



# Understanding the rheology of novel guar-gellan gum composite hydrogels

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## ABSTRACT

Hydrogels are hydrophilic polymeric materials, prepared from either synthetic or natural macromolecules. However, synthetic hydrogels are now gradually being replaced with natural hydrogels owing to their non-toxicity, biocompatibility and biodegradability. The present work focused on synthesizing novel composite hydrogels of guar gum and gellan. The synthesized guar-gellan composite hydrogels were further characterized rheologically to understand their functional properties. Arrhenius and power law models were fitted for elucidation of their steady flow behavior. Interestingly the guar-gellan composite hydrogels showed remarkable stability and maintained elasticity at high temperatures and angular frequency. The comprehensive analysis of rheological data of novel guar-gellan gum composite hydrogels suggested their potential advantages over gellan gum and its applicability in diverse industrial sectors.

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## 1. Introduction

Hydrogels are three dimensional networks of polymeric chains consisting of two or multi-component systems. They are hydrophilic in nature and sometimes found as colloidal gels having water as dispersion medium. Hydrogels can be synthesised from synthetic compounds that offers longer service life, high water absorption capacity and high gel strength. However, synthetic hydrogels are now being replaced with natural gels, owing to their ease of availability, biodegradability and lower toxicity [1,2]. Moreover, majority of natural gums or polymers are safe for consumption and hence are being applied in wide array of industries.

Rheological characterisation of these polymeric hydrogels gives insight to the internal structure complexities of the composite. Rheological tests helps in elucidating the behaviour of hydrogels by scrutinising the viscosity, degree of cross linking, and elasticity of the hydrogels [3]. Recently, several researchers are focussing on development of natural hydrogels based on natural polymers or combination of natural and synthetic polymers that are biocompatible and safe for human use. Gellan gum and guar gum are two such polymers that are Generally Recognised As Safe (GRAS) for their use for human consumption. Independently, they have been extensively exploited in terms of their production as well as their applicability in different industries including food and

pharmaceuticals. For instance, guar gum acts as potential hydrophilic matrix carrier for oral drug delivery. It has also been used as thickening and gelling agent in food industries [4]. Similarly, gellan is also an industrial important polymer due to its various functional properties and is widely used in food, pharmaceutical and even in plant tissue and microbial sector [5]. Although substantial work has been done for understanding the basic rheology of respective gellan and guar gum solutions, however as per our investigations, literature regarding guar-gellan gum mixtures/composite is not available.

Guar gum have extraordinarily high viscosity even at low concentration, but it lacks gel forming ability. On the other hand, gellan can form gels but lacks intrinsic toughness and stability. Multifarious research suggests that blending of two polymers can result in synergistic effects that can be desirable for various applications [6]. Therefore, making guar-gellan gum composite hydrogels can help in overcoming respective incongruity.

The present work aims to prepare novel guar-gellan gum composite hydrogels and to further understand their rheological behaviour. The detailed rheological studies of the composites have been carried out that assisted in understanding its viscoelastic and steady flow behaviour.

## 2. Experimental procedures

2% solutions of both gellan (Gelzan, G1910) and guar gum (GRM 1233) were prepared in distilled water. For preparation of

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guar-gellan gum composite hydrogels, the prepared solutions of gellan and guar gum were then mixed in three different ratios namely; 1:1(GE:GU), 1:2(GE:GU) and 2:1(GE:GU). The 1 M solution of  $\text{CaCl}_2$  was added in each mixture and then kept overnight at 4 °C allowing the polymers to form complex 3-D network. Gelation time of hydrogels was determined by test tube inversion method [7].

The prepared hydrogel mixtures were lyophilised and weighed ( $W_1$ ). The weighed samples were dissolved in deionised water and after 24 h, excessive water was eliminated from the swollen gels and were weighed ( $W_2$ ). The swelling percentage (SR%) was determined from the Eq. (1), earlier reported by Azam *et al* (2017) [8].

$$\text{SR\%} = W_2 - W_1 / W_1 \quad (1)$$

For the estimation of water retention capacity, the appropriate amount of dried hydrogels were weighed ( $W_1$ ) and dispensed in water for 24 h. The swollen hydrogels were wiped off to remove the excessive water and then were placed in a desiccator at room temperature. The samples were weighed ( $W_2$ ) at regular intervals till 24 h. The percentage of water retention (WR) was calculated from using Eq. (2).

$$\text{WR\%} = W_2 \times 100 / W_1 \quad (2)$$

Rheological measurements were carried out using rheometer (MCR 102, Anton Paar, Austria) with parallel plate geometry (40 mm diameter, 1 mm gap). For each test, the appropriate amount of sample was loaded onto the peltier plate, equipped with temperature controlled system for fast and accurate thermoregulation ( $\pm 0.001$  °C). All measurements were carried out in duplicates and the rheological data was analysed using the Anton Paar rheo-plus software.

Steady flow measurement was conducted under the shear rate range of 0.01–100  $\text{s}^{-1}$  at 28 °C. In relation to different concentrations namely GE:GU [1:1, 1:2 & 2:1], the flow behaviours of composites were accurately characterised using power law model by using the following equation:

$$\tau = K\gamma^n \quad (3)$$

where  $\tau$  = shear stress (Pa)

$K$  = consistency coefficient ( $\text{Pa}\cdot\text{s}$ )

$\gamma$  = shear rate ( $\text{s}^{-1}$ )

$n$  = flow behaviour index (dimensionless).

The temperature stability of the hydrogels was determined within temperature range of 20 °C to 80 °C at constant shear rate of 1  $\text{s}^{-1}$ . The correlation between flow behaviour and temperature were assessed by using Arrhenius equation no.4: [9].

$$\eta = A \exp(E_a / RT) \quad (4)$$

where  $\eta$  = viscosity ( $\text{MPa}\cdot\text{s}$ )

$A$  = exponential constant ( $\text{Pa}\cdot\text{s}$ )

$E_a$  = activation energy ( $\text{J mol}^{-1}$ )

$R$  = universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )

$T$  = absolute temperature (K).

For FT-IR analysis, gellan and guar gum composite hydrogels were freeze dried. The dried samples (1 mg) were weighed, thoroughly mixed and milled with KBr powder (99 mg). The Perkin Elmer spectrophotometer was employed to record IR spectrum within a range of 4000  $\text{cm}^{-1}$  and 300  $\text{cm}^{-1}$ .

### 3. Results and discussion

The steady flow behaviour of composite hydrogels was studied. It was evident that at low shear rates, shear stress of all four composite hydrogels showed gradual increase and then gradually approaches towards plateau with further increase in shear rates, indicating shear thinning behaviour. Furthermore, the viscosity of hydrogels showed sharp decline at initial values of shear rate, however at high shear rates, viscosity change was smoothened. This behaviour was more evident as the concentration of gellan gum increased in the composites. It can be seen clearly on flow curves (Fig. 1A), that maximum viscosity was given by GE:GU (2:1)

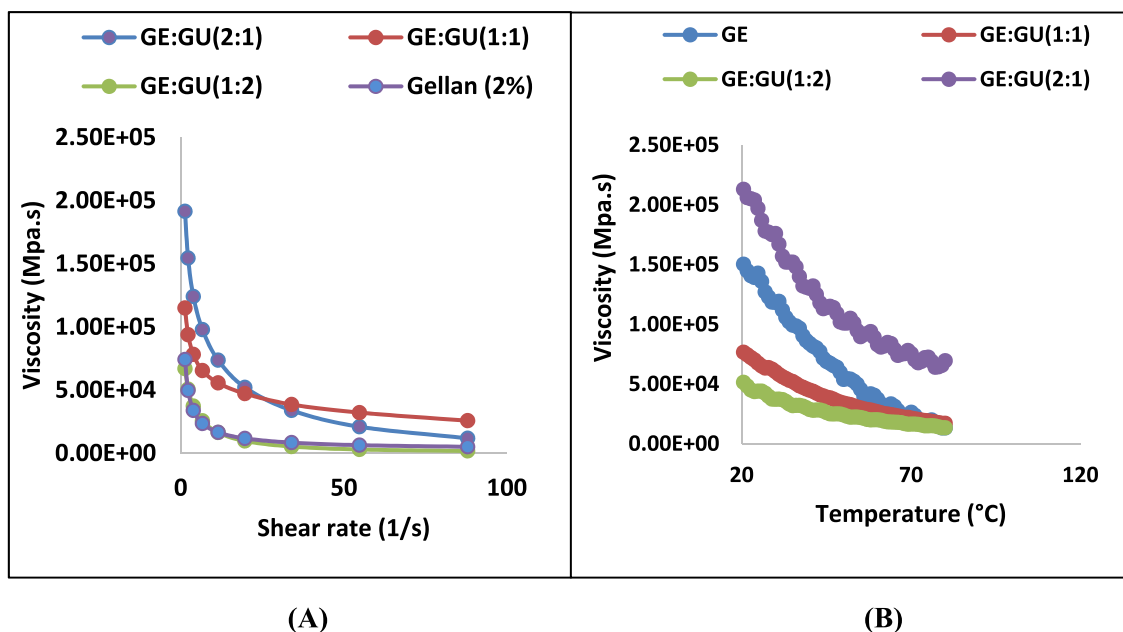


Fig. 1. Steady flow behaviour of gellan (GE)-Guar gum (GU) composites at varying (A) shear rate & (B) temperature.

composite, revealing that addition of guar gum causes decline in overall viscosity of the gellan- guar gum composite hydrogels.

Furthermore, the shear rate data was further analysed by power law flow model and is summarised in Table 1A. As it can be observed that for all four gellan -guar gum composite hydrogels, the power law parameters fitted very well with determination coefficient ( $R^2$ ) value of 0.93 and higher. According to Pongsawatmanit *et al.*, (2006)  $n = 1$ , corresponds to Newtonian fluid and  $n < 1$ , indicates pseudoplastic behaviour of fluid. It has also been reported that higher  $n$  values ( $n > 1$ ) tends to give slimy mouth feel on consumption [10]. Thus for higher viscosities and better mouth feel, composites with lower  $n$  value and higher  $k$  value are required. In accordance to this fact, all four hydrogels synthesised in present work shows lower  $n$  values ranging from 0.23 to 0.47.

Polysaccharides or polysaccharide based composites are processed and stored at wide range of temperatures [11]. Therefore, it is crucial to understand the influence of temperature on hydrogels that can dictate its flow dynamics. Viscosity of the gellan and gellan-guar composite hydrogels was studied over the temperature range of 20 °C to 80 °C at a fixed shear rate of 1 s<sup>-1</sup> (Fig. 1B). Interestingly, all hydrogels showed decline in viscosity with increase in temperature, indicating thermal expansion and increase in intermolecular distances. The temperature-dependent flow behaviour of composite hydrogels was described by the Arrhenius model and the corresponding parameters, including  $E_a$ ,  $\ln A$  and  $R^2$  (Table 1B). Generally,  $E_a$  is defined as threshold energy barrier that must be overcome before the hydrogel achieves flowability. Higher value of  $E_a$  indicates higher temperature-

dependent flowability of the hydrogel. It is evident from the given data that GE showed maximum activation energy of about 538.99 J mol<sup>-1</sup> indicating that its viscosity properties are highly sensitive to temperature variation than other three composites. However, for gellan hydrogels, the value of  $E_a$  sharply declined on addition of guar gum suggesting that guar gum participated in providing higher stability to the system and thus reduced temperature-dependent flowability properties of the hydrogels.

The ability of hydrogels to absorb and retain water are decisive factors while dictating its appositeness in various industrial sectors. The swelling percentage of gellan and guar-gellan composite hydrogels was analysed till 24 h (Fig. 2A). Swelling ratio enhanced with addition of guar gum. Similar pattern was observed for water retention ability (Fig. 2B) in case for all hydrogels. This can be due to hydrophilic nature of incorporated hydrogel network with numerous hydroxyl groups.

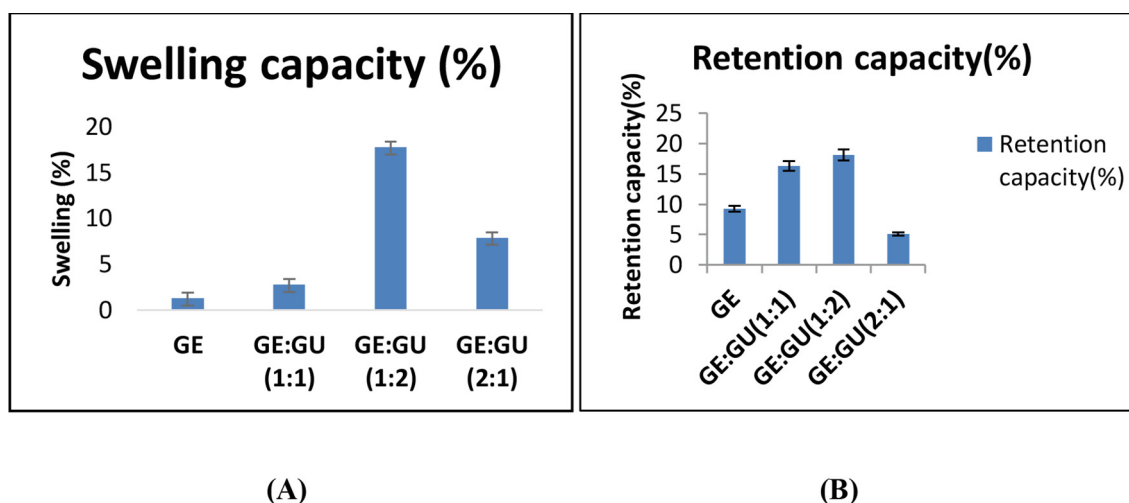
The structure formation of macromolecules in a system can be explained by determining the viscoelastic properties in terms of dynamic measurements, where elasticity is represented by storage modulus  $G'$  while viscous property is explained by loss modulus  $G''$  [12]. The frequency sweep results for gellan-guar composite hydrogels are shown in Fig. 3. It can be observed that both  $G'$  and  $G''$  showed high frequency dependency from 0.1 to 100 rad/s. With increase in frequency, storage modulus grows strongly while  $G''$  decreases, which can be due to incorporation of loose chains and dangling ends into purely elastic gel [13].

The elasticity ( $G'$ ) of the composite hydrogels corresponds to the elasticity of muscle cells (8–15 KPa), cartilage (20–25 KPa) and bone (25–45 KPa). Based on these observations, it can be suggested that these hydrogels can mimic these in tissue micro-environment [14]. These gels can, therefore, be used in tissue engineering and could be further fabricated to attain high mechanical strength.

The crosslinking between gellan and guar gum composites were comprehended by studying FTIR (Fig. 4). The spectrum of guar gum has characteristic peaks at 868 cm<sup>-1</sup> and 813 cm<sup>-1</sup> that are associated with presence of anomeric configurations ( $\alpha$  and  $\beta$  conformers) and glycosidic linkages from  $\alpha$ -D-galactopyranose units and  $\beta$ -D-mannopyranose units respectively [15] while gellan exhibited characteristic peaks at 3448 cm<sup>-1</sup>, 2997 cm<sup>-1</sup>, 1637 cm<sup>-1</sup> and 1420 cm<sup>-1</sup> that corresponds to carboxylic -OH stretching, CH stretching vibration, asymmetric and symmetric COO<sup>-</sup> stretching respectively [16]. The FTIR- spectra of gellan-guar composite hydrogels showed slight shifts in peaks but still corresponds more towards gellan spectrum, thus indicating entrapment of guar gum

**Table 1**  
(A) Power law & (B) Arrhenius model fitting parameters for gellan (GE) and gellan-guar (GE:GU) composites.

A			
Samples	K (Pa.s)	n	R <sup>2</sup>
GE	112.1	0.232	0.93
GE:GU(1:1)	191.6	0.471	0.95
GE:GU(1:2)	61.7	0.341	0.92
GE:GU(2:1)	248	0.393	0.97
B			
Samples	ln A	E <sub>a</sub> (J mol <sup>-1</sup> )	R <sup>2</sup>
GE	3.29	18282.5	0.99
GE:GU(1:1)	2.24	22040.41	0.99
GE:GU(1:2)	3.33	18,166	0.99
GE:GU(2:1)	5.06	17459.4	0.98



**Fig. 2.** (A) Swelling capacity & (B) Retention capacity of hydrogels.

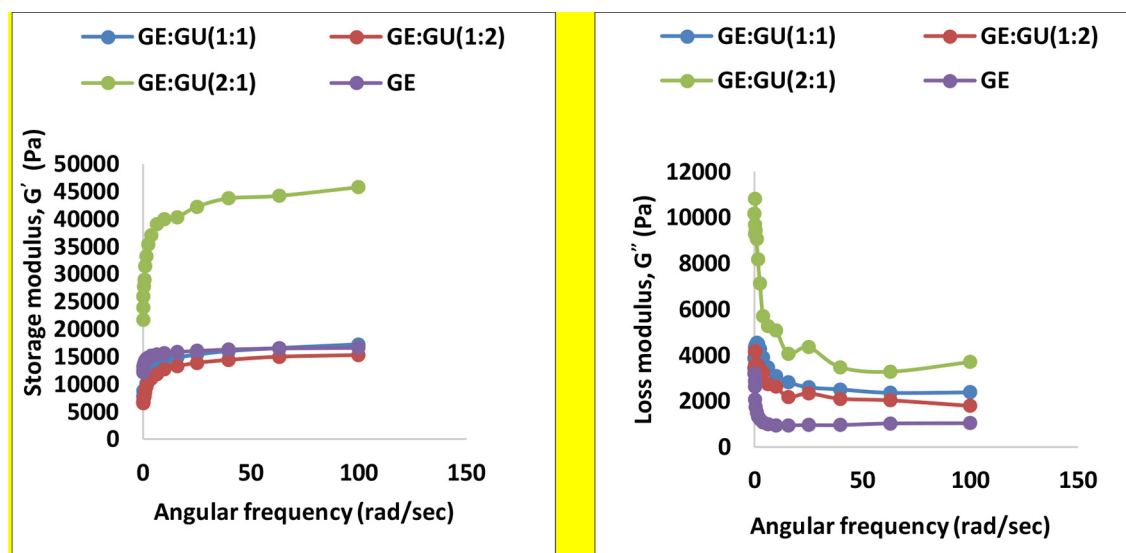


Fig. 3. Dynamic oscillatory rheology of gellan-guar composite (A) Storage modulus,  $G'$  & (B) loss modulus,  $G''$

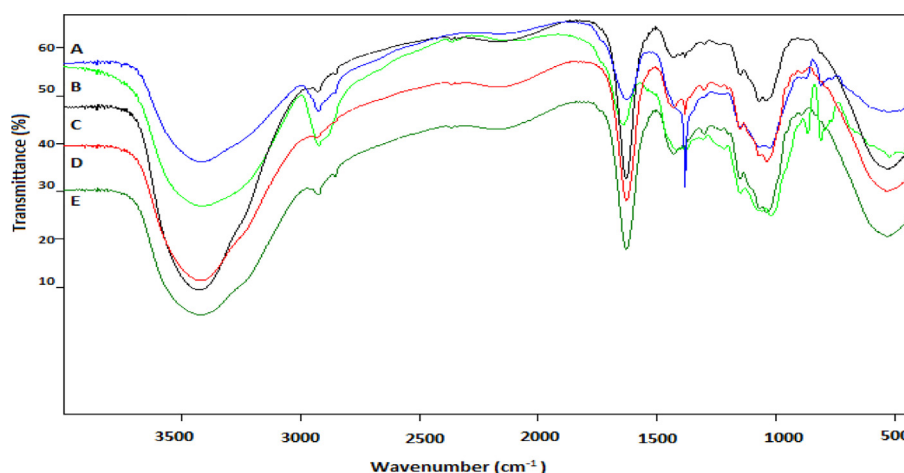


Fig. 4. FTIR spectrum of (A) GE:GU-1:2, (B) Guar gum, (C) GE:GU- 1:1, (D) GE:GU-2:1 and (E) Gellan.

network inside gellan molecular structure. On close observation of the spectrum, decrease in steepness of peaks  $1630\text{ cm}^{-1}$ ,  $1430\text{ cm}^{-1}$  and  $3448\text{ cm}^{-1}$  can be seen, indicating higher occupancy of hydroxyl and carboxylic groups upon crosslinking.

#### 4. Conclusion

The present study focused on developing the novel guar-gellan gum composite hydrogels and further understanding their rheological properties. The major advantage of the guar-gellan gum hydrogels is its chemical free syntheses. It is evident from the aforementioned data that the synthesised hydrogel gives better mouth feel and less temperature dependent flow behaviour, suggesting it as an ideal candidate for numerous food products. Also, elastic modulus of the respective hydrogel was comparable to many tissues in different micro-environment, suggesting its use for biomedical applications.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2019.127234>.

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