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Oleyaei, Seyed Amir

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Authors: Seyed Amir Oleyaei, Seyed Mohammad Ali Razavi, Kirsi S. Mikkonen

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Novel nanobiocomposite hydrogels based on sage seed gum-Laponite:

Physico-chemical and rheological characterization

Seyed Amir Oleyaei^a, Seyed Mohammad Ali Razavi^{a,*}, Kirsi S. Mikkonen^b

^a*Food Hydrocolloids Research Centre, Department of Food Science and Technology, Ferdowsi University of Mashhad (FUM), P.O. Box 91775-1163, Mashhad, Iran*

^b*Department of Food and Nutrition, P.O. Box 66 (Agnes Sjöberginkatu 2), FI-00014 University of Helsinki, Finland*

Research Highlights

- Novel sage seed gum (SSG)-Laponite nanocomposite hydrogels successfully prepared.
- Physicochemical properties of SSG gel tailored by controlling Laponite loading.
- The particle size of SSG hydrogels became larger as the Laponite content increased.
- Large and small deformation behaviors of SSG-Laponite hydrogels were alien overall.
- Laponite rose viscoelastic moduli, complex viscosity, and stiffness of hydrogels.
- Matrix-nanofiller affinity and interactions governed physico-chemical properties.

Abstract

In this study, the physico-chemical and rheo-mechanical properties of sage seed gum hydrogel, reinforced by various ratios (0-25 wt.%) of Laponite, were investigated. Particles size measurements indicated the formation of large SSG-Laponite microstructures upon

*Corresponding author: Tel: +98-51-38805763, Fax: +98-51-38787430, Email: s.razavi@um.ac.ir

nanoparticle adding, due to the interactions generated between the anionic SSG and the charged surfaces of clay platelets. Laponite affected the surface tension and density of the SSG-based systems significantly, but only influenced the ζ -potential above 20 wt.%. The dynamic rheological behavior of SSG-based nanocomposites reflected the reinforcing effect of secondary structures and percolated three-dimensional network, suggested a structural modification of the hydrogels with the Laponite loading. An improvement in texture profile analysis parameters was observed in Laponite content ≤ 5 wt.%, whereas for nanoparticles > 5 wt.%, a significant decrease was obtained. In conclusion, Laponite improved the rheological and physico-chemical properties of SSG-based hydrogel and extended its potential as promising future bio-products for industrial applications.

Keywords: Biocompatible clay; Hydrogel; Galactomannan; Nanostructure; Rheology modifier; Viscoelasticity.

1. Introduction

Hydrogels are three-dimensional (3D) networks of chemically (covalent bonding) and physically (hydrogen and hydrophobic bonds, chain entanglements, van der Waals forces, ionic interactions and crystallites associations) cross-linked hydrophilic polymers that can absorb and retain a significant amount of water or biological fluid. Any flexible or semi-flexible macromolecule can practically formulate hydrogels in a variety of physical forms (Köhnke, Elder, Theliander, & Ragauskas, 2014). Hydrogels are divided into two, synthetic or biopolymer-based categories according to their origin. Considering the eco-friendliness, biodegradability, and biocompatibility of biopolymer-based hydrogels, they have gained increasing attention in recent years. They are applied in various fields such as agriculture,

pharmaceutical, medical materials and biosensors (Shen, Shamshina, Berton, Gurau, & Rogers, 2016). Hydrogels can also offer new opportunities for the efficient design of polymer packaging and coating materials with desirable properties. They can be transformed into highly porous materials, aerogels or act as filmogenic solutions (Ghafari et al., 2015).

Among the biopolymers, polysaccharide-based hydrogels have received significant industrial and environmental interests due to their excellent characteristics, cost, and sustainability. Galactomannans are one of the most common plant food polysaccharides belonging to the legume family consisting of α -(1-4)-linked D-mannosyl backbone grafted with α -(1-6)-linked D-galactosyl stubs to some of the mannosyl residues (Wang & Somasundaran, 2007). In the current trend for a more efficient use of biomass, galactomannans-based biopolymers such as guar and locust bean gum have appeared as a new potential group of polysaccharides in the outreach of novel materials (Kennedy, Kent, & Brown, 2015). A new anionic galactomannan, namely, sage seed gum (SSG), has been recently extracted from the outer pericarp of sage seed, an endemic plant belonging to the genus *Salvia* (Bostan, Razavi, & Farhoosh, 2010). SSG biopolymer has a guar like composition and linear backbone structure with a 1.78-1.93:1 mannose/galactose ratio, a weight average molecular weight of $\sim 4 \times 10^5$ Da and a rigid rod-like conformation. It has a polyelectrolyte nature due to high presence amount of total uronic acids (28.2-32.2 %) and the relative amount of acidic polysaccharides. Based on rheological characterizations, SSG exhibited a stronger shear viscosity, pseudoelasticity, and elasticity in comparison with other commercial galactomannans such as guar and locust bean gums, which are attributed to the presence of a complex network in the gel formed from stiff SSG polymer chains. The hydroxyl (-OH) and carboxyl (-COOH) groups on the repeating units of SSG chains are available for hydrogen bonding of the polymer molecules to mineral surfaces (Razavi, Cui, Guo, & Ding, 2014). Due to the noticeable shear thinning behavior of SSG hydrogels, it can be explored as suspending agent and thickener to improve the stability of

disperse systems in several industrial areas. However, the physico-chemical properties of galactomannans and SSG-based hydrogels are not always optimal for different applications. Nanotechnology provides winning strategies for the development of nanocomposite hydrogels with tailorable features. Polymer-clays nanocomposites have received considerable worldwide attention due to the augmented surface interactions between polymer chains and functional groups such as oxygen and -OH present in clay (Oleyaei, Almasi, Ghanbarzadeh, & Moayedi, 2016).

Laponite is a synthetic version of the biocompatible hectorite clay. The composition, size, crystallinity, shape and, the morphology of nanoparticles are critical parameters of the intrinsic properties of particles and its related nanocomposite. Laponite composition and its bidimensional (2D) crystal structure are intently similar to the naturally occurring in smectite clay such as hectorite. Laponite platelets have a negatively charged surface and positively charged rim and can be quickly dispersed in aqueous media in the form of rigid disk-shaped crystal colloids with an aspect ratio of 1:30 (Dávila & d'Ávila, 2017). Laponite is a rheology modifier that promotes shear-thinning and thixotropic behavior in various waterborne products. In some studies, Laponite was used to augment the gelatin (Karimi, Taheri, & Namivandi, 2013), carrageenan (Mahdavinia, Massoudi, Baghban, & Massoumi, 2012) and cellulose-based (Perotti, Barud, Messaddeq, Ribeiro, & Constantino, 2011) hydrogels. Rheological behavior investigation provides some useful information in perception how these nanostructures are formed and the degree of nanoparticle dispersion in the polymer matrix (Kennedy et al., 2015). Just recently, rheological characterization of alginate-Laponite and scleroglucan-Laponite hydrogels has been carried out to assay the reinforcing effects of Laponite, in particular to analysis the physical gelation due to the electrostatic interactions between the anionic groups of alginate and scleroglucan chains and positively charged rim of Laponite disks (Dávila & d'Ávila, 2017; Lapasin, Abrami, Grassi, Sebenik, & Šebenik, 2017). Although a lot of facts on

the complexation of biopolymer-nanoparticle can be found in literature, the exact nature of the interactions between Laponite nanodisks and galactomannan polymers such as SSG depends on the amount, type and distance of the anionic sites, hydrophilicity and flexibility of the backbone, molecular weight and branching degree in the structure, which are missing.

The aim of this study was to develop a new galactomannan SSG-Laponite nanocomposite hydrogels potentially utilized in coating and therapy applications (drug carrier, skin care, and topical creams) or as a precursor (nanocomposite-forming solution) of microcapsule, film, aerogel, and tissue engineered scaffold materials. Rheological and textural characteristics have a significant effect on stability and functional features of nanohybrid hydrogels as a final product or nanocomposite-forming solutions preparation which is a pivotal phase in highly ordered nanocomposite fabrication. Therefore, the focus of this research was on understanding the roles of Laponite at various concentrations (0-25 wt.%) on matrix-nanofiller system microstructure and polymer-particle interactions by determining the physico-chemical, rheo-textural and macroscopic properties of SSG-Laponite hydrogels. It is believed that developing a database on the rheo-mechanical properties by using various rheological parameters derivatives of biopolymer-based gels is crucial to adjust processing factors, monitoring stability as well as predicting the consistency of matrix-nanofiller systems. Besides, understanding the mentioned database and microstructure-property relation is essential to allow food, cosmetic and biomedical product developers to use the functionality of SSG-based hydrogels in different applications.

2. Materials and methods

2.1. Materials

The mucilage of sage seeds (SSG) was extracted under optimized conditions, using the same procedure as described by Bostan et al. (2010). Laponite[®] XLG powder was procured from Rockwood Additives Ltd., UK. Surface area, cation exchange capacity (CEC) and particle density of this type of Laponite were 370 m²/g, 104 mequiv/100g, and 2.65 g/cm³, respectively. Sodium azide (ReagentPlus[®], assay $\geq$ 99.5%) were supplied by Sigma-Aldrich.

2.2. Hydrogel preparation

The following consecutive manner was applied to SSG-based nanocomposite hydrogels procurement. A stock solution of Laponite (0.01 g/ml) was prepared by stirring (24 hours at 300 rpm) and sonication with 24 kHz Hielscher UP200H ultrasound (Hielscher Ultrasonics, Germany) for two min at ambient temperature. Then, 0, 5, 10, 15, 20 and 25 ml were taken from Laponite stock solution and added to the appropriate amount of de-ionized water containing sodium azide (0.02%) as an antimicrobial preservative. Powdered SSG (1% w/w) was added very slowly with intense stirring (700 rpm, 5 min), and the mixing was continued for 2 hours. T25 Ultra-Turrax (Ika, Germany) was used for 2 min at 4000 rpm speed to homogenate the nanocomposite mixture. Hydrogels were kept on rotating roller mixer (Haematology Cell Mixer, Iran) for 24 h at room temperature to allow complete hydration of the hydrocolloid and also providing enough time to react with nanoparticles for any possible configurationally changes.

2.3. Particle size and Zeta (ζ)-potential measurements

The particle size of SSG-Laponite hydrogels was determined in triplicates by a laser diffraction particle sizer (Cordouan, Vasco 3, and France) at 25°C. The ζ -potential was measured based on micro-electrophoresis mobility at ambient temperature, using dynamic light scattering (DLS)

technique (ZetaCompact, CAD, and France). Before the experiments, the SSG-based hydrogels were diluted 40 fold in deionized water.

2.4. Surface tension and density measurements

Surface tension and density of the SSG-Laponite hydrogels were measured using Wilhelmy plate technique (K100, KRUSS, Germany) with a platinum-iridium plate (width: 10 mm, length: 19.9 mm and thickness: 0.2 mm) at 25 °C. The hydrogels were prepared by the method as described earlier. All samples were kept steady for one h to reach equilibrium before the test, and each measurement repeated three times. Before to the analysis, calibration of the instrument was performed using distilled water.

2.5. Small amplitude oscillatory shear (SAOS) measurements

Dynamic rheological tests of the pure SSG and SSG-Laponite nanocomposite hydrogels were executed by a Physica MCR301 controlled stress/strain rheometer (Anton Paar, Germany, GmbH) equipped with the cone-plate geometry (0.206 mm gap, 50 mm diameter and 4° angle). The temperature was fixed at 20 °C during the experiments using a Peltier-plate system. To structure recovery and temperature equilibration, the samples were left at rest for two minutes. All the samples were covered with a hood accessory along with a layer of silicon oil to prevent water evaporation during the measurements. Rheoplus software (Anton-Paar, version 3.21) was employed to analyze the results of rheological tests.

2.5.1. Stress sweep test

Stress sweep measurements were operated at controlled shear stress state (0.01-100 Pa, 1 Hz, and 20°C) to determine the stress amplitude in the linear viscoelastic region (LVE). In addition, some of the rheological characteristics such as τ_y or dynamic yield stress (the resistance to

mechanical force that can be measured from the limiting value of LVE region in terms of shear stress) with corresponding storage modulus at LVE (G'_{LVE}) as an indicative of the structural strength, viscous modulus at LVE (G''_{LVE}), complex modulus at LVE (G^*_{LVE}), $\tan \delta_{LVE}$ or damping factor at LVE (a view of whether the samples behaved as solids or liquids and can be calculated from G''/G') were determined. Moreover, τ_0 or static yield stress at the limit of the LVE region (calculated by determining the flexion point in a double-logarithmic stress-strain curve or deviation of the linear relationship between strain and stress from the unitary slope), τ_f or flow-point stress (the stress in which internal structure breaks to such an extent that it causes the material to flow or $G' = G''$), with corresponding modulus (G_f : $G' = G''$) for all SSG-based hydrogels were assessed by the amplitude stress sweep test. To have a better perception of gel strength, fracture strain and fracture stress were also calculated. The fracture strain and fracture stress were determined by plotting elastic stress, the product of the elastic modulus and strain amplitude ($G' \cdot \gamma$), as a function of increasing strain and stress, respectively (Razavi, Alghooneh, & Behrouzian, 2017).

2.5.2. Frequency sweep test

The frequency sweep experiments at a constant stress (0.1 Pa) in the LVE region were performed to evaluate the viscoelastic properties of hydrogels samples. The mechanical spectra were characterized by the storage modulus (G') and loss modulus (G''), complex modulus (G^*), complex viscosity (η^*), and the loss tangent ($\tan \delta$) as a function of frequency in the region of 0.01-10 Hz. The frequency dependencies of G' and G'' for SSG hydrogels were determined by a power-law model using Eqn. (1) and Eqn. (2), respectively:

$$G' = K'(\omega)^{n'} \quad (1)$$

$$G'' = K''(\omega)^{n''} \quad (2)$$

Where, K' (Pa.s^n) and K'' (Pa.s^n) are intercepts, n' and n'' are slopes, and ω is the angular frequency (rad.s^{-1}).

In the high-frequency region or near the gel point of the linear viscoelastic regime, the values of Friedrich & Heymann (1988) model parameters were used to describe the hydrogel viscoelastic properties:

$$G^* = \sqrt{G'^2 + G''^2} \cong \sqrt{\frac{2}{\pi}} \times S_\alpha^* \times \omega^\alpha = A_\alpha \times \omega^\alpha \quad (3)$$

Where, S_α^* ($\text{rad}^{-\alpha}.\text{s}^\alpha$) is a parameter associated with the material strength, A_α is the material stiffness ($\text{Pa.rad}^{-\alpha}.\text{s}^\alpha$) and α (dimensionless) is the order of the relaxation function.

2.6. Large deformation mechanical test

Brookfield Texture Analyzer (CT3, USA) was used to characterize the hydrogels texture using the texture profile analysis (TPA) test adopted from Razavi & Mohammadi, (2011). Experiments were performed in a standard size back extrusion container (45 mm diameter) and disk (30 mm diameter). During the measurements at room temperature (25 °C), the disk was proceeded to penetrate twice to a depth of 40% with a rate of 1 mm/s for the test and post-test speed (recovery time was zero). The apparent modulus of elasticity (initial tangent modulus) was considered as the slope of the linear region of the stress-strain curve of the hydrogels. Other critical parameters such as hardness (the height of the force peak on the first compression cycle), adhesiveness (the negative force area of the first cycle), cohesiveness (the ratio of the positive force areas under first and second compressions), and springiness (the distance that the hydrogel recovered its height during the time that elapsed among the end of the first cycle and the start of the second cycle) were derived from the resultant plot.

2.7. Statistical analysis

Statistical analysis based on a completely randomized design was performed using analysis of variance (ANOVA) procedure in SPSS software (Version19, SPSS Inc., Chicago, IL) and the differences between mean values were evaluated by Duncan's Multiple-Region tests ($P < 0.05$).

3. Results and discussion

3.1. Zeta (ζ)-potential

The variations of the ζ -potentials (mV) of the SSG-Laponite nanocomposite hydrogels are shown in Table 1. The ζ -potential of Laponite solution and pure SSG gel were found to be about -57.09 and -53.09 mV, respectively, indicating Laponite and SSG carried negatively charged (anionic hydrocolloids), which is expected and close to the values obtained in literature (Au & Leong, 2015; Mohammadzadeh, Koocheki, Kadkhodae, & Razavi, 2013). The high and negative ζ -potentials magnitudes, preventing aggregation and sedimentation phenomena, are indicative of stable systems. Indeed, it has been reported that, for a physically steadfast nanocomposite, mainly stabilized by electrostatic repulsion, a ζ -potential value close to ± 30 mV is required as a minimum (Bendahou, Bendahou, Seantier, Grohens, & Kaddami, 2015) and, as stated by Derjagin-Landau-Verwey-Overbeek (DLVO) theory, the higher the zeta potential magnitudes, the more stable system (He, Zhang, Cai, & Wang, 2016). Laponite platelets have positive edge charges, typically about 10% of the total negative charge due to the local positive ions present in its structure (Au & Leong, 2015). This allows the Laponite to interact with SSG chains, having a negative ζ -potential.

Table 1

Zeta potential, particle size, surface tension and density for 1% dispersion of sage seed gum (SSG) and SSG-Laponite hydrogels at 25°C.

Samples	Zeta potential (mV)	Particle size (nm)	Surface tension (mN/m)	Density (g/ml)
Laponite	-57.1 $\pm$ 0.2 ^b	-	-	-
SSG	-53.1 $\pm$ 0.4 ^a	277.6 $\pm$ 40.3 ^a	62.2 $\pm$ 0.2 ^a	1.47 $\pm$ 0.01 ^a
SSG-5%Laponite	-52.9 $\pm$ 1.0 ^a	671.6 $\pm$ 56.1 ^b	53.8 $\pm$ 0.1 ^b	1.44 $\pm$ 0.03 ^b
SSG-10%Laponite	-52.1 $\pm$ 0.1 ^a	819.8 $\pm$ 77.5 ^c	66.8 $\pm$ 0.2 ^d	1.32 $\pm$ 0.01 ^c
SSG-15%Laponite	-52.7 $\pm$ 0.9 ^a	882.6 $\pm$ 67.1 ^{c,d}	64.8 $\pm$ 0.0 ^c	1.23 $\pm$ 0.01 ^d
SSG-20%Laponite	-52.9 $\pm$ 0.3 ^a	932.2 $\pm$ 55.0 ^{d,e}	66.1 $\pm$ 0.2 ^d	1.15 $\pm$ 0.02 ^f
SSG-25%Laponite	-56.5 $\pm$ 0.4 ^b	1090.3 $\pm$ 100.2 ^e	69.5 $\pm$ 0.3 ^e	1.19 $\pm$ 0.04 ^e

Different letters indicate significant differences between samples at $P < 0.05$ by Duncan test.

Addition of Laponite into the SSG hydrogel did not affect ζ -potential significantly, even in the high concentration of Laponite (20 wt.%) used (Table 1). It was in good accordance with reported results for gelatin-montmorillonite (MMT) solutions (Jorge et al., 2014). Only a significant increase of the negative value of the ζ -potential observed when the Laponite concentration increased to 25 wt.% (-56.46 mV), which approved that the polymer chains adsorbed on the particle surface. Similar results have been obtained with a mixture of both negative charge cellulose and inorganic nano-zeolites solutions (Bendahou et al., 2015). The results of the study of M'Bodj, Ariguib, Ayadi, & Magnin (2004) also revealed that xanthan adsorbed on the surface of the clay and increased the negative charges on the nanoparticle surface, due to its ionic character.

3.2. Particle size

Particle size is a crucial factor in predicting the rheological behavior of the material, as micro- in comparison to nano-particle interactions with the polymer chains can be different utterly. Particles size distribution of the SSG was monomodal with an average size of about 277 nm (Table 1). Laponite disks are much smaller than SSG rod, can produce strong polymer bridging

interactions especially at high nanoparticle fractions. In the low Laponite content (5 wt.%), particle size increased abruptly to 671 nm. The rate of size increment for high clay concentration, slowed down and size of particles reached to 882 and 1090 nm with 15 and 25 wt.% Laponite adding, respectively. This observation might be explained by the formation of flexible secondary structures due to the polymer bridging which increased particles size. With high enough particle volume fraction, polymer bridging might be responsible for forming a more massive percolated 3D network resulting in a stronger, elastic hydrogel structure (Kennedy et al., 2015). These results agreed with other authors who have found the larger size aggregate structures in gelatin-MMT (Jorge et al., 2014), gelatin-TiO₂ filmogenic solutions (He et al., 2016) and wheat gluten-montmorillonite gel (Mascheroni, Chalir, Gontard, & Gastaldi, 2010), upon nanofiller contents increasing.

3.3. Surface tension

The influence of Laponite on surface activity of SSG-based hydrogels is shown in Table 1. Two different behaviors were seen depending on Laponite percentage. For Laponite contents lower than 5 wt.%, an abruptly decrease of surface tension from 62.1 to 53.8 mN/m was obtained, whereas for higher nanoparticle contents (>5 wt.%), an increase in surface tension could be noted, demonstrating surfactant-like activity of Laponite disks at low concentrations (Yang et al., 2013). Obtained data approved the particle size dependence of surface tension for SSG-Laponite nanocomposite hydrogels except the SSG-5%Laponite. The surface tension was found to be higher for larger particle sizes at high nanoparticle concentrations (≥ 10 wt.%). At low Laponite percentage, the space between the particles was larger than the particle size; hence, the surface free energy at liquid-gas interface reduced due to the electrostatic repulsive forces; which caused the surface tension to diminish. Also, the increment in surface tension observed at high Laponite concentrations is a result of the fact that particles were getting closer

to each other; therefore, rising the van der Waals attractive forces. Furthermore, according to literature, polysaccharides with high molecular weight and rigid chains structure have low tendency to adsorb at air/water interface (Naji-Tabasi, Razavi, Mohebbi, & Malaekheh-Nikouei, 2016). This result was consistent with the findings of Ranjbar, Khosravi-Nikou, Safiri, Bovard, & Khazaei (2015) for Tri Ethylene Glycol- Al_2O_3 and -MgO nanofluids; and with the observation of Tanvir & Qiao (2012) for n-decane and ethanol-based solutions. It should be noted, that the surface tension of SSG-Laponite system illustrated an irregular increment trend at nanoparticle contents above 10 wt.%. The surface tension of SSG-10%Laponite was 66.8 mN/m. It reduced significantly to 64.8 mN/m upon 15 wt.% Laponite addition, then increased gradually to 69.5 mN/m in SSG-25%Laponite. This irregular behavior of surface tension at higher Laponite loading might be contributed to the high viscosity of SSG-Laponite nanohybrid hydrogel at higher nanoparticle concentrations, which made interfacial properties measurement difficult by common techniques.

3.4. Density

Density is an indispensable parameter in materials thermodynamic properties and fluid mechanics calculations. The functional properties of hydrogels such as drug release are depended on the porosity and pore size in hydrated gels (Assaad, Maire, & Lerouge, 2015), which strongly related to the density. Besides, the structural morphology and physical characteristics of films, foams, and aerogels are linked to the real structures and density of the filmogenic and foamogenic hydrogels, even though drying and freeze-drying process create artifacts on the final product structure.

It would be expected that increasing the Laponite concentration would increase the density of hydrogels, due to an increase in solid matter fraction. However, it decreased continuously from 1.47 g/ml in pure SSG to 1.19 g/ml for SSG-25%Laponite (Table 1), leading to conclude that

Laponite particles, especially at high concentrations, have allowed increasing the volume of 3D polymer-particle network. The increase of specific volume (inverse of density) with the increment of mass ratio was more complicated. This phenomenon might be related to the increase of water binding capacity upon clay loading and decrease of SSG polymer mass fraction from 1 in pure SSG gel to 0.8 in SSG-25%Laponite nanocomposite hydrogel. As Laponite content increased, the number of negative charges in the system increased and, thus the interaction between the anionic groups of the hydrogels components and water molecules was enhanced (Li, Kim, Siddaramaiah, & Lee, 2009). Besides, with lower polymer mass fraction, the polymer chains distance and void volume fraction increased, which led to the low-density structure. The third hypothesis involved in the density reduction is the formation of the light-density house of cards microstructure by negative face-positive edge electrostatic attractions between Laponite platelets. It is interesting to notice that this microstructure is responsible for the rheological properties improvement and the shear-thinning behavior of hydrogel (Dávila & d'Ávila, 2017). A literature search indicated a lack of reporting on the effect of nanoparticle loading on hydrogel density investigation. However, similar results were reported for the density of resorcinol-formaldehyde-graphene oxide (Guo, Song, Chen, Du, & Zhong, 2014) and natural rubber-montmorillonite (Pojanavaraphan, Schiraldi, & Magaraphan, 2010) aerogels as a function of nanofiller content.

3.5. *Stress sweep*

Before making detailed viscoelastic nature assessment, the LVE range was defined by performing an amplitude stress sweep. Therefore, the applied stress in the linear viscoelastic domain for frequency sweep measurements was limited to 0.1 Pa. Moreover, the macromolecular and structural solidity information and distinguishing strong and weak hydrogels were based on stress sweep data. The structural strength of gels was indicated by the

value of elastic modulus in the LVE region (G'_{LVE}). The LVE range is attributed to the existence of a balance between the rates of structural breakdown and rebuilding. As demonstrated in Fig. 1, for SSG and SSG-25%Laponite hydrogels, with increasing stress, two different regions namely linear viscoelastic region where G' and G'' were almost parallel and stress independence; and nonlinear region (n-LVE) in which G' and G'' started to decrease were discriminated.

Fig. 1. Typical changes of G' (filled symbols) and G'' (open symbols) in stress sweep of SSG and SSG-25%Laponite nanocomposite hydrogels ($f = 1$ Hz and temperature 20°C).

Table 2

LVE region parameters, crossover point, fracture strain and fracture stress for 1% dispersion of sage seed gum (SSG) and SSG-Laponite hydrogels ($f = 1$ Hz and $T = 20^\circ\text{C}$).

Parameters/Samples	SSG	SSG-5%Laponite	SSG-10%Laponite	SSG-15%Laponite	SSG-20%Laponite	SSG-25%Laponite
G'_{LVE} (Pa)	39.8 $\pm$ 1.2 ^a	39.7 $\pm$ 2.0 ^a	47.7 $\pm$ 3.3 ^b	52.4 $\pm$ 2.1 ^c	50.8 $\pm$ 1.6 ^c	64.5 $\pm$ 0.9 ^d
G''_{LVE} (Pa)	16.8 $\pm$ 0.6 ^a	16.2 $\pm$ 1.1 ^a	18.3 $\pm$ 0.8 ^b	19.8 $\pm$ 1.3 ^b	18.9 $\pm$ 0.9 ^b	21.5 $\pm$ 0.4 ^c
G^*_{LVE} (Pa)	43.2 $\pm$ 1.0 ^a	42.8 $\pm$ 0.8 ^a	51.1 $\pm$ 1.5 ^b	56.1 $\pm$ 1.2 ^c	54.2 $\pm$ 0.6 ^c	68.0 $\pm$ 1.3 ^d
$\tan \delta_{\text{LVE}}$	0.42 $\pm$ 0.11 ^a	0.41 $\pm$ 0.06 ^a	0.38 $\pm$ 0.08 ^b	0.38 $\pm$ 0.04 ^b	0.37 $\pm$ 0.03 ^c	0.33 $\pm$ 0.07 ^d
τ_y (Pa)	4.45 $\pm$ 0.23 ^a	1.44 $\pm$ 0.12 ^b	0.45 $\pm$ 0.09 ^c	0.45 $\pm$ 0.13 ^c	0.46 $\pm$ 0.19 ^c	0.46 $\pm$ 0.08 ^c
τ_0 (Pa)	6.27 $\pm$ 0.18 ^a	5.78 $\pm$ 0.06 ^b	5.84 $\pm$ 0.10 ^b	5.14 $\pm$ 0.22 ^c	4.16 $\pm$ 0.14 ^d	4.88 $\pm$ 0.17 ^c
τ_f (Pa)	18.82 $\pm$ 0.43 ^a	16.00 $\pm$ 0.31 ^b	15.49 $\pm$ 0.24 ^b	14.36 $\pm$ 0.13 ^c	14.59 $\pm$ 0.40 ^c	14.87 $\pm$ 0.26 ^c
G_f (Pa)	13.6 $\pm$ 0.1 ^a	12.9 $\pm$ 0.1 ^b	13.9 $\pm$ 0.3 ^a	14.5 $\pm$ 0.2 ^c	16.0 $\pm$ 0.2 ^c	16.8 $\pm$ 0.1 ^d
Fracture strain (%)	92.3 $\pm$ 3.1 ^a	104.3 $\pm$ 2.3 ^b	120.3 $\pm$ 4.2 ^c	140.9 $\pm$ 3.3 ^d	137.3 $\pm$ 5.4 ^e	161.5 $\pm$ 2.8 ^f
Fracture stress (Pa)	24.1 $\pm$ 0.7 ^a	25.1 $\pm$ 0.3 ^a	26.0 $\pm$ 0.5 ^b	31.1 $\pm$ 0.2 ^c	31.0 $\pm$ 0.4 ^c	31.9 $\pm$ 0.6 ^c

Different letters indicate significant differences between samples at $P < 0.05$ by Duncan test.

As shown in Table 2, in the LVE range the G'_{LVE} was greater than G''_{LVE} for all hydrogels. The G'_{LVE} value increased with Laponite incorporation, showed the increase of SSG-based gels rigidity. Complex modulus (G^*_{LVE}) which consist of both elastic and viscous elements, showed a similar trend with G'_{LVE} , and demonstrated that the total structural strength of hydrogels generally increased, probably due to the formation of elastically effectual junction zones between the Laponite and the SSG segments (Abdurrahmanoglu & Okay, 2010). Loss tangent ($\tan \delta_{LVE}$) of all hydrogels was less than 1, significantly decreased and came close to 0.1 upon Laponite addition, approved that nanocomposite gel had more solid-like behavior at higher nanoparticle fraction.

The limiting value of linearity is considered of the dynamic yield stress (τ_y , the first non-linear changes in the structure), and can be regarded as the starting point of the weakening of the gel strength (Razavi, Alghooneh, & Behrouzian, 2017). The τ_y value significantly decreased from 4.45 to 0.45 Pa with increase nanoparticle content (Table 1). Static yield stress (τ_0) showed a similar trend and decreased significantly from 6.27 Pa, in pure SSG sample to 4.16 Pa in SSG-20%Laponite hydrogel. This behavior was in excellent accordance with the finding of Oliveira, Monteiro, Barros-Timmons, & Lopes-Da-Silva (2010), which have reported the decrease of the limit of the linearity and yield stress of locust bean gum (LBG)-SiO₂ hydrogels by adding nanoparticles which attributed to the high-stress sensitivity of the developed 3D network structure. We believe, longer lasting structure of plain SSG compared to SSG with higher Laponite fraction along the stress axis may be a result of stronger interaction in SSG-Laponite than pure SSG, which confined the freedom of movement of SSG chains and consequently increased the time needed to form new bond to replace those demolished by the external deformation.

For all samples with exceeding shear stress, the LVE entirely gives up and G' can cross G'' ($G'=G''$). At crossover point (flow point), storage modulus value remarkably reduced, so the

corresponding modulus (G_f) shows the modulus at which material behavior changes from viscoelastic to elastoviscous and indicates the stiffness of the system. Similar to other viscoelastic moduli, G_f increased significantly from 13.64 to 16.79 Pa as a function of Laponite concentration indicated the effect of polymer-particle interaction dominated the effect of deformation force. G_f is an effective parameter that can be used to show the ability of the hydrogel to keep its constituents in place and inhibition of nanoparticles aggregation. The stress at the crossover point (τ_f) represents the stress of viscoelastic to elastoviscous behavior transformation and indicates resistance to flow (Alghooneh, Razavi, & Behrouzian, 2017). The highest τ_f value was obtained for plain SSG (18.82 Pa), showing the least propensity to flow. The opposite trend of viscoelastic moduli in the LVE range (G'_{LVE} , G''_{LVE} and G^*_{LVE}) and G_f , with τ_y , τ_0 , and τ_f , obviously illustrated the development of coexistence relatively rigid and fragile ordered structure upon Laponite loading. Also, yielding up phenomenon happens in the frailest section of the hydrogel lattice. It seems, with an increase of the Laponite, although the strength of network increased, the sensitive polymer-particle interaction in SSG-Laponite matrix encountered more microscopic damage at higher nanoparticle concentration.

Fractal analysis through SAOS technique has been attracted a great deal of interest as a simple quantitative method to characterize physical properties of gels. However, fracture properties of hydrogels should be discriminated from yielding. Fracture is considered to occur when; (1) all bonds between the structural components forming the gel network in a certain macroscopic level defeat; (2) breakdown of the structure of the gel over length scales much larger than the structural elements; and (3) ultimately, the falling apart of the gel system. Yielding takes place in the microscopic plane (plastic deformation) and does not include the latest property; it results in the materials which flow (van Vliet, 1996). In addition, the fracture is acting to separate one atomic plane from another. Yield, conversely, is sliding one plane along another and unlike in fracture, the broken bonds during the sliding are allowed to reform in new positions (Roylance,

2008). At larger stress, viscoelastic moduli declined quickly, as the material fractures. Fracture stress and fracture strain were determined as the stress/strain at which visible macroscopic cracks appear in the samples. The fracture characteristics can be used whether the hydrogel is brittle or ductile, which affect its suitability for proposed applications. Fig. 2 compared the fracture stress of the pure SSG and the nanoparticle-filled hydrogel with 25 wt.% Laponite. Both fracture stress and fracture strain enhanced significantly ($P < 0.05$) with the presence of Laponite (Table 2), indicated the formation of rigid structure. The opposite behavior of τ_y and τ_0 in the LVE range and fracture properties in the n-LVE range demonstrated that the LVE information alone was not adequate to characterize biopolymer-based hydrogels without understanding the n-LVE data such as fracture strain and fracture stress. Similar observations have been reported for the poly(*N*-isopropylacrylamide)-hectorite (Haraguchi & Li, 2006) and poly(2-acrylamide-2-methylpropane sulfonic acid)-SiO₂ (Wang, Hou, Cheng, & Fu, 2012) hydrogels, where the fracture stress increased upon nanoparticle loading. They concluded that a denser nanocomposite network had higher fracture properties. Our results challenged this idea and, indicated the producibility of strong-uncompact biopolymer-clay hydrogels.

Fig. 2. The typical effect of increasing stress amplitude on elastic stress ($G' \cdot \gamma$) of pure SSG (open symbols) and SSG-25%Laponite (filled symbols) hydrogels.

3.3. Frequency sweep

Dynamic mechanical experiments were performed at constant amplitude and temperature ($\tau = 0.1$ Pa and $T = 20^\circ\text{C}$) over a frequency range of 0.01-10 Hz. In this range, the plateau-like G' dominated over the G'' and no crossover point was observed (Fig. 3 a & b), confirmed the solid-like viscoelastic behavior of the system.

Fig. 3. Frequency sweeps of G' (filled symbols) and G'' (open symbols) moduli for pure SSG (a), SSG-25%Laponite (b), and complex viscosity (η^*) of SSG (open symbols) and SSG-25%Laponite (filled symbols) (c) hydrogels at LVE region ($\tau = 0.1$ Pa) and $T = 20$ °C

Table 3 showed the G' , G'' , G^* , η^* and $\tan \delta$ at a frequency of 1 Hz for different SSG-Laponite hydrogels. Increasing the nanoparticles fraction enhanced the G' , reflecting the reinforcing effect of Laponite on increasing the strength of SSG-based hydrogels structure due to the formation of elastically effective junction zones between the SSG segments and Laponite disks,

which are in agreement with the results obtained from stress sweep test (Table 2). The values of G'' , G^* , $\tan \delta$, and η^* decreased significantly ($P < 0.5$) with rising in Laponite in the range of 0-5 wt.%, and afterward, they along with G' increased upon nanoparticle addition (Table 3). The increase of loss tangent at Laponite concentration above 5 wt.%, can be explained by the uprose contribution of the viscous component in comparison with the elastic element. SSG-5%Laponite possess lower η^* value compared to pure SSG hydrogel (Table 3). This was probably because of the change in molecular relaxation due to which shear thinning events overcome at lower Laponite percentage. The η^* was enhanced with increasing nanoparticle fraction, accentuated the influence of the Laponite on the segmental relaxation dynamics of the polymer chains (Pojanavaraphan et al., 2010) and formation of a stronger 3D network as hydrogel showed more rigidity at higher Laponite contents. Based on a double logarithmic scale, η^* of all hydrogels reduced linearly with increasing frequency (Fig. 3c), illustrated that at high frequency (not enough time interval to rebuild the broken intra- and inter-molecular interactions), the permanent disentanglement of long-chain polymers, and consequently, diminution in η^* occurred. Slope of complex viscosity (η_s^*) almost decreased with the increase of Laponite from zero to 10 wt.% (-0.79), whereas it increased and reached the highest value of -0.91 in SSG-15%Laponite hydrogel, which was considerably steeper than the maximum amount of -0.76 which used to describe a weak polysaccharide-based gel, formed by overlapping and entangled flexible random coil chains. These results demonstrated a non-Newtonian shear thinning behavior, may be due to the disappearing of the house of cards microstructure and planer alignment of the particle-matrix towards the flow direction under shear force (Dávila & d'Ávila, 2017; Taki, John, Arakawa, & Okamoto, 2013).

The power-law models (Eqs. (1) and (2)) were used to assess the exponents (n' and n'') and intercepts (K' and K'') from a double logarithmic plot of G' and G'' versus frequency (Table 4). From the structural point of view, it was found that all SSG-based hydrogels displayed gel-like

behavior because of the slopes ($n' = 0.11-0.27$ and $n'' = 0.27-0.52$) were much lower than those reported for a Maxwellian gel ($n' = 2$ and $n'' = 1$). The magnitudes of n' and n'' decreased with Laponite addition, showed that the frequency dependency of gels became weaker. Thus Laponite disks promoted the solid-like elastic behavior (Razavi, Alghooneh, & Behrouzian, 2017). The K' and K'' values increased with Laponite content, which suggested an increase in the stiffness of nanocomposite hydrogels due to the formation of an associative 3D network, which could be attributed to a large number of polymer-particle connections. These observations were in accordance with the obtained results of stress sweep test and particle size measurement.

Table 3

Storage modulus (G'), viscous modulus (G''), loss-tangent ($\tan \delta$), complex modulus (G^*), complex viscosity (η^*) at $f = 1$ Hz, slope of complex viscosity (η_s^*) for 1% dispersion of sage seed gum (SSG) and SSG-Laponite nanocomposite hydrogels at $\tau = 0.1$ Pa and $T = 20$ °C.

Parameters/Samples	SSG	SSG-5%Laponite	SSG-10%Laponite	SSG-15%Laponite	SSG-20%Laponite	SSG-25%Laponite
G' (Pa)	35.9±2.1 ^a	33.2±3.4 ^a	41.0±1.1 ^b	49.5±1.0 ^c	52.9±3.3 ^{c,d}	55.5±1.7 ^d
G'' (Pa)	15.4±1.2 ^b	10.6±2.1 ^a	20.6±0.1 ^c	25.2±0.4 ^d	27.7±1.2 ^e	26.3±0.8 ^{d,e}
$\tan \delta$	0.42±0.06 ^b	0.31±0.05 ^a	0.5±0.08 ^d	0.51±0.09 ^{d,e}	0.52±0.04 ^e	0.47±0.08 ^c
G^* (Pa)	39.1±1.9 ^b	34.9±2.7 ^a	45.9±1.5 ^c	55.6±2.4 ^d	59.8±1.3 ^e	61.4±2.1 ^f
η^* (Pa.s)	6.22±0.16 ^b	5.55±0.49 ^a	7.3±0.32 ^c	8.84±0.13 ^d	9.51±0.28 ^e	9.77±0.19 ^e
η_s^*	-0.82±0.00 ^b	-0.82±0.01 ^b	-0.79±0.00 ^a	-0.91±0.01 ^d	-0.89±0.00 ^c	-0.89±0.00 ^c

Different letters indicate significant differences between samples at $P < 0.05$ by Duncan test.

Material stiffness parameter (A_α) and the order of relaxation function (α) were used to determine the strength of hydrogel network and the number of possible interactions between the components, respectively (Table 4). The interfacial interaction was found to be a critical variable in the nanocomposite hydrogels stability. The A_α values increased upon Laponite loading, indicated the increase in the polymer-particle molecular binding. On the other hand, α declined, confirmed a higher number of interfacial interactions and shear thinning in small deformation (Alghooneh et al., 2017).

Based on the results of dynamic oscillatory shear test, it was indicated that Laponite, especially above 5 wt.% content, improved the rheological characteristics performance, attributed to the polymer-particle bridging interaction via the formation of Van der Waals forces, ionic and hydrogen bonds (between the hydrogen and hydroxyl of clay and those of the groups D-glucuronic, D-mannose of the SSG chains), and electrostatic attractions (between anionic groups of SSG molecules and positively charged edges of nanoclay platelets) as already mentioned in literature (Dávila & d'Ávila, 2017; Lapasin et al., 2017; Zlopasa, Norder, Koenders, & Picken, 2016). When nanoparticle concentrations increased, the number and size of agglomerated (soft flocks) and aggregated (hard clusters) SSG-Laponite increased and bridging interaction was strengthened. Thus, a percolated polymer-particle 3D network was progressively developed, resulted in elastic effects. The presence of large agglomerated and aggregated structures as a function of filler concentrations was confirmed by particle size measurement (Table 1).

Table 4

Frequency dependence of the elastic and viscose moduli, the Friedrich-Heymann model parameters and the subtraction of average G' from G'' for 1% dispersion of sage seed gum (SSG) and SSG-Laponite nanocomposite hydrogels ($\tau = 0.1$ Pa, $T = 20$ °C).

Samples	$G' = K' \times (\omega)^{n'}$			$G'' = K'' \times (\omega)^{n''}$			$G^* = A_\alpha \times (\omega)^\alpha$		
	$n' (-)$	$K' (\text{Pa})$	R^2	$n'' (-)$	$K'' (\text{Pa})$	R^2	$\alpha (-)$	$A_\alpha (\text{Pa} \cdot \text{rad}^{-\alpha} \cdot \text{S}^\alpha)$	R^2
SSG	0.28±0.01 ^a	27.83±0.50 ^a	0.94	0.52±0.01 ^a	5.58±0.33 ^a	0.96	0.29±0.01 ^a	28.69±1.52 ^a	0.98
SSG-5%Laponite	0.27±0.00 ^a	26.14±0.41 ^b	0.98	0.40±0.01 ^b	6.57±0.27 ^b	0.93	0.28±0.04 ^a	27.12±1.66 ^a	0.95
SSG-10%Laponite	0.19±0.01 ^b	29.60±0.12 ^c	0.96	0.37±0.00 ^c	11.12±0.60 ^c	0.96	0.22±0.03 ^b	31.95±2.47 ^b	0.95
SSG-15%Laponite	0.17±0.01 ^c	37.44±0.39 ^d	0.94	0.34±0.02 ^d	13.54±0.50 ^d	0.99	0.20±0.01 ^b	40.27±1.12 ^c	0.97
SSG-20%Laponite	0.11±0.01 ^e	44.55±0.64 ^f	0.96	0.28±0.00 ^e	16.11±0.39 ^f	0.93	0.14±0.02 ^d	47.96±2.35 ^d	0.94
SSG-25%Laponite	0.15±0.00 ^d	41.85±0.23 ^e	0.92	0.34±0.01 ^d	14.59±0.43 ^e	0.93	0.17±0.01 ^c	44.97±1.03 ^d	0.94

Different letters indicate significant differences between samples at $P < 0.05$ by Duncan test.

3.4. Texture profile analysis

To further appraise the hydrogel properties and the effect of Laponite reinforcement, large deformation behavior of hydrogel was studied by using texture profile analysis (TPA). The textural parameters were derived from the force-time plot (Table 5). The hardness of SSG-based hydrogels abruptly increased with the presence of 0-5 wt.% Laponite, whereas it decreased when the nanoparticle exceeded. Surprisingly, the SSG-5%Laponite had the highest hardness (327 g) compared to the other hydrogels may be due to the strain-stiffening (-hardening) phenomenon, which was reported for xanthan-LBG, pectin, alginate-pectin and iota-carrageenan (Michon, Chapuis, Langendorff, Boulenguer, & Cuvelier, 2004) and oxidized tamarind seed galactoxyloglucan-5%nanofibrillated cellulose (Ghafar et al., 2015) hydrogels. This phenomenon can be attributed to the higher non-linear stretchability, looser consistency and finite extensibility of the network strands connecting network junctions of the SSG-5%Laponite in comparison to the other samples, leading to different flow characteristics and resistance against damage from exposure to large deformation (Creton, Hu, Deplace, Morgret, & Shull, 2009; Ghafar et al., 2015). The decrease in hardness at higher nanoparticle concentration (≥ 15 wt.%) might be related to the uneven microstructure resulting from more agglomeration and aggregation of Laponite disks.

Adhesiveness is more of a surface property which attributed to a combined effect of viscosity and viscoelasticity. It affected the pumping power friction coefficient and fluidal thermal functions of hydrogel during transportation and heating/cooling processes. Cohesiveness refers to the strength of the internal connections building up the frame of the gel (Naji & Razavi, 2014), and demonstrates how the product endures a second deformation in proportion to its behavior under the first deformation (Ghafar et al., 2015). As shown in Table 5, increasing amount of Laponite (0-5 wt.%), resulted in a gradual increase of the cohesiveness, suggested that SSG hydrogel can preserve its integrity during processing operations in the presence of

low Laponite concentration. Unlike, for Laponite contents more than 5 wt.%, a pronounced decrease in the cohesiveness was observed, presumably due to the heterogeneous distribution of aggregated nanoparticle, leading possibly partly phase separation in the nanocomposite hydrogels (Wang, Zhang, Teng, & Liu, 2017).

Springiness or elastic recovery indicates physically spring back samples after they have been deformed during the first compression cycle. Variation in hardness and cohesiveness of bio-based hydrogel caused gumminess alteration because it is a function of hardness and cohesiveness (Naji & Razavi, 2014). With increasing Laponite, the change trend of adhesiveness, springiness, and gumminess of the hydrogels was similar to that of cohesiveness (Table 5).

The apparent modulus of elasticity (initial tangent modulus) is an index of the material stiffness at low deformation level. Similar to hardness, two different behaviors were observed depending on Laponite contents. For Laponite concentrations lower than 5 wt.%, an increase of apparent modulus of elasticity could be noted, whereas for nanoparticle contents higher than 10 wt.%, a reduction was obtained, but it was still comparable with that of the plain SSG hydrogel. Majdzadeh, Navarchian, & Sadeghi (2010) suggested that the transformation of clay platelets distribution pattern from complete exfoliation in low nanoparticle content to intercalate in high clay concentration reduced nanocomposite apparent modulus of elasticity. Therefore, it can be concluded that the intercalated and exfoliated structures were created during preparation of SSG-Laponite hydrogels which was in agreement with other reported results (Li, Kim, Hui, Rhee, & Lee, 2009; Mahdavinia, Massoudi, Baghban, & Massoumi, 2012). It can be mentioned that although the nanoparticle dispersion pattern is mostly evaluated by X-ray diffraction, determination of small and large deformation rheological properties can be used as an alternative way to estimate particles dispersion state.

A comparison between the obtained results of SAOS and TPA tests suggested that different segment-segment and polymer-particle interactions with different time scales and stress sensitivity (steady/oscillatory, shear/normal, rate, and magnitude) existed in SSG-Laponite nanocomposite hydrogels. The opposite trend of small and large deformation behavior with respect to nanoparticle concentration indicated the formation of coexisted small shear sustainable and large normal deformation sensitive interactions upon laponite loading (> 10 wt.%), and those which were more sensitive to small shear and resistant to large normal stress presented in SSG-5%Laponite hydrogel structure (Tables 2, 3 and 5).

Table 5

Instrumental texture profile analysis (TPA) for 1% dispersion of sage seed gum (SSG) and SSG-Laponite nanocomposite hydrogels at 25 °C.

Parameters/Samples	SSG	SSG-5%Laponite	SSG-10%Laponite	SSG-15%Laponite	SSG-20%Laponite	SSG-25%Laponite
Hardness (g)	255.1±3.2 ^c	327.0±4.7 ^a	270.2±6.3 ^b	259.3±5.5 ^c	219.6±2.5 ^d	207.3±7.1 ^e
Deformation at hardness (%)	36.9±1.2 ^b	32.7±0.3 ^a	35.4±0.9 ^b	38.8±0.7 ^c	39.2±1.0 ^c	32.6±0.5 ^a
Adhesiveness (mJ)	12.5±0.5 ^b	16.1±1.1 ^a	11.4±0.8 ^{b,c}	12.2±1.1 ^{b,c}	9.4±0.6 ^d	10.0±1.2 ^c
Cohesiveness (-)	0.68±0.01 ^b	0.71±0.02 ^a	0.68±0.02 ^b	0.61±0.01 ^d	0.65±0.00 ^c	0.59±0.02 ^d
Springiness (cm)	0.93±0.03 ^c	1.12±0.03 ^a	0.98±0.04 ^b	0.88±0.02 ^d	0.91±0.01 ^c	0.88±0.01 ^d
Gumminess (g)	173.1±4.0 ^c	232.1±6.2 ^a	185.1±3.3 ^b	157.1±6.0 ^d	143.0±3.1 ^e	122.0±5.1 ^f
Apparent modulus (g/s)	106.4±2.4 ^d	172.6±3.2 ^a	129.1±3.8 ^b	110.9±2.2 ^c	112.9±3.2 ^c	106.2±2.0 ^d

Different letters indicate significant differences between samples at $P < 0.05$ by Duncan test.

4. Conclusions

Stress and frequency sweep tests demonstrated a solid-like response, which became stronger with clay adding, may be due to the SSG-Laponite high compatibility, intermolecular association and consequently the formation of a percolated 3D network. Under high shear stress, these structures initiated to break down, resulting in shear thinning behavior. It was also found that the higher the Laponite concentration, the higher the particle size, surface tension, and lower density. The obtained results illustrated the indirect particle size dependence of mechanical behaviors besides the presence of more agglomerates and aggregates microstructures. Density data indicated the generation of the light-density house of cards structures with high water binding capacity upon nanoparticle loading. Depending on the Laponite content (< or >5 wt.%), the TPA parameters evolved in a different pattern. The SSG-5%Laponite showed the highest apparent modulus of elasticity and other crucial texture parameters. Therefore, its most upper mechanical deformation tolerance besides its lowest surface tension can suggest the use of SSG-5%Laponite in bio-based systems where the reinforced structure is desirable.

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Figures caption

Fig. 1. Typical changes of G' (filled symbols) and G'' (open symbols) in stress sweep of SSG and SSG-25%Laponite nanocomposite hydrogels ($f = 1$ Hz and temperature 20°C).

Fig. 2. The typical effect of increasing stress amplitude on elastic stress ($G'\gamma$) of pure SSG (open symbols) and SSG-25%Laponite (filled symbols) hydrogels.

Fig. 3. Frequency sweeps of G' (filled symbols) and G'' (open symbols) moduli for pure SSG (a), SSG-25%Laponite (b), and complex viscosity (η^*) of SSG (open symbols) and SSG-25%Laponite (filled symbols) (c) hydrogels at LVE region ($\tau = 0.1$ Pa) and $T = 20^\circ\text{C}$.