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Effect of Strain on Viscoelastic Behavior of Fresh, Swelled and Mineralized PVP-CMC Hydrogel

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Abstract. Mineralization of calcium carbonate ($CaCO_3$) in hydrogel matrix is one of the most interesting topics of research by material scientists for the development of bio-inspired polymeric biomaterial for biomedical applications especially for bone tissue regeneration. As per our knowledge there was no work reported about rheological properties of $CaCO_3$ mineralized hydrogel though some works have done on mineralization of $CaCO_3$ in various gel membranes, and also it was reported about the viscoelastic properties of Agarose, Cellulose, PVA and PVP-CMC hydrogels. This paper mainly focuses about the effect of strain on viscoelastic properties of fresh, swelled and mineralized ($CaCO_3$) PVP-CMC hydrogel. All these three types of hydrogel sustain (or keep) strictly the elastic properties when low strain (1%) is applied, but at higher strain (10%) the viscoelastic moduli (*G*' and *G*") show significant change, and the nature of these materials turned from elastic to viscous.

Keywords: Hydrogels, Strain, Angular frequency, Viscoelastic, Swelling, Mineralization.
PACS: 83.85.Cg, 83.85.Vb, 87.85.J, 87.16.dm

INTRODUCTION

Biominerals are commonly formed in gel like extracellular network which use their supramolecular assemblies of organized biopolymers to exert wonderful control over the process of biomineralization [1-2]. Hydrogels are often fibrous, porous and hydrated extracellular networks that provide both the structural framework upon which inorganic minerals grow and serve as a source of chemical functionalities to direct nucleation and growth of the crystals [3]. In recent years, the manifestation of hydrogel-organic matrix in bio mineralization has gained much attention for the development of novel bio-inspired polymeric material for bone tissue engineering or other biomedical applications [4]. Grassmann et al. [5-7] prepared $CaCO_3$, in polyacrylamide hydrogels, sulfonic acid based hydrogels and carboxylate groups bearing poly-acrylamide hydrogels, respectively and mostly studied about morphologies of calcites because in gel matrix, the network structure of hydrogel exert different influences on the crystallization of minerals [1].

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Though, some works reported about rheological/viscoelastic properties of hydrogels of fresh ones, before dry condition as well as swelled state for polyvinylpyrrolidone and carboxymethyl cellulose (PVP-CMC) hydrogel [8-10], polyvinyalcohole (PVA) hydrogel [11], cellulose hydrogel [12] and agarose hydrogel [13] but no work reported yet about mineralized hydrogels. The viscoelastic properties of hydrogels correlate strongly with their microstructure and provide useful information for modulating their performance characteristics, moreover the viscoelastic behavior of gels depends on several factors, such as composition and concentration of dispersed materials and preparation condition of hydrogel [8]. Thus, it is important to investigate the viscoelastic properties of calcite ($CaCO_3$) filled PVP-CMC hydrogel which is already been developed by the research team of Polymer Centre, Tomas Bata University in Zlin and granted patent approval by Czech Republic for simple preparation technique of PVP-CMC hydrogel wound cover [14]. The basic viscoelastic properties of fresh, swelled and mineralized PVP-CMC hydrogels were presented in the first paper [15]. This paper mainly focuses about the effect of strain amplitude on the dynamic viscoelastic properties of those above mentioned PVP-CMC hydrogels.

EXPERIMENTAL

Preparation of Hydrogels (Fresh, Swelled and Mineralized)

The PVP-CMC hydrogels were prepared by dissolving polyvinylpyrrolidone (PVP; in concentration 0.2 % w/v), carboxymethyl cellulose (CMC; 0.8 % w/v), polyethylene glycol (PEG; 1.0 % w/v), agar (2.0 % w/v) and glycerin (1.0 % w/v) in distilled water. These polymer solutions were prepared in sealed reagent bottles under 15 lbs pressure and 120°C temperature for 20 minutes. Then, the liquids (50 ml each) were poured into Petri dishes (80 mm in diameter) and allowed to come at room temperature [9-10]. Finally, soft, smooth and transparent round hydrogels were obtained and termed as ‘fresh PVP-CMC hydrogel’. Then, the freshly prepared hydrogels are kept for dry at room temperature (22-25°C) and stored them for the preparation of swelled as well as mineralized hydrogel samples. Parts of the dry PVP-CMC hydrogels were soaked in water for 60 minutes to absorb water and obtained ‘swelled PVP-CMC hydrogel’. Parts of hydrogels were used for mineralization by using liquid diffusion method [15]. For the process of mineralization of calcium carbonate ($CaCO_3$) within PVP-CMC hydrogel two kind of inorganic solutions were used i.e. sodium carbonate (Na_2CO_3; 105 g/L) and calcium chloride ($CaCl_2$; 147 g/L) to achieve ‘mineralized ($CaCO_3$) PVP-CMC hydrogel’ [15-16]. In order to compare the viscoelastic behavior of swelled hydrogel with that of mineralized one, the PVP-CMC hydrogel was mineralized up to 60 minutes (by change of sample in inorganic solution 15 min interval) to deposit/form $CaCO_3$ particles within the hydrogel matrix. The optical images of the hydrogels (fresh, dry, swelled and mineralized) are shown in Figure 1.

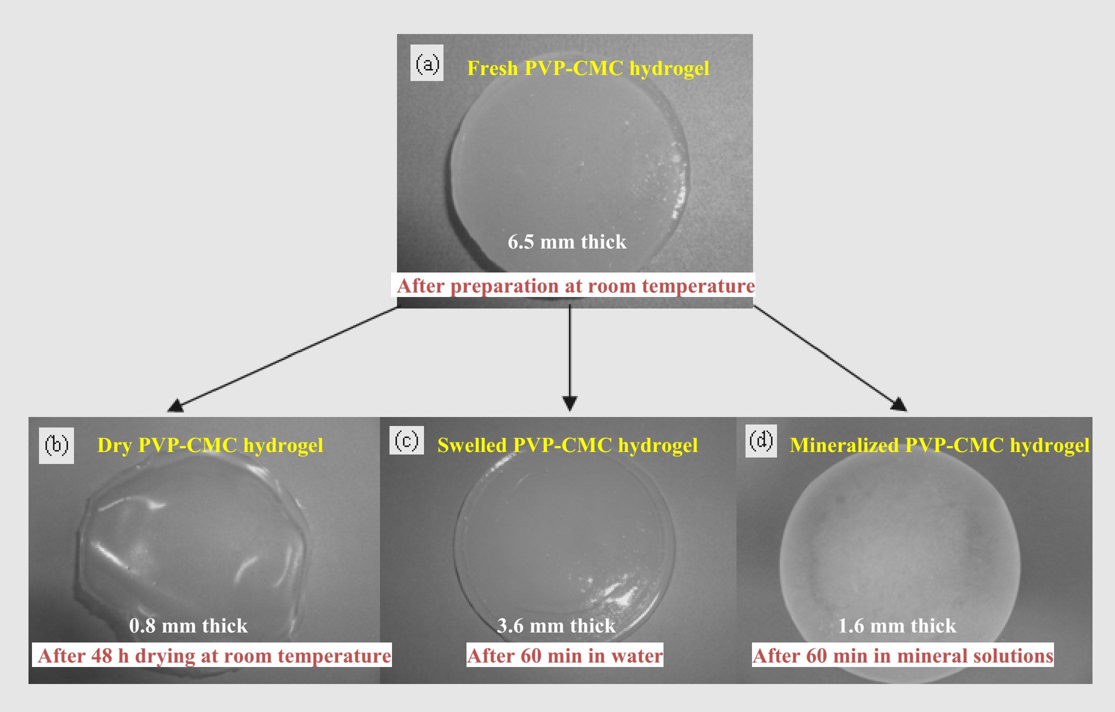

FIGURE 1. An optical image of (a) Fresh, (b) Dry, (c) Swelled and (d) Mineralized ($CaCO_3$) hydrogels.

Measurements of Dynamic Viscoelastic Properties

The viscoelastic properties of hydrogels were examined by using a parallel plate rheometer testing device (ARES, Rheometrics Scientific, USA) and “TA Orchestrator” software for data evaluation. Dynamic frequency sweep tests were carried out at the temperature of 28°C to obtain the storage (*G*’- elastic part) and loss (*G*”- viscous part) moduli, and complex viscosity (η^*). The geometry of measuring parallel plate was 25 mm in a diameter, with a gap between plates depending on sample thickness (approximately from 1 to 3 mm for mineralized, swelled hydrogels and 6 mm for fresh ones). Measurement was conducted in oscillation mode with the frequency range from 0.1 – 100 rad.s^{-1} at two different strain amplitudes i.e. 1% as well as 10%, which is considered as the highest strain limit for the measurements within the linear viscoelastic region (LVER) for homogeneous polymer substances.

RESULTS AND DISCUSSION

To understand the effect of strain on the viscoelastic behavior of hydrogels, the dynamic frequency sweep tests of PVP-CMC hydrogels were carried out in different forms (fresh, swelled and mineralized). Measurements were performed at two different strain amplitudes: 1% and 10%. In our previous research articles based on PVP-CMC and PVP-CMC BA hydrogels, we observed that at low strain (1%), the hydrogels show linear storage (G’) and loss (*G*”) moduli curves and exhibit rubbery consistency throughout the measurement angular frequency range. On the other hand, at the same measurement condition when applied higher strain (10%) the viscoelastic moduli (*G*', *G*") are significantly changed in comparison with those under the low strain measurement [10]. It shows lower value of *G*' and higher value of *G*" when changed the strain of measurement from 1% to 10%. Therefore, to recognize the substantial changes under the strain of 1% and 10% in viscoelastic properties of *fresh*, *swelled* and *mineralized* hydrogels, each hydrogel has been examined individually and mentioned below.

Influence of the Strain on the Viscoelastic Properties of Fresh Hydrogel

The effect of low (1%) and high (10%) strain on the rheological properties (storage modulus: *G*', loss modulus: *G*" and complex viscosity: η^*) of fresh hydrogel is shown in Figures 2 and 3, respectively. It can be seen from Figure 2 that at low strain (1%) the fresh PVP-CMC hydrogel (thickness 6 mm) demonstrates higher value of storage modulus (*G*') than loss modulus (*G*"), however, at higher strain (10%) the same hydrogel sample displays much lower value of *G*' in comparison with that at strain 1% and also shows just opposite behavior between *G*' and *G*".

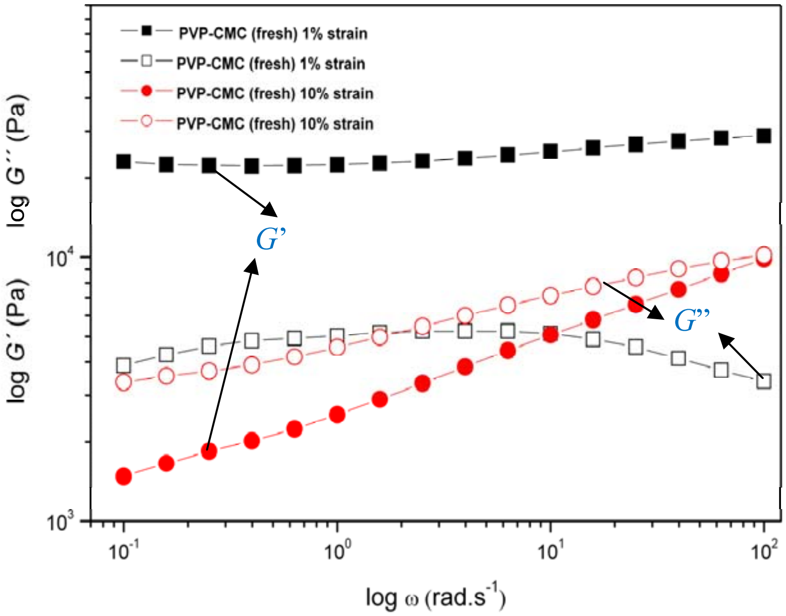

FIGURE 2. Effect of angular frequency (ω) at low (1%) and high (10%) strain on viscoelastic properties of freshly prepared PVP-CMC hydrogels where storage modulus denoted as (*G*', filled symbols) and loss modulus (*G*", unfilled symbols).

It is also noticed that at higher strain of measurement, the value of *G*" is higher than *G*', and both *G*' and *G*" values are gradually increased with the increase of frequency. It means though at higher strain condition, the physical bonding and entanglements/cross linkages of polymers in freshly prepared PVP-CMC hydrogel are broken thus miss their original elastic nature (typical gel character), at higher frequency they start to recover gradually their own characteristics. Like storage modulus (*G*') and loss modulus (*G*"), the fresh PVP-CMC hydrogel also exhibits the lower values of complex viscosity (η^*) at 10% strain compared to those at 1% (depicted in Figure 3), and the slope of η^* versus ω curve decreases from around -1(-45 degs.) at 1% strain to lower value at 10% strain.

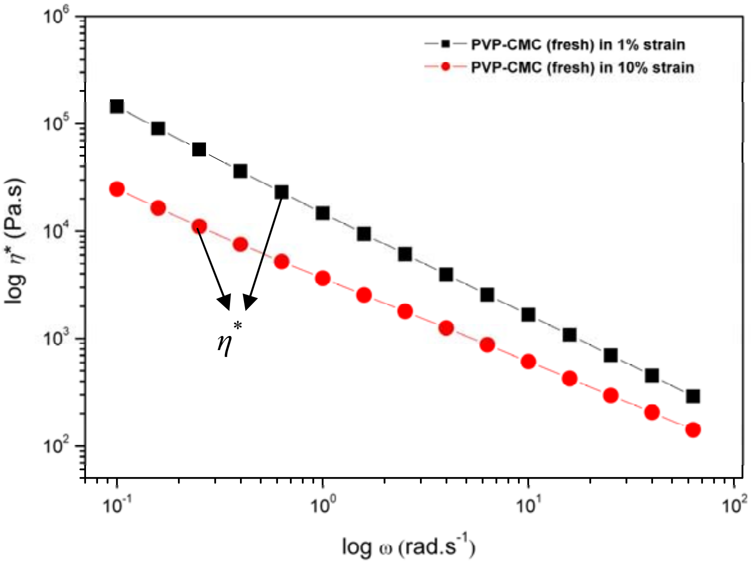

FIGURE 3. Effect of angular frequency (ω) at low (1%) and high (10%) strain on complex viscosity (η^*) of freshly prepared PVP-CMC hydrogels.

Influence of the Strain on the Viscoelastic Properties of 60 Min Swelled Hydrogel

The effect of low (1%) and high (10%) strain on the rheological properties (*G*', *G*", and η^*) of 60 min swelled hydrogel is shown in Figures 4 and 5. It can be seen from Figure 4 that at 1% strain the values of both storage modulus (*G*') and loss modulus (*G*") show the decreased values in the case of swelled (60 min in water) hydrogel in comparison with those of fresh hydrogel, though they display more or less linear curves throughout the whole range of angular frequency which are similar trends with fresh hydrogel. But, at 10% strain the *G*' and *G*" exhibit a little lower values compared to fresh hydrogel, and the values gradually increased , and at the angular frequency of around 10 rad.s^{-1} both the values of *G*' and *G*" merged together and then *G*' becomes higher than *G*", and *G*" value starts to level off or decrease slightly. This behavior seems to be similar with that of simple polymer liquid. It is considered that at higher strain condition, the physical bonding and entanglements/cross linkages of polymers in 60 min swelled PVP-CMC hydrogel are broken higher than fresh hydrogel at low angular frequency ω, however, the increase of *G*' may be attributed to the flexible polymer network which is an evident at higher ω.

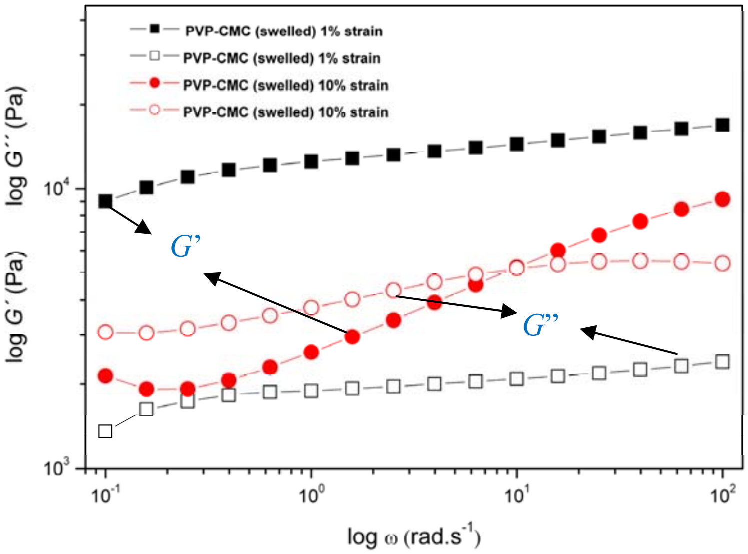

FIGURE 4. Effect of angular frequency (ω) at low (1%) and high (10%) strain on viscoelastic properties of swelled (60 min in water) PVP-CMC hydrogels where storage modulus denoted as (G', filled symbols) and loss modulus (G", unfilled symbols).

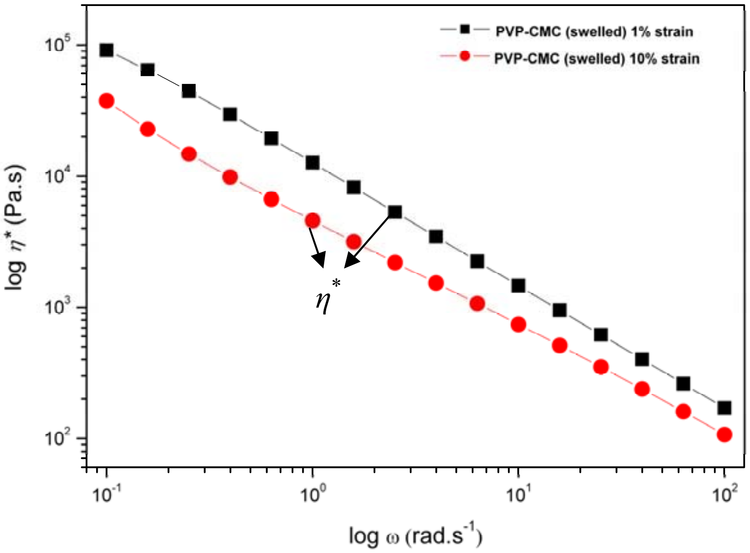

FIGURE 5. Effect of angular frequency (ω) at low (1%) and high (10%) strain on complex viscosity (η^*) of swelled (60 minutes in water) PVP-CMC hydrogels.

When considering the complex viscosity η^* of 60 min swelled hydrogel shown in Figure 5 with respect to fresh one shown in Figure 3, it is noticeable that the values of the former are lower clearly than the latter, but the trend of ω effect is similar as fresh hydrogel, i.e. at low strain the swelled hydrogel also shows higher values of η^* than those at high strain.

Influence of the Strain on the Viscoelastic Properties of 60 Min Mineralized Hydrogel

The effect of low (1%) and high (10%) strain on the rheological properties (*G*’, *G*”, η^*) of mineralized hydrogel is depicted in Figures 6 and 7. It can be seen Figure 6 that at 1% strain, the storage modulus *G*’ and loss modulus *G*” of the 60 min mineralized hydrogel demonstrate the similar trend of curve (i.e. more or less linear curve) like fresh hydrogel as well as swelled hydrogel although *G*’ and *G*” of these hydrogels are different and are in the following order for *G*’: fresh hydrogel ≥ mineralized hydrogel> swelled hydrogel and for *G*”: mineralized hydrogel > fresh hydrogel > swelled hydrogel.

At 10 % strain both *G*’ and *G*” curves of mineralized hydrogel show a little different behavior from fresh hydrogel as well as swelled hydrogel although the trend that *G*’ becomes lower than *G*” over wide range of angular frequency ω are similar for these three type of hydrogels. At the lower ω range (0.1-1 rad.s^{-1}) both *G*’ and *G*” of the mineralized hydrogel (60 min in mineralized solution) show the decreasing value with *ω* and then reveal relatively steady linear curves throughout the wide *ω* range .The steady linear curves of *G*’ and *G*” indicate the firm attachment of $CaCO_3$ with PVP- CMC hydrogel matrix.

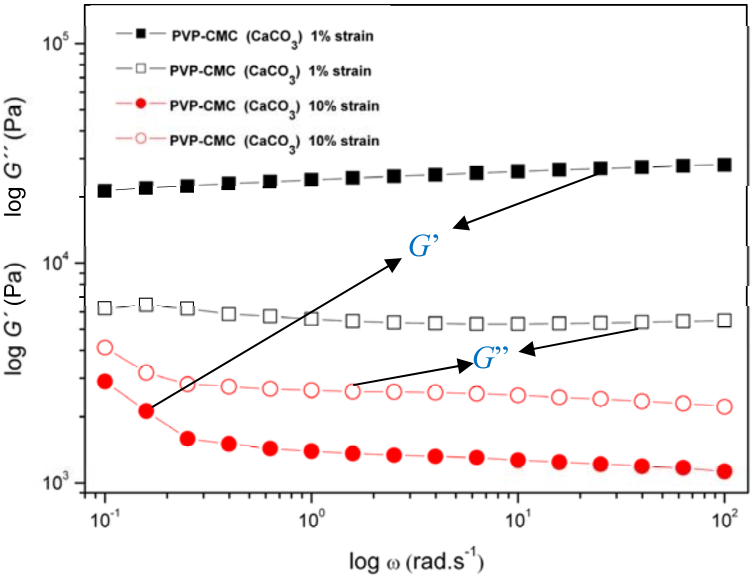

FIGURE 6. Effect of angular frequency (*ω*) at low (1%) and high (10%) strain on viscoelastic properties of mineralized (60 min in mineralized solution) PVP-CMC hydrogels where storage modulus denoted as (*G*’, filled symbols) and loss modulus (*G*”, unfilled symbols).

Like fresh and swelled hydrogels, the mineralized hydrogel also showed the same trend of curve in the case of low and high strain of measurement i.e. at 1% strain the mineralized hydrogel showed high value of η^* than 10% strain. Moreover, from the curve nature (Figures 6 and 7) it can be assumed that even after mineralization with $CaCO_3$, the PVP-CMC hydrogel is able to maintain almost same viscoelastic behavior of fresh hydrogel under the measurement at low strain though there is far difference in thickness of hydrogel sample between fresh hydrogel and mineralized hydrogel (see Figure 1).

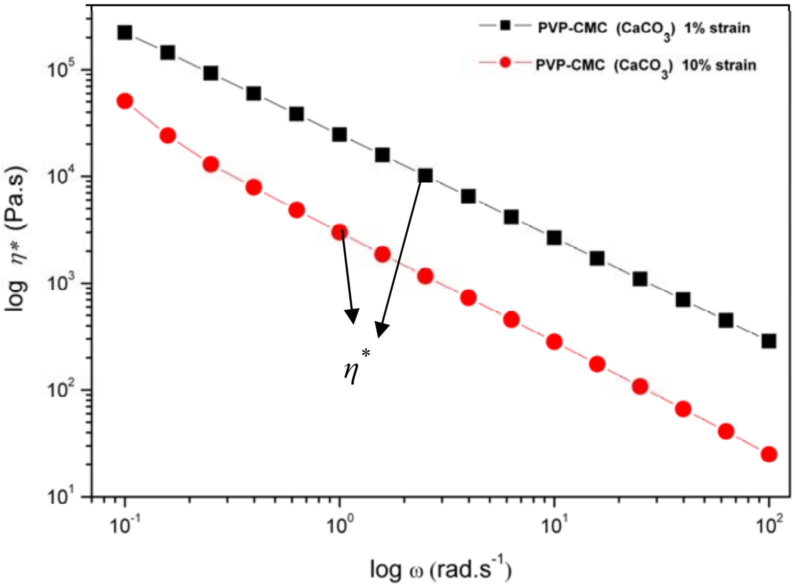

FIGURE 7. Effect of angular frequency (ω) at low (1%) and high (10%) strain on complex viscosity (η^*) of mineralized (60 minutes diffusion of minerals) PVP-CMC hydrogels.

In another paper [15] we showed the relation between absorptivity of $CaCO_3$ into fresh hydrogel and mineralized time, and it was found that the amount of $CaCO_3$ gradually increases with time. Concerning the dynamic viscoelastic properties of the hydrogels with different mineralized time, it was found that both *G*' and *G*" have the tendencies to gradually decrease with mineralized time, which is different rheological behavior from that of general filled systems. In order to clarify the strain dependent viscoelastic properties of mineralized hydrogels we will need the morphological observation in more detail.

CONCLUSION

The dynamic frequency sweep tests by parallel plate rheometer explained that, all three forms of hydrogels (fresh, swelled and mineralized hydrogels) sustain (or keep) strictly elastic properties when low strain amplitude is applied. However, when the higher strain is applied the viscoelastic moduli (*G*' and *G*") show significant change, and their material nature turns from elastic to viscous.

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