



Evaluation and modelling of rheological properties of microwave treated xanthan gum solution

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ABSTRACT

The aqueous solution of xanthan gum has high viscosity and pseudoplastic behavior. This research aimed to analyze the effect of microwave pretreatment at different time intervals (0, 1, 2, and 3 min) on the viscosity and rheological behavior of xanthan gum solution. The results showed that the apparent viscosity of xanthan gum solution (untreated solution) reduced from 0.177 Pa.s to 0.036 Pa.s with increasing shear-rate from 12.2 s⁻¹ to 171.2 s⁻¹. Also, the apparent viscosity of xanthan gum solution reduced from 0.070 Pa.s to 0.046 Pa.s with increasing the microwave pretreatment time from 0 to 3 min (shear-rate=61.2 s⁻¹). The flow behavior of all samples was successfully modeled with Power law, Bingham, Herschel-Bulkley, and Casson models, and the Herschel-Bulkley model was selected as the better model to describe the flow behavior of xanthan gum solutions. The Herschel-Bulkley model had an acceptable performance with the maximum correlation coefficient (r) (higher than 0.9032) and the minimum sum of squared error (SSE) (lower than 0.7165) and root mean square error (RMSE) (lower than 0.2552). The yield stress and consistency coefficient (Herschel-Bulkley model) of xanthan gum solution increased from 0.095 Pa to 0.450 Pa, and from 0.659 Pa.sⁿ to 0.811 Pa.sⁿ, with increasing microwave pretreatment time from 0 to 3 min, respectively. The flow behavior index (Herschel-Bulkley model) of xanthan gum solutions decreased from 0.440 to 0.328 while the duration of microwave treatment increased.

1- Introduction

Natural polymers are macromolecules made up of repeating structural units and originate from natural sources [1]. Natural hydrocolloids, including gums, have received renewed attention in recent years due to their excellent characteristics such as biocompatibility, biodegradability, and nontoxicity [2]. Xanthan gum is a natural high molecular weight heteropolysaccharide produced by the bacterium *Xanthomonas campestris* using carbohydrates as the main raw material [2, 3]. The xanthan gum backbone consists of β -D-glucose linked [4]. Due to its excellent functional and rheological properties, this gum has found numerous applications in many industries such as food, cosmetics, and pharmaceuticals [2-4]. Xanthan gum is a biocompatible, biodegradable, less toxic, bioactive, and cost-effective natural polymer. The native properties of xanthan gum can be improved by cross-linking, grafting, curing, blending, and various modification techniques. Grafted xanthan gum has excellent biodegradability, metal binding, dye adsorption, immunological properties, and wound healing ability [5]. Xanthan gum possesses structural rigidity, providing stability against heat, acid, and alkali conditions. Xanthan gum is characterized by its pseudoplastic flow behavior and high viscosity, with a yield stress even at low concentrations [6, 7].

The rheological behavior of polysaccharides in solution is relevant for fundamental studies, but also from practical point of view. Even added in low content, they are able to change the rheology of aqueous systems, acting as thickening or gelling agents for food industry and eco-friendly applications [8].

The natural polymers can be modified as required and thus can be tailor made for specific applications [1]. The thermal processing including microwave technology has gained acceptance in domestic usage and is gaining popularity in industrial applications [9, 10]. Microwave irradiation to efficiently apply thermal energy is becoming a standard technique in various fields of chemistry [11]. Microwave irradiation creates heat inside the processed materials because of rapid alterations of the electromagnetic field at high frequencies [9]. Hence, microwave irradiation has an effect in a shorter process time, with higher yield, and better quality of products than those obtained by conventional processing techniques [12]. Microwave heating has vast applications in the field of food processing such as cooking, drying, pasteurization and preservation of food materials [13]. The microwave irradiation is an efficient method which results in rapid transfer of energy in the bulk of the reaction mixture. The microwave-assisted graft copolymerization requires a very short reaction time and proceeds even in the absence of any redox initiator [11].

Xanthan gum is a nonionic polysaccharide widely explored in biomedical, nutraceutical, and pharmaceutical fields [1]. Various techniques have been employed to modify xanthan gum, including genetic, enzymatic, ultrasonic, radiative, and chemical modification [3]. The aim of this work was to study the effect of microwave pretreatment at different time (0, 1, 2, and 3 min) on the rheological properties, viscosity, consistency coefficient, and flow behavior index of xanthan gum solution.

2- Materials and methods

2.1. Preparation of gum solutions

Xanthan gum powder (food grade) was purchased from FuFeng Co. (China). The xanthan gum solutions (0.20%, w/v) were provided by solving the gum powder in distilled water using a stirrer.

2.2. Microwave treatment process

To apply the microwave pretreatment on the xanthan gum solution, a microwave oven (Gplus, Model; GMW-M425S.MIS00, Goldiran Industries Co., Iran) was used under atmospheric pressure. In this study, the effect of the microwave pretreatment time at four levels of 0, 1, 2, and 3 min (power=440W) on the xanthan gum solution was examined.

2.3. Apparent viscosity

The rheological properties of untreated and microwave treated xanthan gum solutions was calculated using a rotational viscometer (Brookfield, DV2T, RV, USA) after each treatment at 20°C. The apparent viscosity and shear-stress of xanthan gum solutions at different shear-rates (12.2-171.2 s⁻¹) were studied using UL Adapter Kit [14].

2.4. Mathematical modeling

Hydrodynamic resistance of macromolecules to flow is influenced by the molecular characteristics of the polysaccharide, concentration in solution, but also by the thermodynamic and environmental conditions. Due to the structural and functional complexity of polysaccharides, it is difficult to select an appropriate model to describe their rheological behavior [8]. In this study, various viscous flow models, including Power law (Eq. 1), Bingham (Eq. 2), Herschel-Bulkley (Eq. 3), and Casson (Eq.

4), were used to match the experimental shear stress and shear rate data of the untreated and microwave treated xanthan gum solutions [15, 16]:

$$\tau = k\dot{\gamma}^n \quad (1)$$

where τ is the measured shear stress (Pa), k is the Power law consistency coefficient (Pa.sⁿ), $\dot{\gamma}$ is the shear rate (s⁻¹), and n is the flow behaviour index (dimensionless).

$$\tau = \tau_{0B} + \eta_B \dot{\gamma} \quad (2)$$

where η_B is the Bingham plastic viscosity (Pa.s) and τ_{0B} is the Bingham yield stress (Pa).

$$\tau = \tau_{0H} + k_H \dot{\gamma}^{n_H} \quad (3)$$

where k_H is the consistency coefficient (Pa.sⁿ), τ_{0H} is the yield stress (Pa), and n_H is the flow behaviour index for Herschel-Bulkley model.

$$\tau^{0.5} = \tau_{0C}^{0.5} + \eta_C \dot{\gamma}^{0.5} \quad (4)$$

where η_C is the plastic viscosity (Pa.s) and τ_{0C} is the yield stress (Pa) for Casson model. Data modeling was carried out with multilinear and nonlinear regression analysis parameters and functions associated with various equations calculated from empirical values using Matlab software (version R2012a).

2.5. Statistical analysis

Means were compared via Duncan's multiple range test using an alpha level of 0.05 for significant effects, using SPSS Version 21.

3- Results and discussion

3.1. Apparent viscosity

Due to its unique molecular structure, xanthan gum possesses many outstanding properties, including high viscosity at low concentrations and distinctive rheological characteristics [3]. The rheological characteristics of food hydrocolloids are strongly influenced by temperature, pressure, concentration, and physical state of dispersion [17, 18]. The shear-rate dependence of the viscosity of xanthan gum solutions is shown in Figure 1. It is seen that the apparent viscosity of xanthan gum solution decreases as the shear-rate increases. This shear-thinning probably be caused by the structural decomposition or rearrangement of xanthan gum under the action of shear force [3]. In this study, the apparent viscosity decreased from 0.177 Pa.s to 0.036 Pa.s with the shear-rate increased from 12.2 s^{-1} to 171.2 s^{-1} (untreated solution).

In addition, influence of microwave pretreatment on the apparent viscosity of

xanthan gum solutions as a function of shear-rate are demonstrated in Figure 1. The application of microwave to the xanthan gum solution reduces its viscosity. This behavior was observed at all conditions and 3 min pretreatment leading to a greater reduction in gum viscosity. The results demonstrated that the apparent viscosity of xanthan gum solution reduced from 0.070 Pa.s to 0.046 Pa.s with increment in microwave pretreatment time from 0 to 3 min (shear-rate= 61.2 s^{-1}). Microwave treatment causes a drop in viscosity which may be due to the molecular rearrangements restricted to sections of the hydrocolloids molecules [19]. Effect of microwave irradiation on acid hydrolysis of faba bean starch was examined by González-Mendoza, *et al.* [20]. The results showed that the lowest viscosity values were for the starches with the combination of more severe hydrochloric acid and microwave energy conditions.

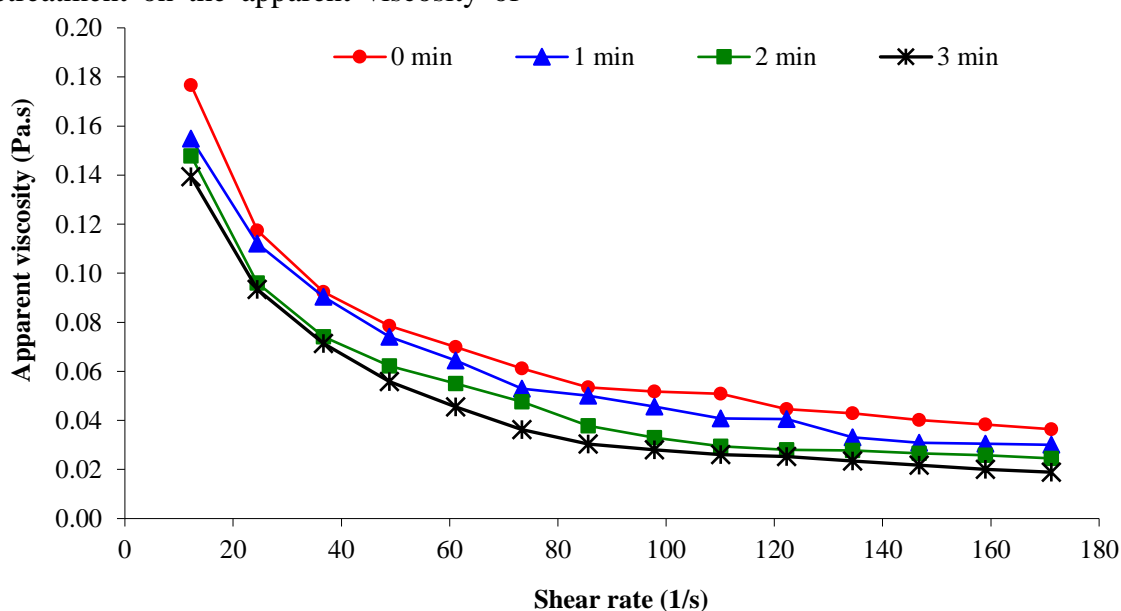


Fig. 1. Impact of microwave pretreatment on the apparent viscosity of xanthan gum solution.

3.2. Mathematical modeling

The flow behavior of xanthan gum solutions was successfully modeled with Power law, Bingham, Herschel-Bulkley, and Casson models, and the Herschel-Bulkley model was found as the better model to describe the flow behavior of xanthan gum solutions. Figure 2

demonstrates the fit of different rheological models to the experimental data. This figure confirms that the Herschel-Bulkley equation can model well the rheological behavior of untreated and microwave treated xanthan gum solution.

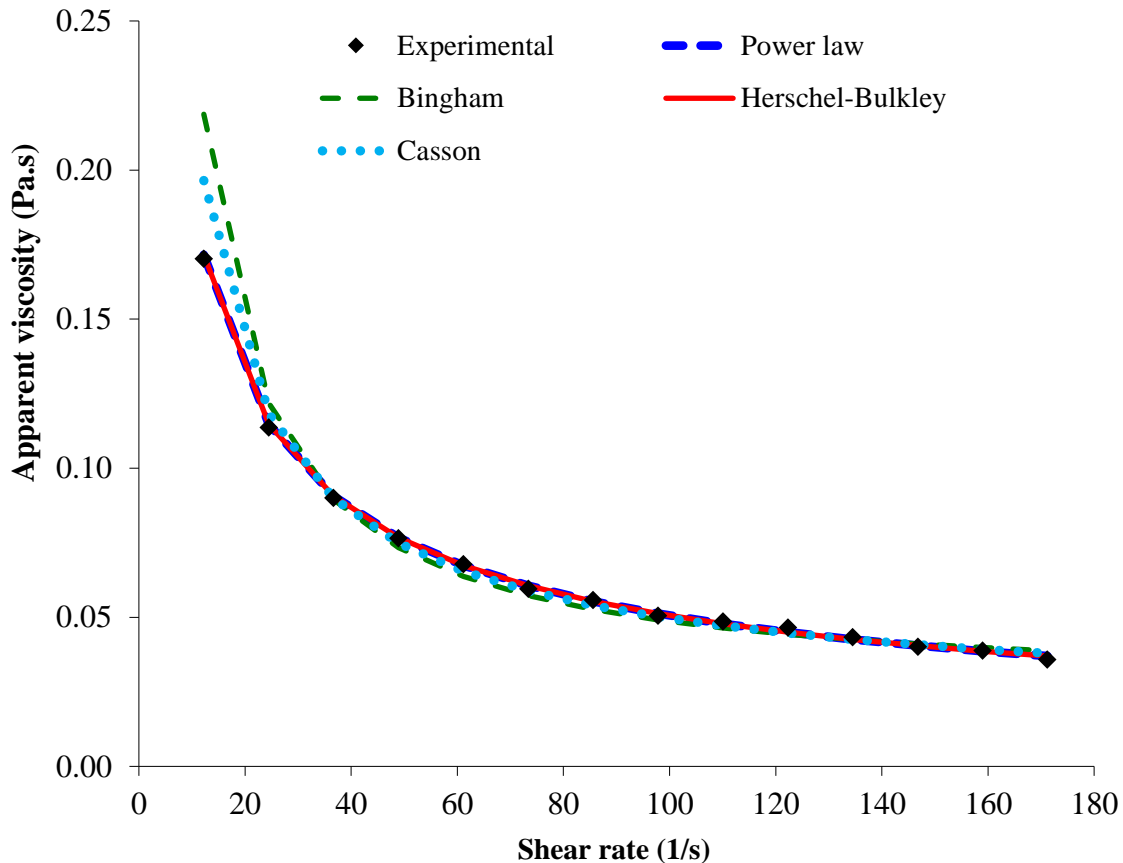


Fig. 2. Fitting ability of different rheological models to experimental data.

3.3. Power law model

The Power law was considered to be the suitable model for characterizing the rheological behavior of many gum solutions [21, 22]. In this study, the Power law model showed an acceptable performance with sum of squared error (SSE) of 0.421, correlation coefficient (r) of 0.968, and root mean square error (RMSE) of 0.171 (Table 1).

In the Power law model, the rheological properties are defined by flow behavior

index (n) and consistency coefficient (k) parameters [15]. The impact of microwave treatment on the consistency coefficient of xanthan gum solutions is reported in Table 1. The consistency coefficient of xanthan gum solution increased from 0.726 Pa.s ^{n} to 1.051 Pa.s ^{n} with increasing microwave pretreatment time from 0 to 3 min.

The rheological characteristics of hydrocolloids are extremely important because of the structural, functional and textural properties of food products [23, 24]. It is clear from the Power law model

that a non-Newtonian fluid ($n \neq 1$) with pseudoplastic behavior has a value of n lower than 1 [25]. The impact of microwave treatment on the flow behavior index of xanthan gum solutions is reported in Table 1. The flow behavior index of xanthan gum solutions decreased significantly from 0.422 to 0.235 ($p < 0.05$) (increases in

pseudoplastic behavior) while the duration of microwave treatment increased. The change in the k and n indexes of the xanthan gum solution may be due to the structural change of the gum during microwave treatment.

Table 1- The coefficients of Power law model for calculating shear-stress values of microwave treated xanthan gum solution

Microwave treatment time	Consistency coefficient (Pa.s ⁿ)	Flow behavior index	Sum of squared error	Correlation coefficient	Root mean square error
0 min	0.726±0.071 ^a	0.422±0.020 ^a	0.114	0.997	0.096
1 min	0.835±0.181 ^a	0.362±0.049 ^a	0.637	0.975	0.230
2 min	0.794±0.193 ^a	0.350±0.075 ^{ab}	0.432	0.972	0.156
3 min	1.051±0.141 ^a	0.235±0.040 ^b	0.502	0.928	0.201

Different letters within each column represent significance difference ($p < 0.05$)

3.4. Bingham model

Rheological properties play an important role in process design. The experimental shear-stress versus shear-rate values of untreated and treated xanthan gum solutions was fitted with the Bingham model and the determined constant coefficients of the Bingham equation consisting of Bingham yield stress (τ_{0B}) and Bingham plastic viscosity (η_B) are presented in Table 2 together with the

corresponding statistical error values. The results of Bingham model showed that the values of the Bingham yield stress ranged from 2.054 Pa to 2.348 Pa, and the Bingham plastic viscosity ranged from 0.009 Pa.s to 0.025 Pa.s. Based on the Bingham model fitting results, the values of SSE, r , and RMSE for xanthan gum solutions ranged from 0.636-1.113, 0.876-0.985, and 0.202-0.389, respectively.

Table 2- The coefficients of Bingham model for calculating shear-stress values of microwave treated xanthan gum solution

Microwave treatment time	Yield stress (Pa)	Plastic viscosity (Pa.s)	Sum of squared error	Correlation coefficient	Root mean square error
0 min	2.348±0.120 ^a	0.025±0.001 ^a	0.938	0.978	0.278
1 min	2.281±0.230 ^a	0.019±0.002 ^{ab}	1.113	0.952	0.298
2 min	2.080±0.142 ^a	0.016±0.004 ^b	0.963	0.941	0.280
3 min	2.054±0.069 ^a	0.009±0.002 ^c	0.636	0.901	0.229

Different letters within each column represent significance difference ($p < 0.05$)

3.5. Herschel-Bulkley model

The experimental shear-stress versus shear-rate values of untreated and treated xanthan gum solutions was fitted with the Herschel-Bulkley model and the determined constant coefficients of the Herschel-Bulkley

equation consisting of τ_{0H} , k_H , and n_H are presented in Table 3 together with the corresponding statistical error values for all solutions. Based on the Herschel-Bulkley model, all xanthan gum solutions demonstrated pseudoplastic behavior,

described by the flow behavior index (n_H) values lower than 0.710 under all conditions. The results of Herschel-Bulkley model showed that the values of the yield stress ranged from 0.095 Pa to 0.769 Pa, consistency coefficient ranged from 0.460

Pa.sⁿ to 0.811 Pa.sⁿ, and the flow behavior index ranged from 0.328 to 0.509. The values of SSE, r, and RMSE for xanthan gum solutions ranged from 0.063-0.717, 0.903-0.999, and 0.076-0.255, respectively.

Table 3- The coefficients of Herschel-Bulkley model for calculating shear-stress values of microwave treated xanthan gum solution

Microwave treatment time	Yield stress (Pa)	Consistency coefficient (Pa.s ⁿ)	Flow behavior index	Sum of squared error	Correlation coefficient	Root mean square error
0 min	0.095±0.134 ^a	0.659±0.105 ^a	0.440±0.029 ^a	0.127	0.997	0.104
1 min	0.769±0.582 ^a	0.460±0.328 ^a	0.509±0.152 ^a	0.621	0.975	0.237
2 min	0.205±0.290 ^a	0.705±0.302 ^a	0.384±0.119 ^a	0.426	0.972	0.192
3 min	0.450±0.636 ^a	0.811±0.478 ^a	0.328±0.170 ^a	0.492	0.929	0.208

Same letters above the values means non-statistically significant differences among the groups ($p > 0.05$)

3.6. Casson model

The experimental shear-stress versus shear-rate values of untreated and treated xanthan gum solutions was fitted with the Casson model and the determined constant coefficients of the Casson equation consisting of Casson yield stress (τ_{0C}) and Casson plastic viscosity (η_C) are reported in Table 4 together with the corresponding

statistical error values for all solutions. The results of Casson model showed that the values of the Casson yield stress ranged from 1.378 Pa to 1.678 Pa, and the Casson plastic viscosity ranged from 0.048 Pa.s to 0.105 Pa.s. The values of SSE, r, and RMSE for xanthan gum solutions ranged from 0.355-0.767, 0.893-0.996, and 0.132-0.308, respectively.

Table 4- The coefficients of Casson model for calculating shear-stress values of microwave treated xanthan gum solution

Microwave treatment time	Yield stress (Pa)	Plastic viscosity (Pa.s)	Sum of squared error	Correlation coefficient	Root mean square error
0 min	1.389±0.113 ^a	0.105±0.004 ^a	0.355	0.992	0.170
1 min	1.678±0.138 ^a	0.084±0.011 ^a	0.767	0.968	0.249
2 min	1.378±0.233 ^a	0.078±0.018 ^a	0.613	0.960	0.219
3 min	1.578±0.130 ^a	0.048±0.009 ^b	0.540	0.919	0.210

Different letters within each column represent significance difference ($p < 0.05$)

4- Conclusion

In this study, the effect of microwave pretreatment on the rheological characteristics of xanthan gum solution was examined. This gum demonstrated the pseudoplastic flow behavior. The application of microwave to the xanthan gum solution reduces its viscosity. The results showed that the Herschel-Bulkley model became the most accurate model to show the rheological characteristics of

xanthan gum solutions compared to three other confirmed rheological models. The consistency coefficient value of the samples was increased with an increment in microwave process time to 3 min. The values of SSE, r, and RMSE for xanthan gum solutions ranged from 0.063-0.717, 0.903-0.999, and 0.076-0.255, respectively.

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ارزیابی و مدل‌سازی خواص رئولوژیکی محلول صمغ گزانتان تیمار شده با مایکروویو

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چکیده

اطلاعات مقاله

محلول آبی صمغ گزانتان دارای ویسکوزیته بالا و رفتار سودوپلاستیک است. این تحقیق با هدف تجزیه و تحلیل اثر پیش تیمار مایکروویو در فواصل زمانی مختلف (۰، ۱، ۲ و ۳ دقیقه) بر ویسکوزیته و رفتار رئولوژیکی محلول صمغ زانتان انجام شد. نتایج نشان داد که ویسکوزیته ظاهری محلول صمغ گزانتان (محلول تیمار نشده) با افزایش سرعت برشی از ۱۲/۲ برثانیه به ۱۷۱/۲ برثانیه، از ۰/۱۷۷ پاسکال ثانیه به ۰/۰۳۶ پاسکال ثانیه کاهش یافت. همچنین، ویسکوزیته ظاهری محلول صمغ گزانتان با افزایش زمان پیش تیمار مایکروویو از ۰ به ۳ دقیقه، از ۰/۰۷۰ پاسکال ثانیه به ۰/۰۴۶ پاسکال ثانیه، کاهش یافت (سرعت برشی = ۶۱/۲ برثانیه). رفتار جریان همه نمونه‌ها با موفقیت با مدل‌های قانون توان، بینگهام، هرشل بالکلی و کاسون مدل‌سازی شد و مدل هرشل بالکلی به عنوان مدل بهتر برای توصیف رفتار جریان محلول‌های صمغ گزانتان انتخاب شد. مدل هرشل بالکلی با حداکثر ضریب تبیین (R) (بیشتر از ۰/۹۰۳۲) و حداقل مجموع مربعات خطا (SSE) (کمتر از ۰/۷۱۶۵) و جذر میانگین مربعات خطا (RMSE) (کمتر از ۰/۲۵۵۲) عملکرد قابل قبولی داشت. تنش تسلیم و ضریب قوام محلول صمغ گزانتان (مدل هرشل بالکلی) با افزایش زمان پیش تیمار مایکروویو از ۰ به ۳ دقیقه به ترتیب از ۰/۰۹۵ پاسکال به ۰/۴۵۰ پاسکال و از ۰/۶۵۹ Pa.sⁿ به ۰/۸۱۱ Pa.sⁿ افزایش یافت. شاخص رفتار جریان محلول‌های صمغ گزانتان (مدل هرشل بالکلی) با افزایش مدت تیماردهی با مایکروویو، از ۰/۴۴۰ به ۰/۳۲۸ کاهش یافت.

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هرشل بالکلی

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