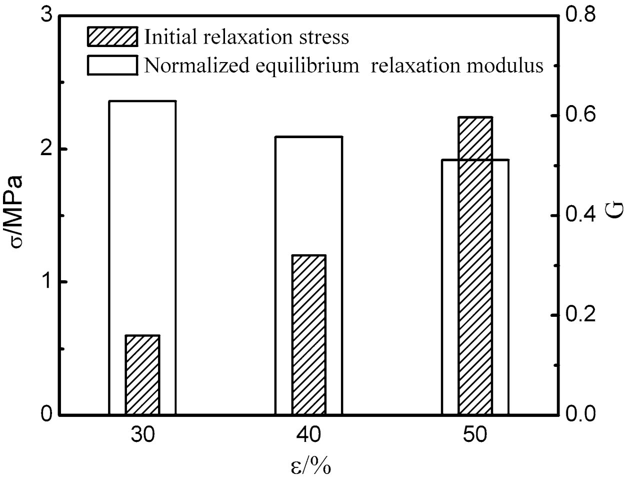

Fig. 5 Relationship between initial relaxation stress and equilibrium normalized relaxation modulus under different compressive strain levels

levels. It can be clearly seen from Fig. 5 that the change of behavior of normalized equilibrium relaxation modulus with the compressive strain is inversely proportional to that of the initial relaxation stress with the compressive strain, i.e., the initial relaxation stress increases with the rise of compressive strain, but normalized equilibrium relaxation modulus decreases with the rise of strain. For example, while the compressive strain rises from 30% to 50%, the initial compressive relaxation stress increases from 0.599 to 2.238 MPa, almost rising three times. Contrarily, the normalized equilibrium relaxation modulus decreases from 0.629 to 0.511.

The result is mainly attributed to the intensified network deformation of the composites with the increase of the initial relaxation stress. The acceleration of the network deformation in the composites would increase the flow speed of the free water that is squeezed out in the network of the composites, thus increasing the relaxation rate of the composites. Meanwhile, the acceleration movements of the macromolecular chain and cross-linked network nodes are beneficial to improve the stress relaxation rate of the composites. Furthermore, the variation degree of the bond angle and bond length would increase with the rise of initial stress, and then resulting in the rise of the regular elastic modulus of the composites. According to the stress relaxation mechanism of the polymer, on the initial relaxation processing, the decreased amplitude of the regular elastic modulus increases, thus causing the stress, which maintains the constant strain level, reduces distinctly and ultimately resulting in the normalized equilibrium relaxation modulus decreasing with the rise of strain.

It can be concluded from the above discussion that the variation of the relaxation rate and normalized equilibrium relaxation modulus with the strain ratio mainly depend on the flow speed of the free water in the network squeezed out and the movement of the macromolecular chain. It should be noted that the increase of relaxation rate and the decrease of normalized equilibrium relaxation modulus with the rise of strain both are beneficial to the application of nano-HA/PVA gel composites as an artificial articular cartilage. While nano-HA/PVA gel composites used as articular cartilage repair material bear high compressive stress, the rapid relaxation rate is beneficial to the dissipation of stress concentration quickly. Moreover, the lower the equilibrium relaxation modulus, the more effect on the dissipation stress is. These results would ultimately protect articular cartilage repair material effectively and improve the service life of the repair material.

Effect of HA content

Figure 6 shows the effect of nano-HA content on the stress relaxation of the composites under a certain compressive strain ratio. It can be concluded from Fig. 6 that: first, for a given strain level, the relaxation rate of the composite firstly increases with nano-HA content up to 6% and then decreases with increasing nano-HA content. For example, while the relaxation time is 100 s, the normalized relaxation modulus firstly decreases from 0.709 for pure PVA gel to a minimum value of 0.628 at 6% for filled PVA gel composites, and then increase to 0.688 with 7.5% nano-HA filled PVA gel composites. Second, the relaxation rate of the composites declines rapidly with the rise of relaxation time. The decrease amplitude of the relaxation modulus of all the composites takes up 50–60% of the total decrease amplitude at initial 100 s relaxation time. The remaining 40%–50% complete in 2300 s. Third, the normalized equilibrium relaxation modulus of the composites was strongly influenced by nano-HA content. With increasing

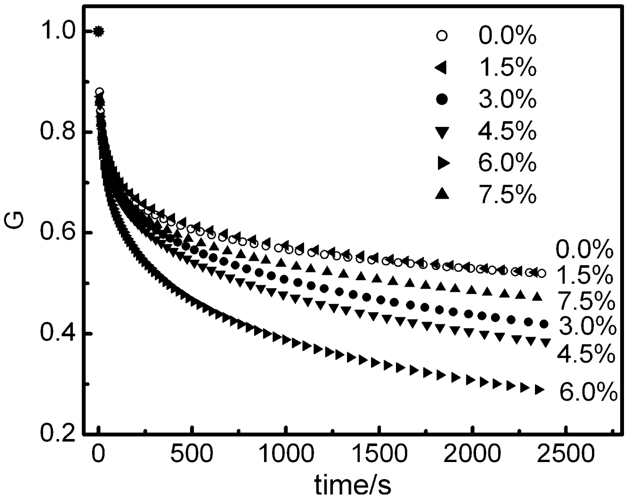

Fig. 6 Effect of nano-HA content on the stress relaxation behavior

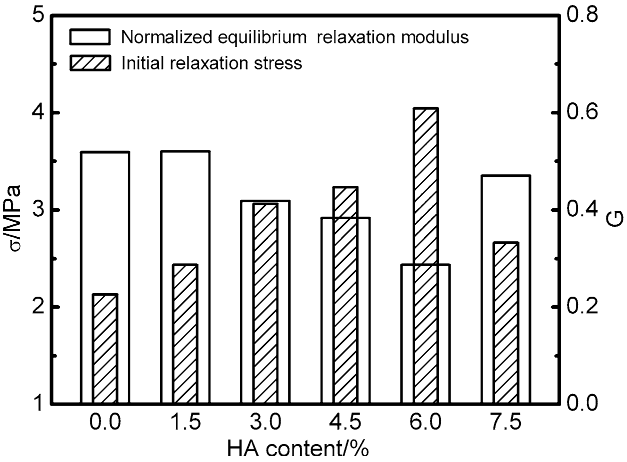

Fig. 7 Effect of nano-HA content on the initial relaxation stress and equilibrium normalized relaxation modulus

amount of nano-HA, the normalized equilibrium relaxation modulus decreased from 0.519 for unfilled PVA gel until a minimum value of 0.287 at 6% for filled PVA gels. Then, the normalized equilibrium relaxation modulus of the composites rises to 0.471 for 7.5% of nano-HA.

Figure 7 shows the relationship between normalized equilibrium relaxation modulus and initial relaxation stress under different nano-HA content. It can be seen from Fig. 7 that the initial relaxation stress of the composites first increases and then decreases with the rise of nano-HA content. It reaches maximum at 6% of nano-HA content. Conversely, the normalized equilibrium relaxation modulus of the composites first decreases and then increases with the rise of nano-HA content. It reaches minimum at 6% nano-HA content. It can be concluded that the normalized equilibrium relaxation modulus is inversely proportional to the initial relaxation stress. That is, under the same strain level, the higher initial relaxation stress, the lower the normalized equilibrium relaxation modulus is.

It is well known that the mechanical properties of the polymer are expected to be improved effectively by adding inorganic nano-particles into polymer matrix as their high mechanical strength and surface energy [14, 15]. Thus, addition of nano-HA particle in PVA gel matrix can obviously improve the mechanical strength of nano-HA/PVA gel composites. 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. The agglomerated nano-HA particles ultimately deteriorate the mechanical properties of the composites. According to the above discussion, it can be concluded that the mechanical properties of the gel composites deteriorates while nano-HA content in the PVA matrix is more than 6%.

Conclusions

The stress relaxation behavior of nano-HA/PVA gel composites has been investigated. The following points can be summarized for the present investigation.

1. The stress relaxation process of nano-HA/PVA gel composites included fast and slow relaxation stages. The stress relaxation mechanism of the composites was determined by both the stress relaxation characteristics analogous to those of the natural articular cartilage and the polymer.
2. The relaxation rate of the composites increased with the rise of strain ratio, but it declined with the relaxation time. The decline rate of the normalized relaxation modulus presents exponential decrease trend with the relaxation time.
3. Under the same strain ratio, the relaxation rate of the composite presented a trend of rising first and then falling with the rise of nano-HA content. Contrarily, the normalized equilibrium relaxation modulus of the composites first decreased and then presented increasing trend with the rise of nano-HA content. Both the relaxation rate and normalized equilibrium relaxation modulus reached to the peak value while nano-HA content is 6%. Furthermore, the normalized equilibrium relaxation modulus of the composites decreased with the rise of strain.
4. The stress relaxation characteristic of nano-HA/PVA gel composites is similar to that of natural articular cartilage and nano-HA/PVA gel composite is an excellent articular cartilage repair material.

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