

REVIEW ARTICLE

Rheological and Structural Properties of k-Carrageenan/Xanthan Gum Gummies Architected With a New Natural Additive

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Received: 19 December 2024 | **Revised:** 26 January 2025 | **Accepted:** 27 January 2025

Funding: This work was supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico, 302434/2022-4, FCT, CEECINST/00156/2018, UID/CTM/50025/2020, Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, 88887.878787/2023-00, 88887.936575/2024-00.

Keywords: carrageenan | natural additives | rheology | soft materials | xanthan gum

ABSTRACT

Biohybrids (BHs) based on bentonite and anthocyanins can be produced as alternatives to synthetic colorants. However, no information is available on the interaction of biohybrid with food system. This research studies the rheological properties of gummies containing k-carrageenan and xanthan gum incorporated with a BH. The incorporation of BH ($\leq 2\%$ w/w) increased the flow consistency index and shear thinning effect in melted gummies at 85°C. During cooling from 90°C to 25°C, the presence of BH altered the sol–gel transition temperature typical in carrageenan systems, probably by the formation of carrageenan complexes. At 25°C, all gummies had a solid-like response with elastic modulus (G') higher than viscous modulus (G''). G' values increased linearly with BH concentration, and the linear viscoelastic region and breaking strain decreased with BH concentration, indicating that this natural additive acted as a reinforcing material.

1 | Introduction

The use of synthetic colorants in food formulations has been associated with toxic and allergic effects, as well as attention-deficit hyperactivity disorder in children [1, 2]. In this way, natural colorants have emerged as an alternative to synthetic colorants in food products. Furthermore, the use of natural colorants can increase food acceptance because consumers have recently demanded healthier food products with clean labels, over the recent years [3].

Anthocyanins are natural and non-toxic pigments responsible for the red, blue, and purple colors in fruits and vegetables [3]. In recent years, more studies have focused on recovering anthocyanins from agri-food wastes (e.g., pomace and peels) [4].

The recovery of anthocyanins has been appointed as an alternative to the sustainable production of food colorants in consideration of the different Sustainable Development Goals of the United Nations (SDGs-UN) [5].

Natural and synthetic clays have been used to recover anthocyanins from agri-food waste. The recovery of anthocyanins involves adsorption, where the pigment is stabilized through physical interaction with clay platelets. In this way, anthocyanins from eggplant (*Solanum melongena*) and jambolan (*Syzygium cumini*) peel extracts have been recovered using a synthetic clay called Laponite (Lap). The adsorption process was carried out at room temperature and pH 1, and 93% of the anthocyanins from the extract were adsorbed on the clay surface. In both studies, it was possible to absorb approximately 15 mg of anthocyanins per gram of Lap [6, 7],

and the resulting material was named biohybrid (BH) because it is composed of organic (anthocyanins) and inorganic (nanoclay) materials. The stabilization of anthocyanins onto the clay surface is due to a chemical reaction between anthocyanin ions and the functional groups present on the clay surface [8]. Recently, Koop et al. [8] used bentonite to recover anthocyanins from jambolan (*S. cumini*) peel extracts and concluded that the adsorption process was similar to that observed with Lap. However, the adsorption capacity of bentonite was higher than that of Lap. Hence, the adsorption capacity was 212 mg of anthocyanins per gram of bentonite, suggesting that this clay has potential for food applications. Bentonite is a colloidal-hydrated aluminum silicate containing varying quantities of iron, alkalies, and alkaline earth. This mineral is considered a GRAS (generally recognized as safe) ingredient for food applications [9].

Recently, Caicedo Chacon et al. [10] developed a biohybrid (BH) based on bentonite and the phenolic compounds from propolis extract. The authors concluded that this BH can be used as a natural additive in carrageenan hydrogels. Carrageenan hydrogels are often blended with xanthan gum to improve the mechanical properties of the resulting hydrogel aiming at food applications as vegan gummies [11]. Gummies are a class of food widely consumed by the entire population and are usually colored with synthetic additives [12].

To date, no study has explored the food application of bentonite adsorbing anthocyanins (BH), as well as the stability and interaction when mixed with food systems based on biopolymers. Therefore, the current research study aimed to produce gummies based on carrageenan and xanthan gum containing BH and to investigate the chemical interactions and structures in gummies in view to rationalize the effect of BH concentration on the rheological behavior of gummies.

2 | Materials and Methods

2.1 | Raw Materials

Jambolan fruits were harvested manually in a fully ripe stage, in Florianopolis city, SC, Brazil (−27.5999, −48.5219). The fruits were immediately washed, and the pulp and skin were manually separated from the seeds and stored at $-18^{\circ}\text{C} \pm 2^{\circ}\text{C}$ [8]. Bentonite (CP31-Bentonisa, Brazil) was used as the adsorbent clay. Distilled water was used as the solvent. K-carrageenan (Sigma Aldrich, 22048-100G-F) and xanthan gum (Fluka, 95465; both 1053246) were used as the macromolecules. All reagents were of analytical grade.

2.2 | BH Production

The BH was produced following the protocol informed by Koop et al. [8]. BH was obtained by adding bentonite to the anthocyanin extract at a ratio of 0.027 g of bentonite per mg of anthocyanins and keeping it under agitation at 500 r.p.m. by mechanical stirring for 15 min in the absence of light. The mixture was stored overnight at 4°C to sediment the BH. After removing the supernatant, BH was dried at 35°C for 24 h in a convective oven before being stored in desiccators containing silica gel until

analysis. A complete characterization of the BH was previously reported by Koop et al. [8]. A commentary characterization of BH was performed in relation to its morphology and particle size (see Supporting Information).

2.3 | Gum Production

Carrageenan/xanthan gummies were produced as proposed by Song et al. [13], who used these biopolymers to produce gummy candies. Gummies were prepared by dispersing carrageenan (2 g) and xanthan gum (1 g) in 100 mL of distilled water followed by stirring and heating (70°C) for 30 min. In sequence, BH was added based on the weight of the formulation (0%, 0.5%, 1%, and 2%). The resulting dispersions containing BH were stirred at 50°C for 15 min before characterization. Gummies containing only carrageenan (2%) were also produced and used as controls. The addition of BH did not exceed 2% of the formulation weight of the formulation, as proposed by the legislation for food additives [14].

2.4 | Gum Characterization

2.4.1 | Morphology

The morphology of the gummies was studied using optical transmission microscopy (Olympus BH2, Olympus, Tokyo, Japan, $20\times$) coupled to a LEICA DFC 280 digital camera. Melt samples ($\approx 85^{\circ}\text{C}$) were placed on microscope slabs, gently squeezed with a glass cover, and cooled to 25°C .

2.4.2 | Chemical Bonds and Crystalline Structure

The chemical bonds of the dried gummies at 40°C for 30 min were studied using an FTIR spectrometer (Spectrum, PerkinElmer, Waltham, MA, USA) equipped with a Universal Attenuated Total Reflection (ATR). FTIR spectra were obtained in the infrared region between 1800 and 600 cm^{-1} with 16 scans, a resolution of 1 cm^{-1} [15].

X-ray Diffraction (XRD) of the dried gummies was performed using an X-ray diffractometer (D8 Discover, Bruker, Billerica, MA, USA), operating at 40 kV and 15 mA ($\text{CuK}\alpha\ 1 = 1.5406\text{ \AA}$ radiation). Diffractograms were obtained at room temperature in the diffraction range (2θ) between 4.5° and 70° , with a scan rate of $2^{\circ}/\text{min}$ and a step size of 0.04° . The interplanar distance d (nm) was calculated using Bragg's law equation (Equation 1) with the angle of diffraction θ at the maximum intensity of the peak observed in the diffractogram as follows:

$$n \times \lambda = 2 \times d \times \sin(\theta) \quad (1)$$

where λ is the wavelength (nm), and n is the reflection order ($n = 1$, dimensionless).

2.4.3 | Rheometry

2.4.3.1 | Flow Curve. The flow curves of the melted gummies were carried out using a modular compact rheometer (MCR

302, Anton Paar, Graz, Australia) with a 40-mm parallel-plate geometry and a gap of 230 μm . Samples were studied at 85°C in a shear rate range between 1 and 1000 s^{-1} , using the following experimental protocol: first, a constant strain of 10% with a frequency of 1 Hz was applied for 5 min to erase any flow history and rejuvenate the melted sample, thus ensuring test reproducibility. Later increasing and decreasing shear rate sweeps were applied to study the rheological behavior of samples [16]. The Power law (Equation 2) was used to calculate the rheological parameters of apparent viscosity (η) versus shear rate ($\dot{\gamma}$):

$$\eta = K\dot{\gamma}^{(n-1)}. \quad (2)$$

where K is the flow consistency index ($\text{Pa}\cdot\text{s}^n$) and n is the flow behavior index (dimensionless) [17].

2.4.3.2 | Viscoelastic Properties. The viscoelastic properties were measured using a rotational rheometer (AR G2, TA Instruments, New Castle, DE, USA) equipped with a 25-mm parallel-plate geometry and a gap of 500 μm . A temperature sweep test from 90°C to 25°C was carried out to investigate the effect of BH on the carrageenan sol–gel transition temperature. The applied strain amplitude and frequency were set at 0.5% and 1.0 Hz, respectively. Water evaporation in the samples was avoided using an oil (dodecane 44030-1L, Sigma-Aldrich). During cooling, the rheometer's gap was compensated for the thermal expansion of the plates, and the normal force was kept to $0 \pm 0.1 \text{ N}$ to accommodate for the possible change of volume occurring during the sol to gel transition [18].

In sequence, the mechanical spectra of the hydrogels at 25°C was measured with a frequency sweep from 100 to 0.01 Hz performed using a strain amplitude of 0.5%. Finally, the linear and large deformation viscoelastic behaviors of the hydrogels were determined at 25°C by performing an oscillatory shear strain amplitude sweep between 0.01% and 1000% and at a frequency of 1 Hz [16, 19].

All rheological results were analyzed using the Rheology Advantage Data Analysis software (TA Instrument, New Castle, DE, USA).

2.5 | Statistical Analyses

All tests were performed in triplicate, and the results are expressed as means $\pm$ standard deviation. Analysis of variance (ANOVA) and Tukey's test with a 5% significance level were performed using TIBCO Statistica software, version 13.5.0.17. Fitting of the models to data was performed using a dedicated software (OriginPro, version 8.5, OriginLab, USA).

3 | Results and Discussion

3.1 | Morphology

Gummies based on carrageenan and carrageenan/xanthan gum displayed a homogeneous macroscopic visual appearance (Figure 1a,b). The formation of carrageenan-based gels is accompanied by the aggregation of polymer chains and the separation from the solvent, which may lead to microscopic spatial heterogeneities [20, 21]. In this way, at microscopic scale, zones

with gray and white colors could be correlated with the phase separation (heterogeneities) between the polymers and water (Figure 1), suggesting that macromolecular aggregates and/or possible xanthan-rich regions are with size smaller than the resolution achieved by optical microscopy.

Gummies containing BH had a homogeneous visual aspect and exhibited wine color, independently of the BH concentration (Figure 1c,d). Optical microscopy images revealed aggregates of BH in the gummy matrix. These aggregates had a red color, irregular shapes, and particle sizes between 4 and 42 μm (Figure 1c–e). Scanning electron micrographs revealed that the BH is composed of aggregates of particles at the microscale (Figure S1). When dispersed in distilled water, the BH had a trimodal distribution with particle sizes between 0.13–0.18, 0.20–0.55, and 0.57–0.64 μm (Figure S2). Particularly, the second particle size distribution of BH (0.20–0.55 μm) was the most representative in this additive (see cumulative results in Figure S2). Bentonite has platelets shapes with a broad distribution of particle sizes ranging from 0.8 to 2000 μm [22, 23]. Discrepancies between particle shapes and particle size distribution observed in the BH when compared with bentonite probably were due to the clay modification during the adsorption of anthocyanins [8], and the dispersion methods used to quantify particles sizes. Results from particle size distribution of BH in water (Figure S2) and optical microscopy of gummies (Figure 1c–e) revealed that, in spite of the good distributive mixing, the BH was not well dispersed during the gummy production in contrast to the good dispersion achieved by the mixing of sample before particle size characterization. Despite the poor dispersion of BH into the carrageenan/xanthan gum matrix, it was possible to obtain gummies with a homogeneous visual appearance (Figure 1).

3.2 | Chemical Bonds and Crystalline Structure

Dried samples had FTIR spectra typical of carrageenan (Figure 2a), being observed the stretching of: carboxylate anions (1638 cm^{-1}), sulfate esters (1225 cm^{-1}), glycosidic groups (1007 cm^{-1}), 3,6-anhydro-galactose (920 cm^{-1}), and sulfated CO (842 cm^{-1}) [24, 25]. Dried gummies containing xanthan gum had a shift of the band previously observed at 1638 cm^{-1} to the right (1620 cm^{-1}) due to the interactions between carboxylate anions (RCOO^-) and carboxyl groups (ROOH) from carrageenan and xanthan gum, respectively (Figures 2a and S3) [26]. Furthermore, the incorporation of xanthan gum shifted the band previously observed at 1225 cm^{-1} to the left (1232 cm^{-1}), indicating that the sulfate ester groups of carrageenan interacted with xanthan gum (Figure 2a). The incorporation of BH did not alter the FTIR spectra of gums, suggesting that this material can interact with macromolecules by means of hydrogen bonds [15, 27, 28].

X-ray diffractograms of dried carrageenan gummies displayed a small reflection centered at $2\theta = 7.4^\circ$ ($d_{01} = 11.9 \text{ \AA}$) and a broad band centered at $2\theta = 21^\circ$ ($d_{02} = 4.2 \text{ \AA}$) (Figure 2b), which were associated with the cross-linking domain in double helix and the amorphous structure of this macromolecule, respectively [29–31]. The blending with xanthan gum did not modify the crystalline structure previously observed in carrageenan gummies (Figure 2b), this result was due to the amorphous nature of xanthan gum [32], and to the fact that in case of phase separation, this occurs on larger scales than those resolved by WAXD.

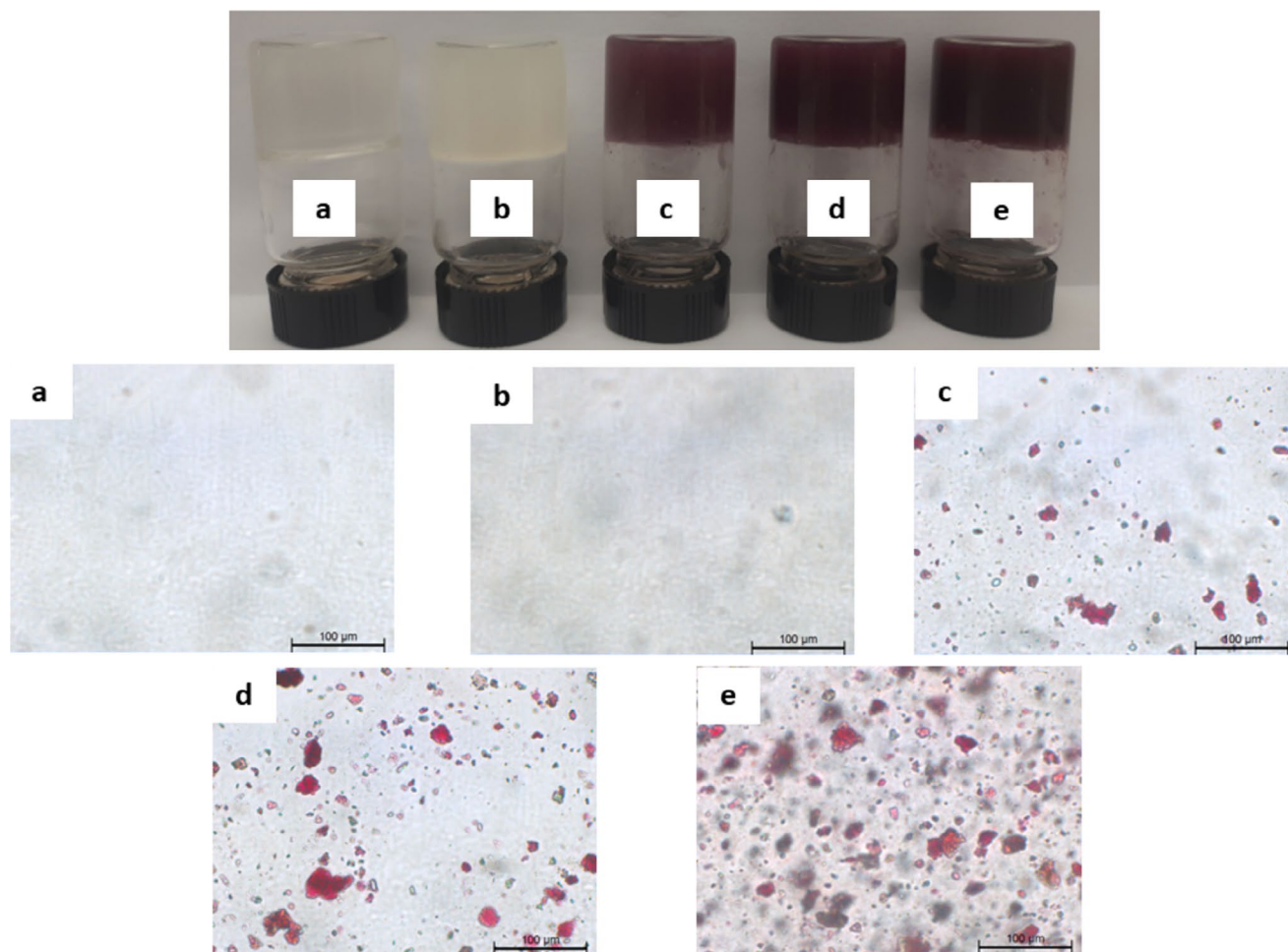


FIGURE 1 | Visual appearance and optical microscopy of carrageenan gummy (a) and gummies based on carrageenan and xanthan gum incorporated with: (b) 0, (c) 0.5, (d) 1, and (e) 2% of BH (biohybrid). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

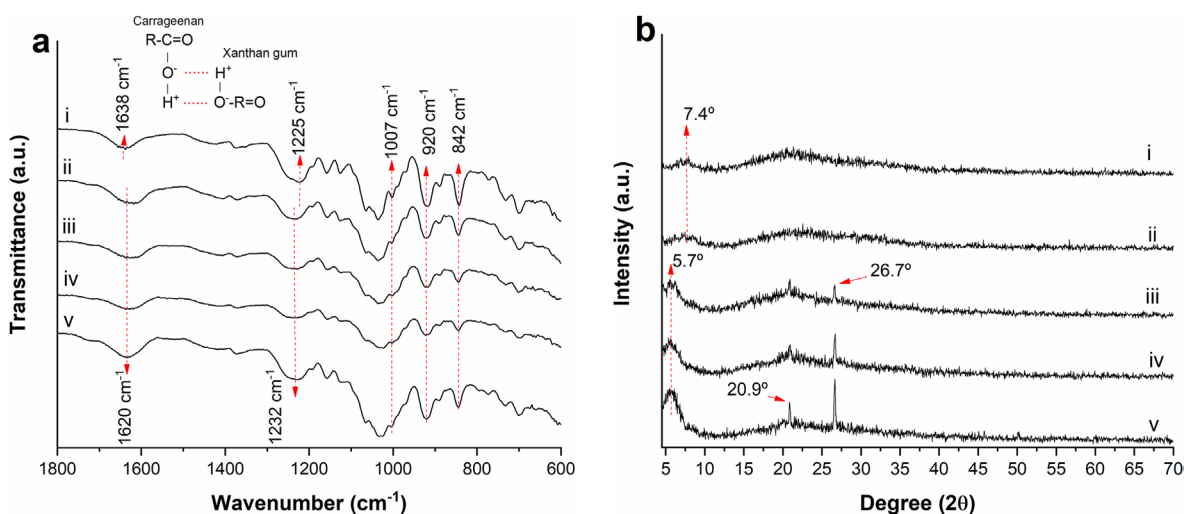


FIGURE 2 | Fourier-transform infrared spectra (a) and X-ray diffractograms (b) of gummies. Carrageenan gummies (i) and gummies based on carrageenan/xanthan gum incorporated with: (ii) 0, (iii) 0.5, (iv) 1, and (v) 2% of BH (biohybrid).

The incorporation of BH led to a displacement of the d_{01} from $2\theta = 7.4^\circ$ to 5.7° ($d_{01} = 15.5 \text{ \AA}$) due to the intercalation of biopolymers into clay platelets and their interaction by means of

hydrogen bonds [28, 33]. Furthermore, two diffraction peaks centered at $2\theta = 20.9^\circ$ ($d = 4.2 \text{ \AA}$) and $2\theta = 26.7^\circ$ ($d = 3.3 \text{ \AA}$) were observed in gummies containing BH (Figure 2b), this

diffraction peaks are typical of bentonite and increased with BH [34].

3.3 | Flow Properties

The flow curve of the 2% w/w carrageenan solution exhibits a Newtonian viscosity plateau at low shear rate and a decreasing viscosity at higher shear rates (Figure 3). This overall non-Newtonian behavior indicated that carrageenan chains were in the semi-diluted or entangled regime, where polymer-polymer interactions and flow-induced chain orientation were responsible for the shear rate dependence of the viscosity. In the current research, carrageenan chains could be in the helical conformation even at such high temperature as suggested by Westberry et al. [35]. As such, the shear thinning behavior was expected since this was reminiscent from the rheological behavior of non-dilute solutions of worm-like chains (Figure 3).

Adding xanthan gum to carrageenan enhanced the viscosity and the shear thinning of the solutions, which intrinsically contain more polymers (Figure 3). However, the non-reproducibility at lower shear rates between the flow curves measured by sweeping up or down the shear rates suggested time and flow-history dependences in the measured viscosity, probably related to the spatial heterogeneity

previously observed in optical microscopy results (Figure 1b). Additional rheological testing and morphological characterization of possible flow-induced structures would be needed to

TABLE 1 | Rheological parameters (upward curve) of melted gummies.

Gummy sample	K (Pa·s ^{<i>n</i>})	n	R^2
Carrageenan	0.26 ± 0.00^e	0.85 ± 0.01^a	0.9508
Carrageenan/ xanthan gum	3.45 ± 0.03^d	0.56 ± 0.01^b	0.9974
Carrageenan/ xanthan gum with 0.5% BH	6.17 ± 0.00^c	0.27 ± 0.00^c	0.9999
Carrageenan/ xanthan gum with 1% BH	8.67 ± 0.05^b	0.13 ± 0.01^d	0.9995
Carrageenan/ xanthan gum with 2% BH	9.06 ± 0.07^a	0.01 ± 0.00^e	0.9990

Note: Means in the same column followed by different lowercase are significantly different ($p < 0.05$). Abbreviations: BH = biohybrid, K = flow consistency index; n = flow behavior index.

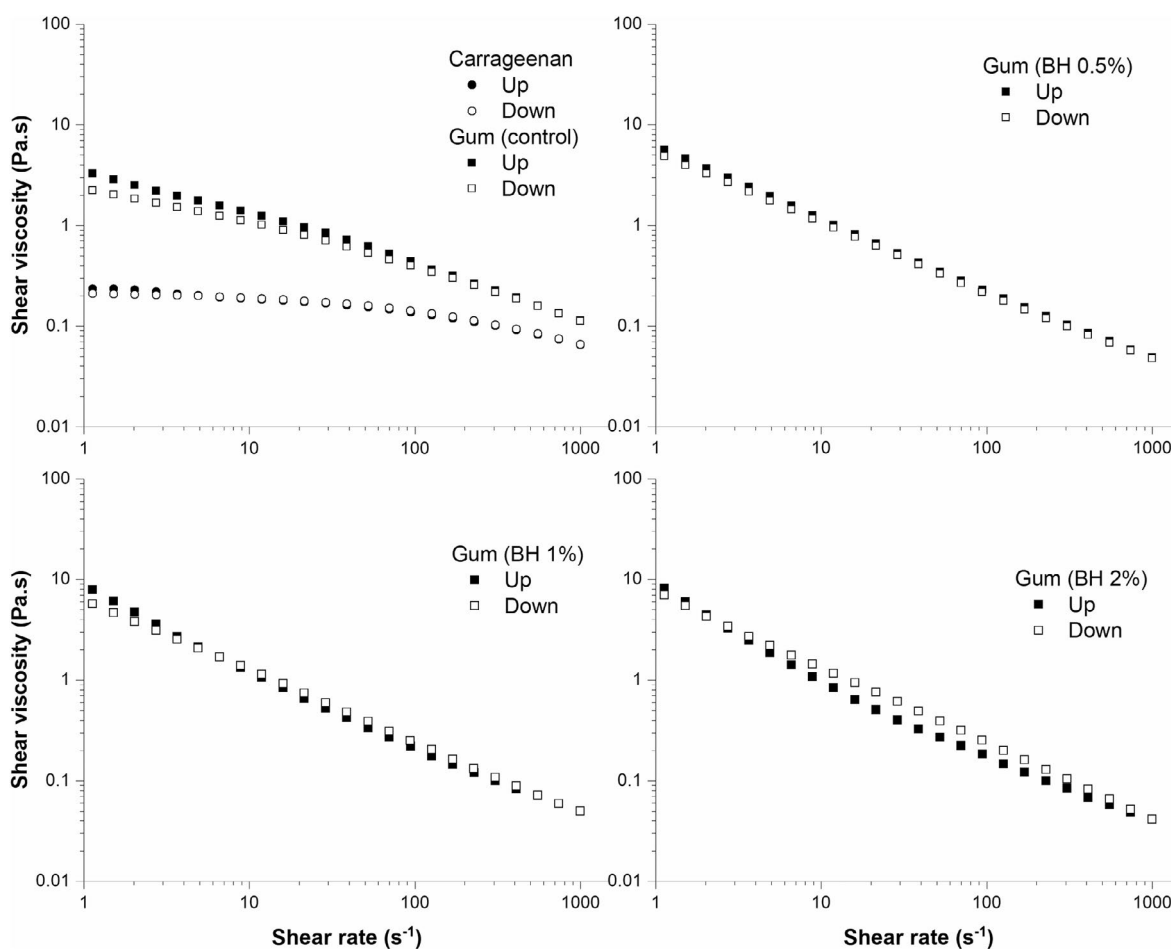


FIGURE 3 | Flow curves of carrageenan, carrageenan/xanthan gum (control), and carrageenan/xanthan gum containing different BH (biohybrid) concentrations.

relate such behavior with possible thixotropy, time-dependent chain aggregation, or flow-induced demixing/mixing between the two components.

Melted gummies containing xanthan gum and BH also had a shear-thinning behavior, with higher η values at $\dot{\gamma} = 1 \text{ s}^{-1}$ (Figure 3). The flow curves were well described by the Power law model (Table 1) as no Newtonian plateau is measured at lower shear rates, and results are overall insensitive to ramping up or down the shear rates. The incorporation of BH drastically increased the flow consistency index and shear thinning effect ($n < 1$) in melted gummies, see Table 1. In addition, gummies containing BH show a linear increase of K values for BH concentrations between 0% and 1%, whereas n decreased exponentially for the whole BH concentration range (Figure S4). Both effects could be due to the increase in solid content, the linear increase in K being reminiscent from a Stokes–Einstein effect of solids on the matrix viscosity, whereas the increased shear thinning relates to increased local shear rates between flowing particles.

3.4 | Gel Properties

Gummies showed an increase in the elastic (G') and viscous (G'') moduli as the samples were cooled from 90°C to 25°C (Figure 4). However, the rheological behavior of each gummy was impacted by its formulation. Gummies based on carrageenan and carrageenan/xanthan gum (blended) had $G'' > G'$ at 90°C, as expected from the data displayed in Figure 3. Both moduli increased with decreasing temperature and had a crossover point ($G' = G''$) at $45.7^\circ\text{C} \pm 1.0^\circ\text{C}$ and $40.6^\circ\text{C} \pm 0.8^\circ\text{C}$ in carrageenan and blended gummies ($p < 0.05$), respectively (Figure 4). This crossover point is typical of physical gels that undergo sol–gel ($T_{\text{sol-gel}}$) transitions when the systems are cooled [36, 37]. According to the literature, below $T_{\text{sol-gel}}$, helices from carrageenan molecules are formed and consequently aggregate into higher-order assemblies to create a three-dimensional network and consequently elastic gels [36, 38]. The reduction of $T_{\text{sol-gel}}$ in blended gummies when compared with carrageenan gel could be attributed to the physical–chemical interactions between these macromolecules as seen in FTIR spectra, or simply to a change

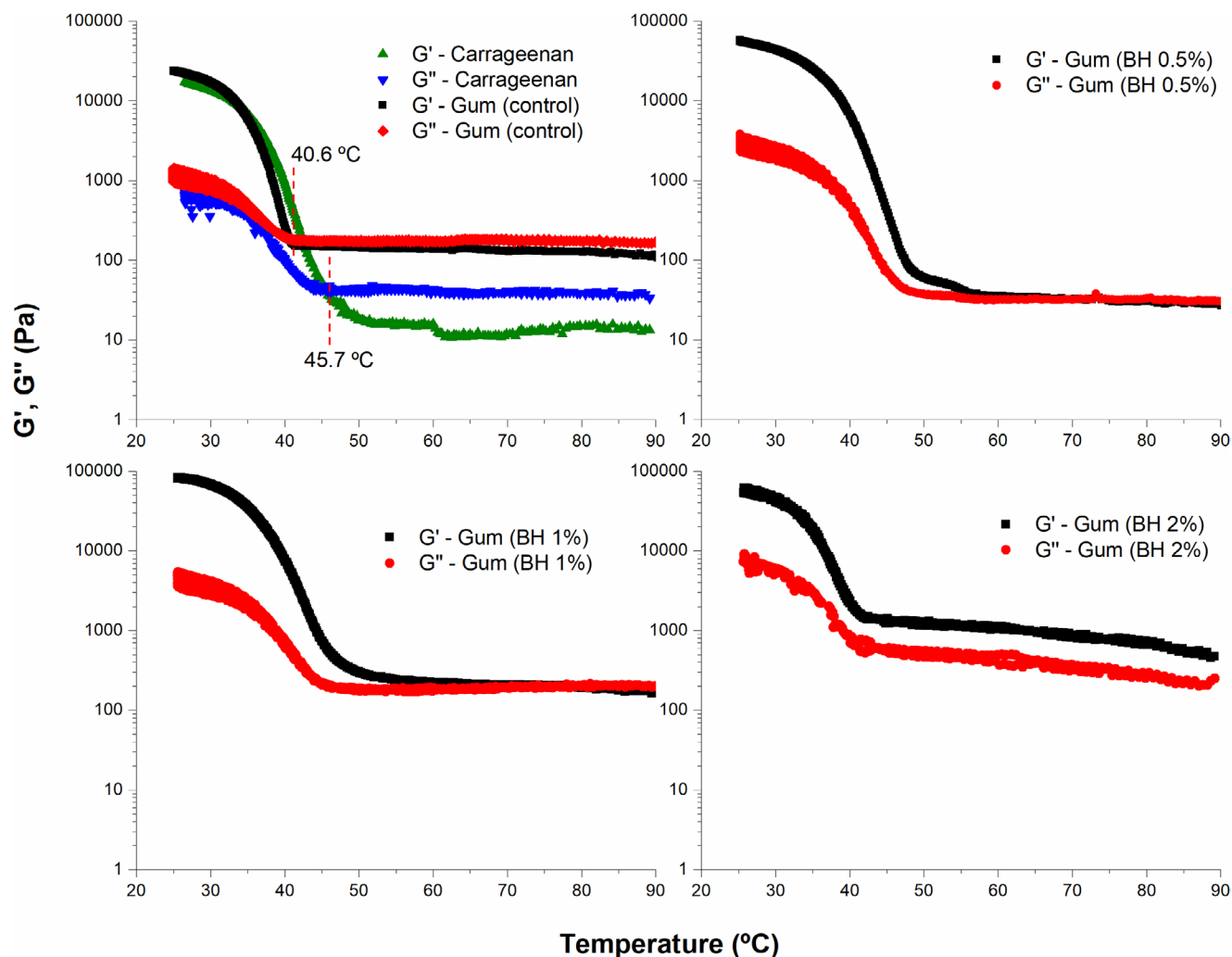


FIGURE 4 | Examples of curves of viscoelastic moduli (G' and G'') of carrageenan gummies, carrageenan/xanthan gum (control) gummies, and carrageenan/xanthan gum gummies containing different BH (biohybrid) concentrations as a function of temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

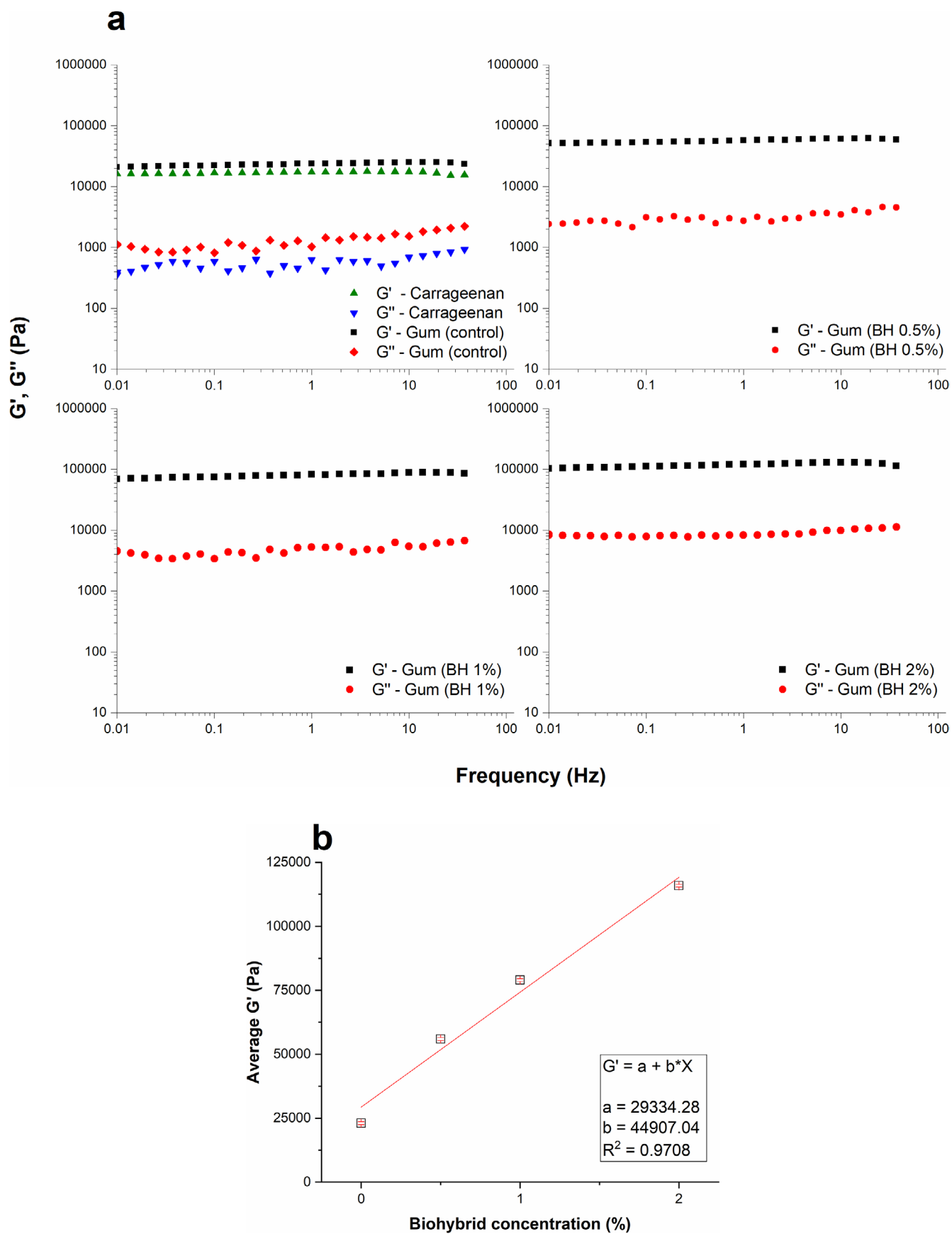


FIGURE 5 | (a) Typical mechanical spectra of carrageenan gummies, carrageenan/xanthan gum (control) gummies, and carrageenan/xanthan gum gummies containing different BH (biohybrid) concentrations; (b) average elastic modulus (G') as a function of BH concentration. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article).

in solvent-carrageenan electrostatic interactions, reducing the rate of gelation in carrageenan (see Section 3.2). Note here that the increase in the sol viscosity at larger temperatures (see also Figure 3) cannot explain the shift in the cross-over between G' and G'' , since the slope of G' with temperature is also affected at lower temperature below the onset of gelation.

The addition of BH strongly affects the thermal behavior of blended gummies (Figure 4). Therefore, gummies containing 0.5% and 1% BH had $G'' = G'$ at 90°C, whereas gummies with 2% BH showed $G' > G''$ for the entire temperature range tested. This behavior could be due to additional elasticity originating from BH-BH contacts at highest BH concentration. For 0.5% BH, the shear moduli at higher temperature are smaller than the shear moduli of the suspending matrix. In light of the reinforcing behavior inferred from the flow curves, this drop in shear moduli at larger temperature can only be explained by the larger frequency dependence of G' and G'' . The mechanism underlying the shift of the gel setting of filled gummies to lower temperatures with more added BH is however less clear.

The mechanical spectra of the gummies revealed that these systems had a solid-like response at 25°C with $G' > G''$ for the entire

frequency range tested (Figure 5a). Furthermore, all gummies had large moduli with weak frequency dependence for the whole range of tested frequencies, where G' was constant and significantly larger than G'' (Figure 5a), typical of carrageenan gels [39]. Furthermore, G' increased linearly with BH concentration (Figure 5b), suggesting that this additive played the role of a reinforcing filler in the diluted regime, that is, without filler-filler interaction.

The large deformation behavior of gummies revealed that carrageenan gels had the onset of strain softening (end of linear viscoelastic region, LVR) occurring at 2.5% strain (Figure 6), followed by an abrupt drop in the moduli typical of kappa-based carrageenan systems [21, 40]. A crossover between G' and G'' is measured for a shear strain (breaking strain) in the range of 11%, which suggests a fluidization process where the rheological response of the sheared gummy was dominated by the shear loss modulus G'' (Figure 6). The addition of xanthan gum is accompanied by increased in the LVR and breaking strain of approximately 5% and 107%, respectively. These results suggest that the xanthan gum, in addition to increasing G' values (Figure 5a), also increased the resistance to deformation (Figure 6). In contrast, the incorporation of BH led

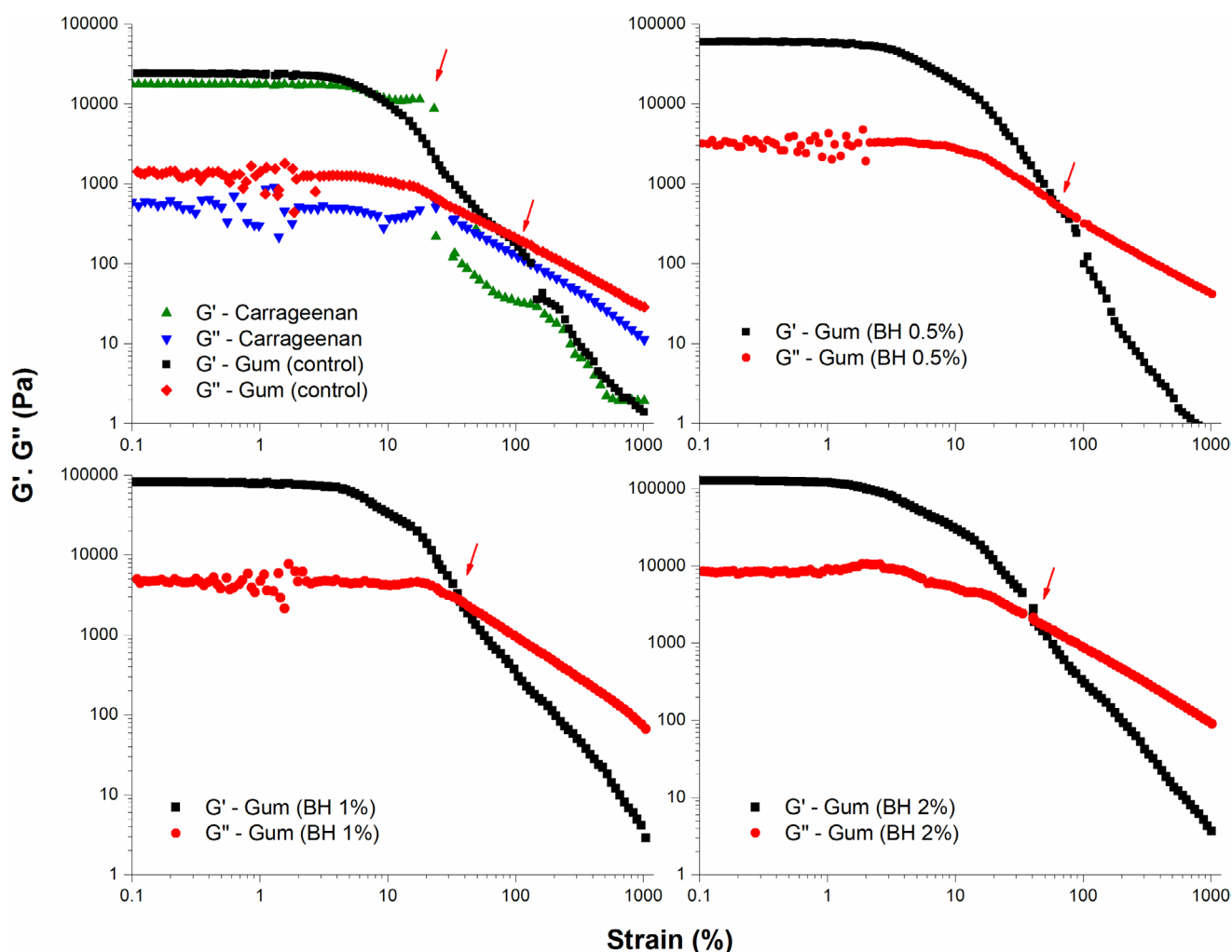


FIGURE 6 | Viscoelastic moduli (G') as a function strain for carrageenan gummies, carrageenan/xanthan gum (control) gummies, and carrageenan/xanthan gum gummies containing different BH (biohybrid) concentrations. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

to a decrease in both parameters (LVR and breaking strain), suggesting that this additive acted as a reinforcing material where only G' was improved, whereas BH/matrix interface was not strong enough to sustain larger strain than the matrix strain resistance. In other words, BH particles act as stress-weakening points.

4 | Conclusions

This research reports, for the first time, the production and structural-rheological characterization of vegan gummies based on carrageenan and xanthan gum incorporated as a new BH. Gummies with homogeneous visual appearance and wine color were obtained after BH incorporation. BH was dispersed into biopolymer chains with good spatial distribution, and no specific chemical interaction with the biopolymer matrix could be inferred from FTIR analysis. Important modifications were observed in the rheological properties of gummies after BH incorporation, suggesting that this natural additive can be used to impart color and modulate both linear and nonlinear elastic properties in food formulations.

Acknowledgments

This work was supported by the Fundação para a Ciência e Tecnologia (FCT), through the E2B2-PHACAR project, grant number: PTDC/BII-BIO/5626/2020 (<https://doi.org/10.54499/PTDC/BII-BIO/5626/2020>). G. A. Valencia would like to thank the National Council for Scientific and Technological Development (CNPq) (grant 302434/2022-4) and CAPES (88887.936575/2024-00) for financial support. I.C.F. Moraes also thanks CAPES (88887.878787/2023-00) for financial support. G. C. Leandro gratefully acknowledges the CAPES for the PhD fellowship. L. Hilliou acknowledges the financial support by the FCT under the framework of Strategic Funding grant: UID/CTM/50025/2020 and grant CEECINST/00156/2018. The authors gratefully acknowledge the Central Laboratory of Electronic Microscopy (LCME—UFSC) and the LINDEN (UFSC) nanotechnology for the SEM and LDS analyses, respectively.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.