

Changes in Functional Properties of Food Gels Treated Under High-Hydrostatic Pressure

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ABSTRACT

The effect of high pressure on the flow behavior of hydrogels containing locust bean gum (LBG), guar gum (GG), pectin, gellan gum, xanthan gum (XG) and tragacanth was undertaken in this study. Hydrogels containing 1% (w/v) of each of the hydrocolloids were subjected to a high-hydrostatic pressure of 200-500 MPa for 30 min at 25°C. The rheological data obtained was analyzed by ANOVA using MS Excel 2010. All the samples exhibited a shear thinning flow behavior which was analyzed using Power Law model and Herschel Buckley model ($R^2 > 0.95$). However, the effect of high pressure treatment on the model parameters like consistency (K) and flow behavior index (n) was not same for all the samples. The consistency of LBG and GG increased significantly ($P \leq 0.01$) with the applied pressure; whereas, it has significantly decreased in case of gellan gum. However, XG behaved the same way after treatment as that of before treatment. Moreover, the pectin and tragacanth dispersions behaved as free flowing solutions at the concentrations used. The flow behavior of the hydrogels was confirmed by the functional spectrum analysis using Fourier transform infrared spectroscopy (FTIR), in which a prominent difference in peaks was observed between the samples at 900-1150 cm^{-1} and 3000-3500 cm^{-1} wavenumber.

Keywords: Flow Behavior Index, High pressure processing, Hydrogels, Power law model, Viscosity.

1. INTRODUCTION

There are various hydrocolloids like guar gum, locust bean gum, gellan gum, pectin, tragacanth, and xanthan gum used in food products. Guar gum is a linear chain of galactomannan unit (Fig. 1a) obtained from the endosperm of guar beans. It is easily soluble in cold water but shows weak synergism with other gums [1]. LBG also consists of galactomannan which is extracted from the carob tree seeds and has been observed to form gels in combination with carrageenan [2,3]. Gellan gum, a heteropolysaccharide (Fig. 1b), is derived from a microbial (*Pseudomonas elodea*) source and is having gel forming properties. Xanthan gum is obtained by fermentation of sucrose, lactose or glucose by *Xanthomonas campestris*. It is a polysaccharide chain consisting of glucose, mannose, and glucuronic acid. Gasper et al. [4] found a synergistic effect of gellan gum, xanthan gum and locust bean gum in a proportion of 1:1:1.7 on the overall acceptability of jelly. Pectin is a heteropolysaccharide obtained mainly from citrus fruits and apple. It is a linear polymer of partly esterified α -(1-4)-linked D-galacturonic and mannuronic acid. Tragacanth (sap of legumes) is composed of arabinogalactan and tragacanthic acid. The viscosity of a solution containing tragacanth gum depends upon the solubility of its components in water and their proportions present in the solution.

Food hydrocolloids have important functions in various food products like ice cream, whipped cream, jam, jelly, desserts, candies, yogurt, etc. They function as thickeners, stabilizers, gelling agents, etc. in these food products. Nowadays, people prefer reduced-sugar products, and hydrocolloids are favoring the texture formation in those food products as an alternative to sugar for texture development. Hence, the rheological study (a study of flow behavior) of these texture modified products is important to characterize and compare their properties.

The food materials are usually processed by thermal treatment for the microbial and enzyme inactivation, new product development, and so on. But, it has a detrimental effect on bioactive compounds present in the food materials especially in fruits and vegetables which are rich sources of these compounds. Further, the viscosity of hydrocolloids like gellan and galactomannans is reduced (10%) by thermal sterilization [5]. Hence, novel technologies like microwave heating, ohmic heating, pulsed electric field, UV irradiation, freezing, ultrasonication, high pressure processing, ultrafiltration, etc. have evolved to reduce the lethal effect on bioactive compounds during processing. High pressure processing (HPP) is a non-thermal technology in which a pressure of 100-1000 MPa is applied to a food product to kill the microorganisms and inactivate the enzymes. Besides, it maintains the nutritional quality particularly the bioactive components. Moreover, high pressure processing favors a decrease in system volume which could improve the intermolecular interactions like hydrogen and hydrophobic interactions, and enhance the functionality of a food product [6]. A limited literature is available on the effect of HPP on rheological properties of the hydrocolloids. Little knowledge can be found for the effect of HPP on the individual hydrocolloids without the addition of any solutes. Hence, this study was conducted to evaluate the effect of high pressure treatment on flow behavior of the hydrogels, to evaluate the rheological model fitting of the data obtained, and to validate the results obtained from rheological study by analysis of functional spectra of the samples using FTIR (Fourier Transform Infrared Spectroscopy).

2. METHODOLOGY

2.1. Sample Preparation

The food grade hydrocolloids (gellan gum, guar gum, locust bean gum, pectin, tragacanth, and xanthan gum) were procured from Harsh and Company, Rajasthan, India. Each of the hydrocolloids were separately mixed with distilled water at room temperature (26 ± 2 °C) on a magnetic stirrer at 500 rpm for 120 min. The concentrations used were 1% (w/v) for each of the samples. The prepared samples (50 ml each) were vacuum packed in double polyethylene pouches for high pressure treatment.

2.2. High Pressure Processing

A batch mode high pressure processing unit (Stansted Fluid Power System, UK) was used to treat the samples (Fig. 2a). The high pressure processing system consisted of four components (a) *press module* comprising of a pressure vessel where the samples were loaded to be pressurized, conditioning fluid circulation jacket system, top and bottom caps, yoke system, supporting frame, pressurization fluid piping, thermocouples network, and yoke, top cap and tongue actuation systems (b) *power pack unit* containing hydraulic and precharging pumps, intensifier pumps, pressurization valve, pressure intensifiers, decompression valves, main holding frame structure, process fluid tank, hydraulic fluid tank, fluid circulating pumps, heat exchanger and pipe network, and pneumatic actuation switches (c) *console* consisting of a control panel, a SCADA (supervisory control and data acquisition) system, a PLC system, a computer unit, and (d) *calorifier system*. Monopropylene glycol solution

was used as the pressure transmitting medium. The prepared samples were subjected to a high-hydrostatic pressure of 200-500 MPa for 30 min at 25 °C. A ramp rate of 350 MPa/min was selected. The treated samples were used for analysis. The sample prepared at atmospheric pressure (0.1 MPa) was considered as the control sample.

2.3. Rheological Characterization

Steady-state rheological test of the samples was performed using a rotational rheometer (DV-III Ultra Rheometer, Brookfield Engineering, USA) provided with an in build Rheocalc data acquisition software (Fig. 2b). A small sample adapter (spindle SC4-21) was used for testing of the samples. The samples were tested at a shear rate of 0-200 s⁻¹ and a constant temperature (25±0.6 °C) using a water bath which circulated the fluid at required temperature to the insulated jacket of the geometry used.

2.4. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The hydrogel samples were also analyzed by FTIR (Perkin-Elmer spectrometer, Thermo Scientific, USA). The analysis was done within a wavenumber of 500-4000 cm⁻¹ at 25 °C using potassium bromide pellets.

2.5. Statistical Analysis

The data obtained was statistically analyzed using one-way analysis of variance using Microsoft Excel 2013. The rheological models were fitted to the data using Origin software version 8.5. The best fit models with R²>0.9 were selected to evaluate the model parameters. The treatments were done for duplicates and measurements were taken three times. The mean values with standard deviations were reported.

3. RESULTS AND DISCUSSION

3.1. Effect of Pressure Treatment on Rheological Behavior of Hydrogels

The viscosity of all samples decreased with the increase of shear rate as shown in Fig. 3, indicating a shear thinning behavior. The same flow behavior has been reported by Imeson [12] in various hydrocolloids. The viscosity of xanthan gum was highest followed by guar gum, gellan gum, locust bean gum, pectin, and tragacanth. After the pressure treatment, the viscosity of locust bean gum and guar gum increased, whereas that of gellan gum decreased as shown in Fig. 3. But, it was significantly higher than the samples with heat treatment. However, no change was observed in the flow behavior of xanthan gum after high pressure as well as thermal treatment. Further, all the samples showed a pseudoplastic behavior as the change in viscosity with shear rate in up cycle coincided with the down cycle, showing no hysteresis loop (Fig. 4a). Also, a time independent behavior was observed for all the samples as shown in Fig. 4b.

There are various rheological models used to characterize the flow behavior of viscous products as given in Eq. 1-5. However, the power law model (Eq. 2) and Herschel–Bulkley model (HB) (Eq. 3) showed good fit (R²>0.95) to the obtained rheological data as shown in Fig. 5. But the power law model was selected to obtain the rheological parameters (Table 1) as the samples showed small values for yield stress.

Newtonian model

$$\sigma = \eta \dot{\gamma} \quad (1)$$

where,

σ , η , and $\dot{\gamma}$ are stress, viscosity and shear rate, respectively.

Power law model

$$\sigma = K\dot{\gamma}^n \quad (2)$$

where,

σ , K , n and $\dot{\gamma}$ are stress, consistency, flow behavior index and shear rate, respectively.

Herschel–Bulkley (HB) model

$$\sigma = \sigma_0 + K\dot{\gamma}^n \quad (3)$$

where,

σ_0 , K , n and $\dot{\gamma}$ are yield stress, consistency, flow behavior index and shear rate, respectively.

Cross model

$$\eta = \eta_{\infty} + (\eta_0 - \eta_{\infty}) \div (1 + K\dot{\gamma}^n) \quad (4)$$

where,

η_0 , η_{∞} , K and n are zero and infinite shear viscosity, time constant related to the relaxation time and dimensionless exponent, respectively.

Casson model

$$\sigma^{0.5} = \sigma_c^{0.5} + (K\dot{\gamma})^{0.5} \quad (5)$$

where,

σ_0 , K , and $\dot{\gamma}$ are yield stress, consistency, and shear rate, respectively.

From the obtained power law model parameters, it was observed that all the samples showed shear thinning behavior as the flow behavior index was less than 1 i.e. non-Newtonian behavior [13]. The consistency after pressure treatment was higher in guar gum (12-33%) and locust bean gum (27-39%), and less in gellan gum (12-26%) as compared to their respective control samples (before treatment). Moreover, the increase in pressure from 200 MPa to 500 MPa had a drastic effect on the consistency of gellan gum in which the values decreased significantly ($P \leq 0.01$) from 83 to 70 Pa.sⁿ. The flow behavior index also changed significantly with the pressure treatment. The consistency of locust bean gum and guar gum increased significantly from 39 to 43 Pa.sⁿ and 136 to 162 Pa.sⁿ, respectively, with the increase in pressure from 200 to 500 MPa. The difference in results of HPP effect on the viscosity of these gums is not clear, but it might be because of the difference in the molecular composition of the hydrocolloids. A reduction in volume is caused by high pressure which might be favoring the hydrophobic and hydrophilic bond formation, causing an increase in viscosity of the samples. Moreover, the difference in branch chains in chemical structure and their alignment before and after the treatment might be the reason for change in viscosity of the solutions containing these food hydrocolloids. The flow behavior index also varied with the change in consistency and approached towards the value of 1.0, which is characteristic value for Newtonian fluids. Besides, the pectin and tragacanth dispersions behaved as free-flowing liquids at the concentrations used even after the pressure treatment. The pectin concentration at 1% was not sufficient to form a viscous solution as it requires the presence of other solutes like sugar to form a three dimensional network. Similarly, tragacanth solution of 1% was not enough viscous to be measured with the selected geometry, because it has synergistic effect with other hydrocolloids.

Stolt et al. [7] have reported an increase in viscosity of the suspensions of waxy corn starch with an increase in pressure. A complete gelatinization has been reported in a waxy corn starch dispersion (5%) at 600 MPa for 15 min at 20 °C. Michel and Autio [8] reported that the degree of esterification (DE) of pectin decreased by

HPP at pH 7.0 from 65% to less than 60%. And no effect was reported at lower pH (5.0). High pressure processing at 400 MPa and 25 °C increased the viscosity of pectin solution (1.5%) containing 25% sugar by ten times and followed the shear thinning flow behavior, which might be due to structure breakdown. A less effect was observed at 800 MPa for which the reason is not clear. But might be because of changes in molecular linkages. Michel et al. [9] observed a more pronounced effect on sugar-free pectin solution of the same concentration, which might be because of the interference of sugar with the HPP effect on viscosity of the pectin. Also, pectin source has been observed to affect this variation in the results [10]. However, Yen and Lin [11] found no effect of HPP on hydrocolloid solutions. The variation in results could be because of the difference in gum source, molecular structure, and process controls.

3.2. Functional Spectra of Different Hydrogels

The functional spectra indicating the presence of various functional groups in the samples obtained using FTIR is shown in Fig. 6. The functional groups like -OH (at 300-3500 cm^{-1}); -CH (at 2925 cm^{-1}); COO- (at 1647 cm^{-1}); -CCH, -COH (at 1200-1480 cm^{-1}), C-C, and CO- (at 900-1150 cm^{-1}) were observed with different intensities for different samples. The intensity of the peaks for all samples varied with the treatment applied except for xanthan gum. The results obtained through FTIR analysis were in confirmation with the results obtained from rheological study.

4. CONCLUSION

All the samples showed a shear thinning and pseudoplastic flow behavior. The application of high pressure increased the viscosity of the gums except for gellan gum in which it decreased after the pressure treatment. Moreover, a highly significant effect was observed on the viscosity of these gum solutions as the pressure increased from 200 MPa to 500 MPa. The type of flow behavior was same for the control, HPP and thermal treated (TP) samples. However, the change in viscosity with shear was at lower rate in HPP as compared to the TP samples. HPP showed very less effect on the viscosity of hydrogels as compared to thermal processing. The FTIR analysis confirmed the results obtained from rheological study. Hence, it can be concluded that the percent requirement of these hydrocolloids in a food product can be reduced while applying high pressure treatment as compared to that of the thermal-treated products. High pressure can be used not only to preserve foods, but also to improve the rheological and functional properties of foods. Further, the effect of HPP on the flow behavior of these hydrocolloids in various combinations needs to be evaluated in future.

5. Acknowledgement

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Figure captions:

Figure 1: Structure of galactomannan unit of guar gum and locust bean gum (a) and structural unit of gellan gum (b).

Figure 2: High pressure unit (a) and Brookfield rheometer (b).

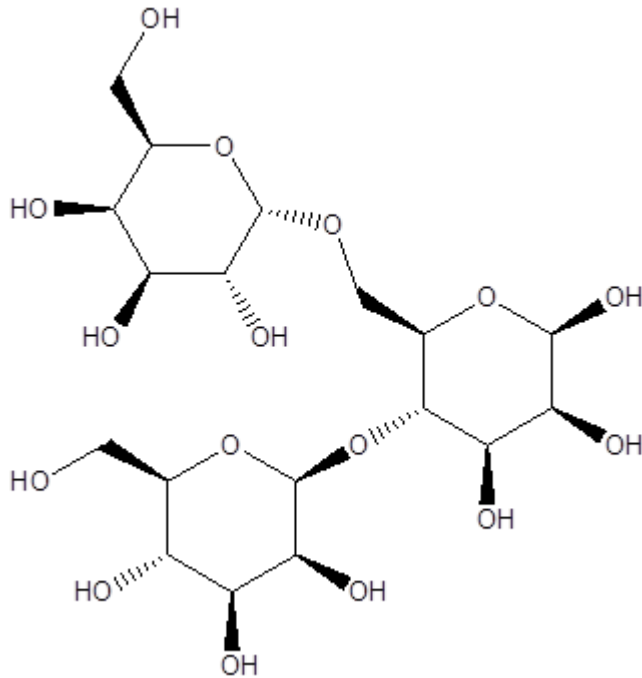
Figure 3: Effect of high pressure treatment on the flow behavior of the hydrogels.

Figure 4: Pseudoplastic (a) and time independent (b) behavior of the hydrogels.

Figure 5: Power law and HB model fit of the rheological data of gellan gum.

Figure 6: Functional spectrum of the samples obtained by FTIR analysis (XG: xanthan gum, GG: guar gum, G: gellan gum, LBG: locust bean gum).

(a)



(b)

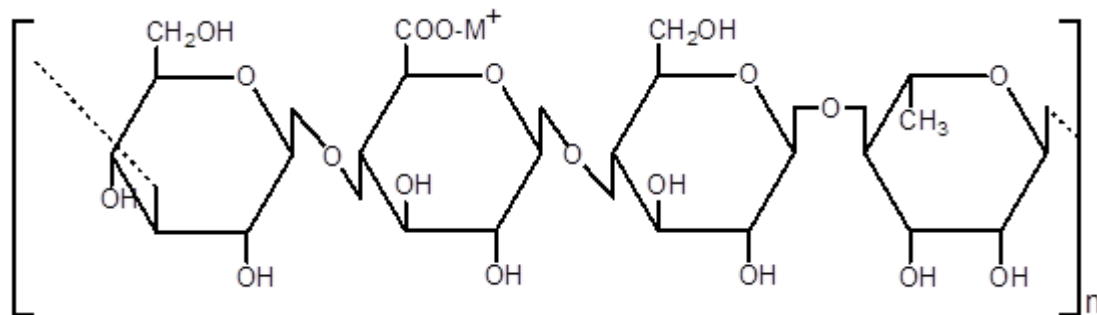


Fig. 1. Structure of galactomannan unit of guar gum and locust bean gum (a) and structural unit of gellan gum (b).

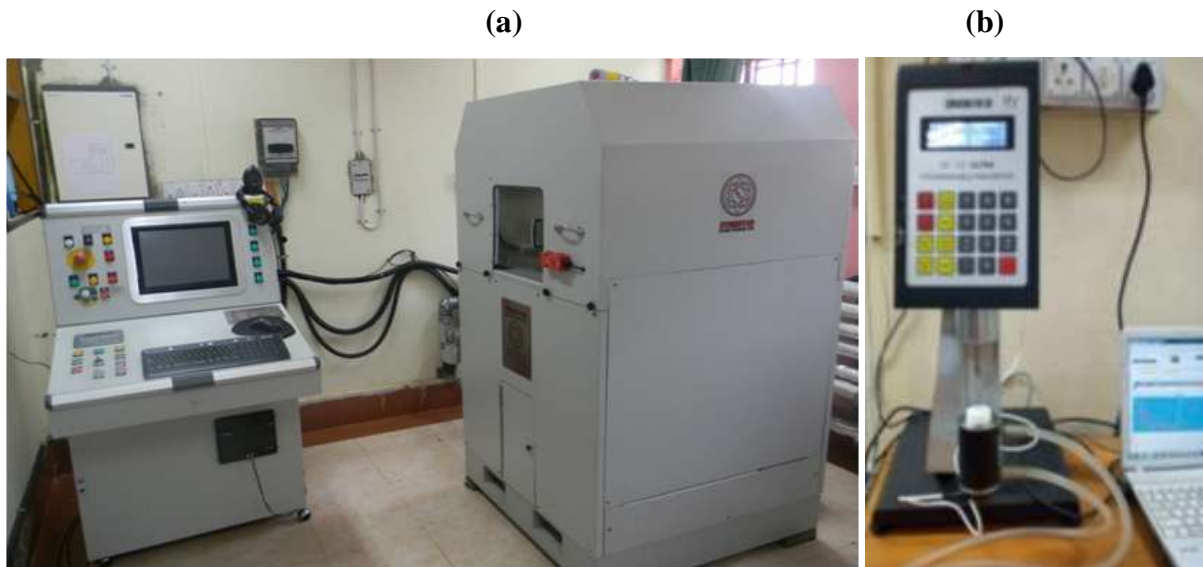


Fig. 2. High pressure unit (a) and Brookfield rheometer (b).

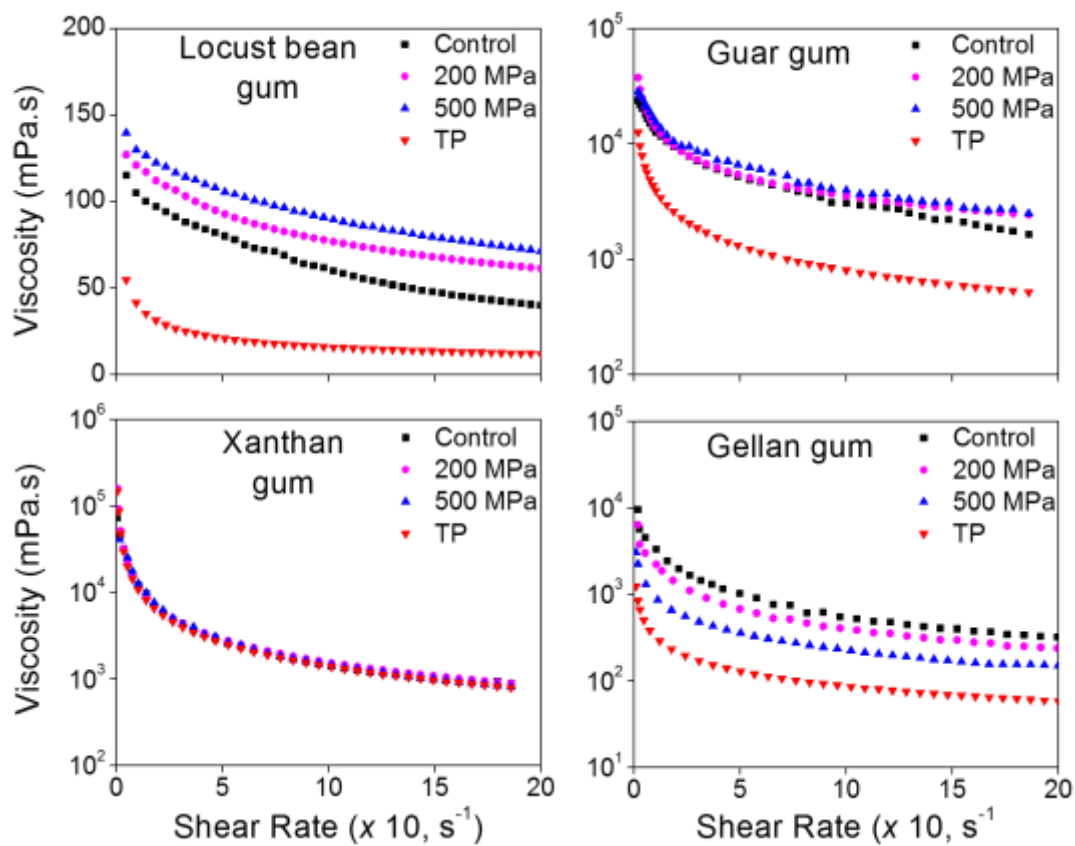


Fig. 3. Effect of high pressure treatment on the flow behavior of the hydrogels.

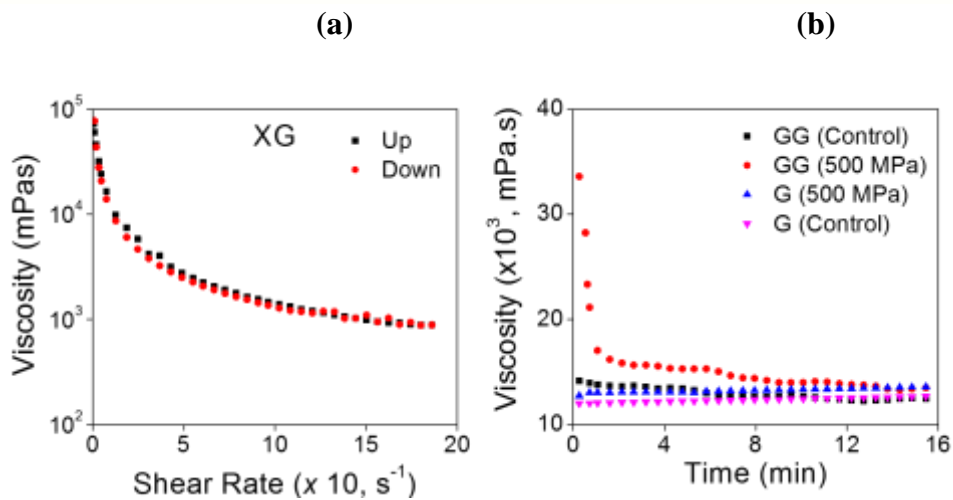


Fig. 4. Pseudoplastic (a) and time independent (b) behavior of the hydrogels.

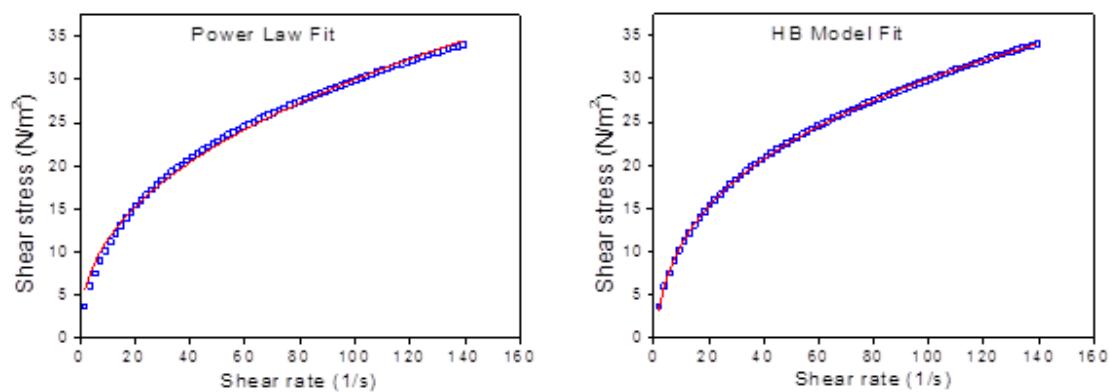


Fig. 5. Power law and HB model fit of the rheological data of gellan gum.

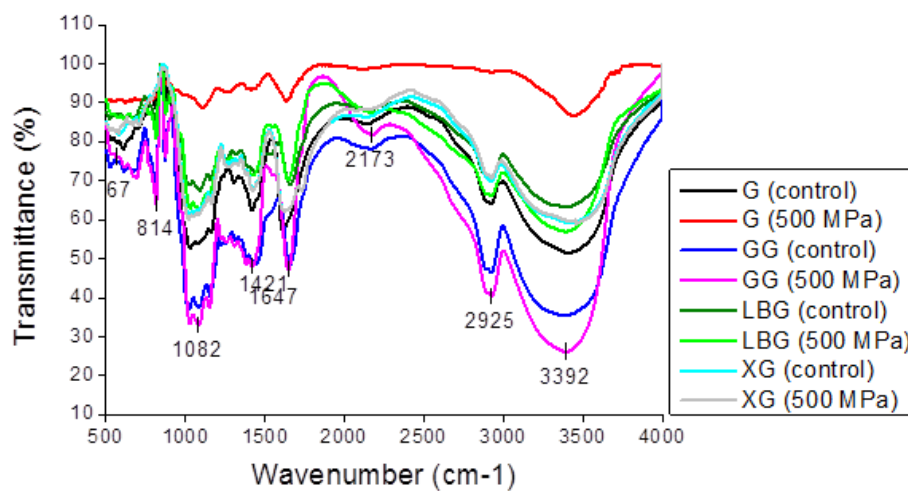


Fig. 6. Functional spectra of the samples obtained by FTIR analysis (XG: xanthan gum, GG: guar gum, G: gellan gum, LBG: locust bean gum).

Table 1. Power law model parameters obtained from the steady-state flow behaviour of the samples.

Sample*	$K (mPa.s^n)$	n	R^2
XG (control)	208.3 ± 4.7	0.699 ± 0.001	0.996
XG (200 MPa)	211.1 ± 3.9	0.704 ± 0.013	0.983
XG (500 MPa)	213.9 ± 1.7	0.695 ± 0.072	0.991
GG (control)	121.5 ± 2.1*	0.423 ± 0.008	0.993
GG (200 MPa)	135.9 ± 1.9*	0.401 ± 0.042	0.957
GG (500 MPa)	161.7 ± 2.6*	0.408 ± 0.031	0.982
G (control)	94.34 ± 0.2*	0.510 ± 0.074	0.991
G (200 MPa)	82.78 ± 0.1*	0.515 ± 0.066	0.985
G (500 MPa)	69.71 ± 0.2*	0.511 ± 0.009	0.991
LBG (control)	30.82 ± 0.1*	0.364 ± 0.017	0.978
LBG (200 MPa)	39.14 ± 0.3*	0.390 ± 0.081	0.990
LBG (500 MPa)	43.09 ± 0.4*	0.392 ± 0.016	0.986

*significantly different ($P < 0.05$), XG: xanthan gum, GG: guar gum, G: gellan gum, LBG: locust bean gum