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Rheological properties of ternary mixtures of yellow fruits

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ABSTRACT. In this work, the rheological behaviour of ternary mixtures of orange juice, pineapple and mango pulps was studied using response surface methodology. The flow curves were adequately described by the Herschel–Bulkley rheological model. All the ternary mixtures studied presented a change in the rheological parameters with an increase in temperature, and the majority of the formulations were shear-thinning fluids. The rheological responses were influenced by different pulp proportions and different temperatures (20 or 60°C). The quadratic and cubic models used to fit the responses were considered suitable owing to the high values of the coefficient of determination.

Keywords: rheology, apparent viscosity, temperature, fruits.

Propriedades reológicas de misturas ternárias de frutas amarelas

RESUMO. Neste trabalho, foi estudado o comportamento reológico de misturas ternárias de suco de laranja e polpas de abacaxi e manga utilizando a metodologia de superfície de resposta. As curvas de fluxo foram adequadamente descritas pelo modelo reológico de Herschel-Bulkley. Todas as misturas ternárias estudadas apresentaram alteração nos parâmetros reológicos com o aumento da temperatura, sendo a maioria das formulações fluidos pseudoplásticos. As respostas reológicas foram influenciadas pela diferença na proporção das polpas a também pelas temperaturas (20 e 60°C). Os modelos quadráticos e cúbicos usados para ajustar as respostas foram considerados adequados devido aos altos valores de coeficiente de determinação.

Palavras-chave: reologia, viscosidade aparente, temperatura, frutas.

Introduction

New product development (NPD) is often recommended as a suitable strategy to build competitive advantage and long-term financial success in today's global food markets. Product innovation is said to help maintain growth (thereby protecting the interests of investors, employees, and food chain actors), spread market risk, enhance the company's stock market value and increase competitiveness (LORD, 2000).

Rheology is an important tool to develop and scale-up a process. The rheological behaviour and flow properties of fruit pulps have a significant role in the food industry as they govern product development, design, and the evaluation of process equipment such as pumps, piping, heat exchangers, evaporators, sterilisers, and mixers (AHMED et al., 2005b).

Additionally, knowledge of fundamental rheological properties of any food can be an indication of how the food is going to behave under various process conditions (AHMED et al., 2005a). Taking into account that there is an increasing tendency to develop products made of mixtures of fruits (yogurts, juices, ice-creams, and soft drinks) and the importance of knowledge of the relevant rheological parameters in manufacturing, this novel study investigated the rheological behaviour of pineapple, mango and orange. The goal of this research was to characterise the rheological behaviour of ternary mixtures of orange juice, pineapple and mango pulps using response surface methodology (RSM) as a mathematical and statistical tool (WU et al., 2009).

Material and methods

Raw material

Pineapple and mango pulps were purchased at a local market in the city of Campo Mourão, Paraná state. Orange juice was generously provided by the company COCAMAR (Maringá, Paraná State, Brazil).

Raw material characterisation

Physico-chemical analyses

Total soluble solids (°Brix) and pH were determined using a refractometer (WY1A, ABBE, USA) and a pH meter with a glass electrode (model 710 A, Orion Research, Boston, USA) at 25°C, respectively. Titratable acidity and moisture content were measured according to the standard method of AOAC (2000).

Rheological measurements

The flow behaviour of the ternary mixtures was studied using a rotational Haake Rheostress 1 rheometer (Haake, Karlsruhe, Germany). A parallel geometry plate (rotor PP35H with a 35 mm diameter and 1.5 mm gap) was used for the non-oscillatory experiments. The temperature was adjusted by a circulating Haake DC-30 bath and a Haake (UTC) Universal Temperature Controller system (Haake, Karlsruhe, Germany). The flow behaviour of the ternary mixtures was determined according to Haminiuk et al. (2006a). The measurements were performed at 20 and 60°C, considering that the former is the usual temperature of thawed pulp and the latter corresponds to the temperature used in industrial pasteurisation. Each experimental was run using an upward curve with a duration of 2 min. and a shear rate ranging from 0 to 300 s^{-1} and 2 min. and a downward curve with a shear rate range from 300 to 0 s^{-1}. While both decreasing and increasing the shear rate, 25 points of shear stress were obtained, resulting in a total of 50 points, whose average value of shear stress was taken for each shear rate. Three experimental runs were performed for each formulation or mixtures, and the resulting shear stress was the average of the three experimental values. The rheological data of shear rate and shear stress of the ternary mixtures were fitted according to the Herschel-Bulkley model (HUANG et al., 2008):

$$\tau = \tau_o + K \gamma^n \tag{1}$$

where:

τ is the shear stress (Pa);

τ_o is the yield stress (Pa);

K is the consistency coefficient (Pa.s^n);

γ is the shear rate (s^{-1});

n is the flow behaviour index of the fluid (dimensionless).

Formulation and experimental design

The proportions of the mixtures using pineapple and mango pulps and orange juice were defined by response surface methodology (RSM) using a simplex-centroid design augmented with ten treatments in order to obtain the formulations. The experimental design and the mean values of the rheological parameters of flow behaviour index (n), consistency coefficient (K), and yield stress (τ_o) at the temperatures of 20 and 60°C are given in Tables 1 and 2.

Table 1. Simplex-centroid design augmented with ten treatments for the mixtures of pineapple and mango pulps and orange juice at 20° C.

Mixtures	Original components (coded)			Responses			
	X'1	X'2	X'3	τ_0	K	n	R^2
1	1	0	0	0.50	0.01	0.97	0.99
2	0	1	0	7.98	0.77	0.53	0.99
3	0	0	1	17.81	1.27	0.54	0.99
4	½	1/2	0	1.10	0.01	0.97	0.99
5	½	0	1/2	2.10	0.19	0.64	0.99
6	0	1/2	1/2	15.56	0.53	0.65	0.99
7	1/3	1/3	1/3	3.26	0.23	0.65	0.99
8	2/3	1/6	1/6	1.36	0.01	0.91	0.97
9	1/6	2/3	1/6	6.09	0.18	0.68	0.99
10	1/6	1/6	2/3	6.96	0.78	0.54	0.99

X'1 – orange juice. X'2 - pineapple pulp. X'3 – mango pulp. τ_0 (yield stress - Pa), K (consistency coefficient – Pa.s^n), n (flow behaviour index – dimensionless) and R^2 (Coefficient of determination). Rheological data were obtained by the fit to the Herschel-Bulkley model. All the measurements were carried out at 20°C.

Table 2. Simplex-centroid design augmented with ten treatments for the mixtures of pineapple and mango pulps and orange juice at 60° C.

Mixtures	Original components (coded)			Responses			
	X'1	X'2	X'3	τ_0	K	n	R^2
1	1	0	0	0.47	0.001	1.24	0.99
2	0	1	0	5.09	0.39	0.62	0.98
3	0	0	1	16.85	0.21	0.77	0.99
4	½	1/2	0	0.59	0.091	0.62	0.95
5	½	0	1/2	3.03	0.015	0.98	0.99
6	0	1/2	1/2	10.97	0.044	0.95	0.99
7	1/3	1/3	1/3	3.05	0.050	0.82	0.99
8	2/3	1/6	1/6	0.75	0.026	0.72	0.94
9	1/6	2/3	1/6	5.93	0.046	0.85	0.98
10	1/6	1/6	2/3	9.76	0.057	0.91	0.99

X'1 – orange juice. X'2 - pineapple pulp. X'3 – mango pulp. τ_0 (yield stress - Pa), K (consistency coefficient – Pa.s^n), n (flow behaviour index – dimensionless) and R^2 (Coefficient of determination). Rheological data were obtained by the fit to the Herschel-Bulkley model. All the measurements were carried out at 60°C.

Statistical analysis was carried out using the value of each replicate. This methodology allows modelling of the results using a second-order equation. Multiple regression models (quadratic and special cubic) were applied to the three rheological parameters studied and are represented by the following equations, respectively.

$$Y = \beta'_1 X'_1 + \beta'_2 X'_2 + \beta'_3 X'_3 + \beta'_1 \beta'_2 X'_1 X'_2 + \beta'_1 \beta'_3 X'_1 X'_3 + \beta'_2 \beta'_3 X'_2 X'_3 \tag{2}$$

$$Y = \beta'_1 X'_1 + \beta'_2 X'_2 + \beta'_3 X'_3 + \beta'_1 \beta'_2 X'_1 X'_2 + \beta'_1 \beta'_3 X'_1 X'_3 + \beta'_2 \beta'_3 X'_2 X'_3 + \beta'_1 \beta'_2 \beta'_3 X'_1 X'_2 X'_3 \tag{3}$$

where:

Y is the rheological variable;

β is the coefficient generated by multiple regression;

X is the proportion of the fruits.

According to Vaikousi and Biliaderis (2005), an analysis of variance is produced for each of the response variables, testing the value of the applied model and determining if a more complex model could have a better fit.

Statistical analysis

The flow curves data were fitted to the Herschel-Bulkley model using Origin 7.0 (OriginLab Corporation, MA, USA) software, generating values of the rheological parameters (τ_0, K and n) and a statistical parameter (R^2). The value of R^2 was used to evaluate the goodness of fit to the experimental results in the Herschel-Bulkley model. Finally, the statistical analysis of the rheological responses was carried out using STATISTICA 7.1 (StatSoft, Tulsa, OK, USA) software. Error terms and model significance were used to judge the adequacy of model fitness. After obtaining the multifactor analysis of variance and the second-order model prediction, contour plots of the responses were generated.

Results and discussion

The pineapple pulp, mango pulp and orange juice proximate compositions are shown in Table 3. The values of the physico-chemical data are consistent with several studies published in the literature (VIDAL et al., 2006).

Table 3. Physico-chemical composition of the fruits.

Parameters	Mango pulp	Pineapple pulp	Orange juice
Soluble Solids (°Brix)	12.50	8.20	11.00
pH	4.40	4.17	3.71
Titratable Acidity (g 100 mL^{-1}*)	0.62	0.93	2.60
Moisture content (%)	82.86	85.02	83.86

*Expressed as citric acid.

The flow curves of the ten ternary mixtures at 20 and 60°C are plotted in Figures 1A and B, respectively. Marked points represent the average values of the rheogram experimental data and continuous lines are the fit results calculated using the Herschel-Bulkley model. According to the values of the flow behaviour index (Tables 2 and 3), different mixtures presented different flow behaviours. At both temperatures studied, the majority of the formulations presented shear-thinning characteristics. The thixotropic effect was not observed in the ternary mixtures.

These results were dependent on the sample composition and interactions between the fruits. Observing the data in Tables 2 and 3, the influence of orange juice on the Newtonian behaviour of these mixtures is clear. On the other hand, mango pulp remarkably influences the pseudoplasticity of these mixtures. Temperature had a great effect on all the parameters studied.

All mixtures presented higher n values at 60°C when compared to the values obtained at 20°C. The flow behaviour index (n) is only slightly affected by temperature (FARAHNAKY et al., 2010; HAMINIUK et al., 2006b). As expected, the majority of the consistency coefficient and the yield stress data decreased with an increase in temperature.

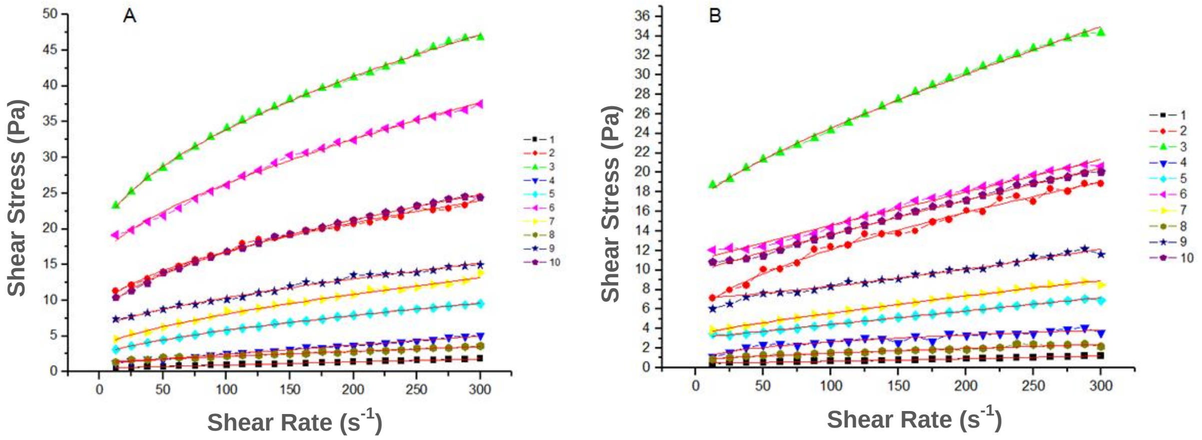

Figure 1. Flow curves of the ternary mixtures of orange juice, pineapple and mango pulps fitted by the Herschel-Bulkley model (A) at 20°C and (B) 60°C. Numbers 1-10 represent the formulation (see Tables 2 and 3).

These results are in agreement with Branco and Gaspareto (2005) who studied the rheological behaviour of ternary mixtures of mango pulp, carrot and orange juices, where the ternary mixtures presented non-Newtonian fluid behaviour. When the rheograms were fitted to the Herschel-Bulkley model, high determination coefficient values were achieved ($0.973 < R^2 < 0.999$ at a temperature of 20°C and ($0.945 < R^2 < 0.993$ at a temperature of 60°C).

The contour plots of τ_o, K, and n are given in Figure 2. According to Figure 2a and b, the yield stress and consistency coefficient of the ternary mixtures were highly influenced by the mango fractions, which was confirmed by the higher values of the linear coefficient shown in equations 4 and 5 (Table 4). Nevertheless, the tendency of turning the ternary mixture into a Newtonian fluid (Figure 2c) was influenced by the orange juice fraction (equation 6). Pineapple and mango pulps had the same effect on the flow behaviour index, presenting almost the same values of linear coefficients. Fitted equations were obtained for the rheological parameters τ_o, K, and n at the temperatures studied and are shown in Table 4. All fitted equations showed high values for the determination coefficients and low values of standard error.

At 60°C, the mango pulp continued to play an important role in yield stress parameter (Figure 3a) when compared with the other fractions, as can be seen in Table 4 (equation 7). On the other hand, the behaviour of the consistency coefficient at 60°C (Figure 3b) changed completely when compared with that at 20°C. This can be confirmed by checking the linear coefficients of equation 8. In this case, the pineapple fraction contributed to higher values of K at this temperature. Finally, the n value was not affected by temperature (Figure 3c). However, at 20°C, the orange juice fraction had higher values of the linear coefficients, indicating the shear-thinning characteristic of this fruit. Haminiuk et al. (2007) found similar results when studying the rheological behaviour of ternary mixtures of blackberry, raspberry, and strawberry pulps.

Tables 5-6 show the analysis of variance of the rheological parameters τ_o, K, and n at 20 and 60°C, fitted according to the quadratic or cubic models. Analysis of variance (P-test) showed that the second-order (quadratic and cubic) models fitted well to the experimental data and the only exception was the flow behaviour index at 60°C where the p value was not significant at 5% of probability.

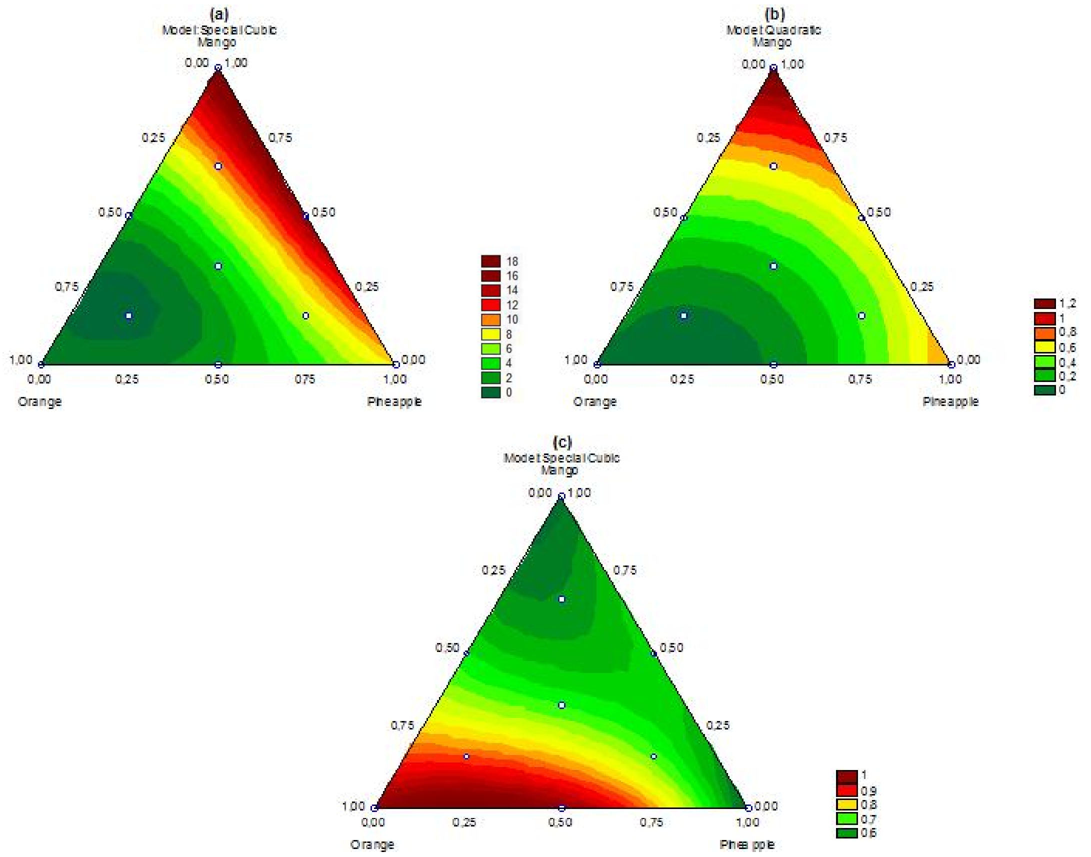

Figure 2. Contour plots for τ_o (a), K (b), and n (c) from ternary mixtures of pineapple and mango pulps and orange juice at 20°C.

Table 4. Regression equations of rheological parameters τ_0, *K,* and n.

Temperatures (°C)	Equations	Number of the equations	Models
20	$\tau_o = 1.28X'1+7.99X'2^{\star}+ 17.08X'3^{\star}-11.27X'1X'2-28.44X'1X'3+9.18X'2X'3-64.07X'1X'2'X3$	4	ECM
	$K = 0.0004X'1+0.71X'2^{\star}+ 1.32X'3^{\star}-1.35X'1X'2-1.45X'1X'3-1.74X'2X'3^{\star}$	5	QM
	$n = 0.99X'1^{\star}+0.53X'2^{\star}+ 0.54X'3^{\star}+0.92X'1X'2^{\star}-0.46X'1X'3+0.42X'2X'3-3.05X'1X'2'X3$	6	ECM
60	$\tau_o = 0.46X'1+5.35X'2^{\star}+ 16.86X'3^{\star}-8.42X'1X'2-22.66X'1X'3^{\star}+0.35X'2X'3$	7	QM
	$K = 0.009X'1^{\star}+0.37X'2^{\star}+ 0.22X'3^{\star}-0.39X'1X'2-0.28X'1X'3-1.02X'2X'3^{\star}$	8	QM
	$n = 1.19X'1^{\star}+0.66X'2^{\star}+ 0.79X'3^{\star}-1.30X'1X'2-0.24X'1X'3+1.06X'2X'3^{\star}$	9	QM

$^{\star}p \leq 0.05$ – Special Cubic Model (ECM); Quadratic model (QM). X'1 – orange juice; X'2 – pineapple pulp; X'3 – mango pulp.

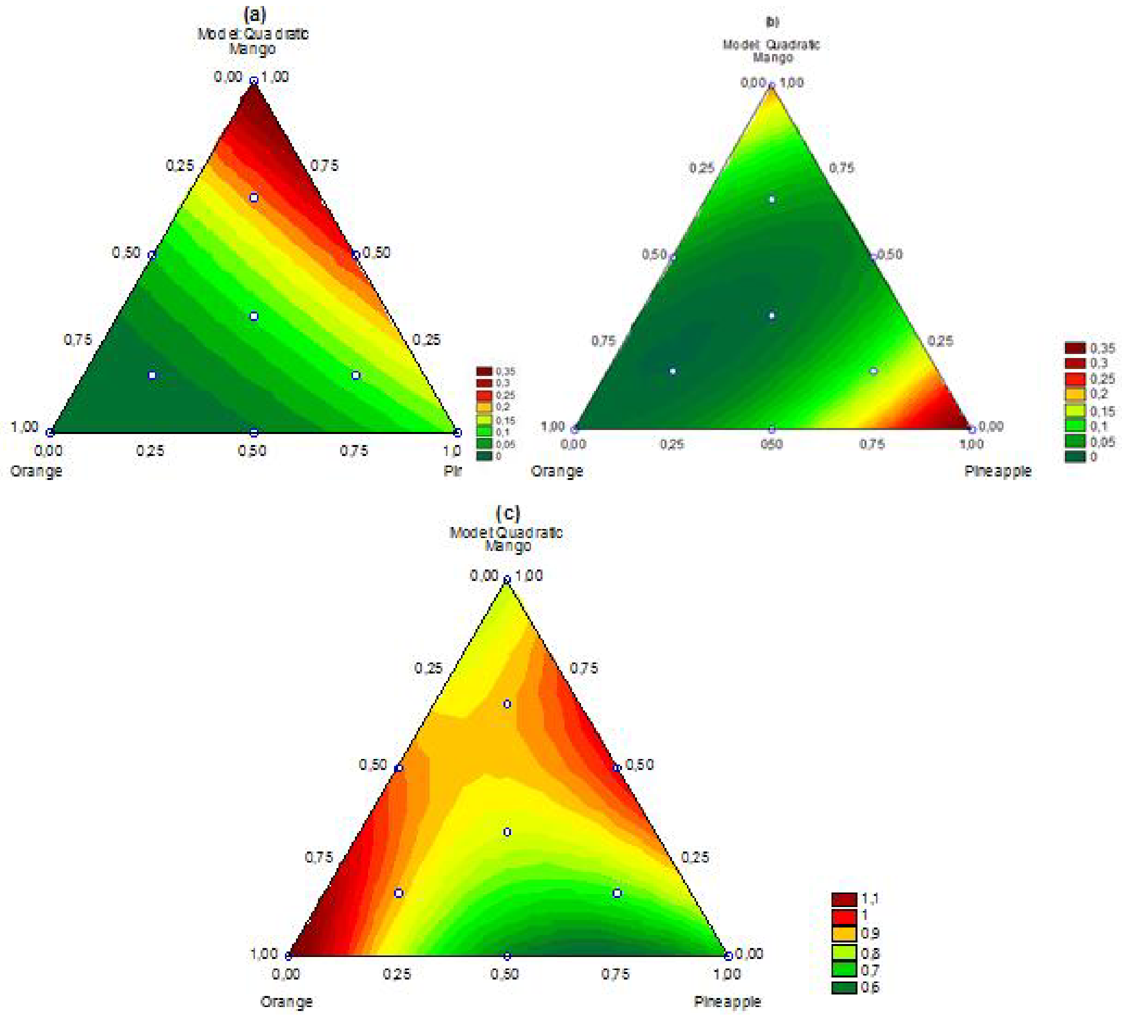

Figure 3. Contour plots for τ_o (a), K (b), and n (c) from ternary mixtures of pineapple and mango pulps and orange juice at 60°C.

Table 5. Analysis of variance of the responses in yield stress (τ_0), the consistency coefficient (*K*), and the flow behaviour index (n).

Parameters	τ_0 $^{\psi}$ (Yield stress)			
Source	Square sum	Degree of freedom	Mean square	P
Model	323.02	6	53.83	0.023★
Total error	10.43	3	3.47	
Total	333.45	9	37.05	
	K $^{\psi}$ (Consistency coefficient)			
Source	Square sum	Degree of freedom	Mean square	P
Model	1.58	5	0.31	0.007★
Total error	0.07	4	0.018	
Total	1.65	9	0.18	
	n $^{\#}$ (Flow behaviour index)			
Source	Square sum	Degree of freedom	Mean square	P
Model	0.27	6	0.04	0.014★
Total error	0.006	3	0.002	
Total	0.27	9	0.03	

$^{\star}p \leq 0.05$ - $^{\#}$ Fitted by the quadratic model - $^{\psi}$Fitted by the special cubic model. All the measurements were carried out at 20°C.

Table 6. Analysis of variance of the responses in yield stress (τ_0), the consistency coefficient (K), and the flow behaviour index (n).

Parameters	τ_0 $^{\#}$ (Yield stress)			
Source	Square sum	Degree of freedom	Mean square	P
Model	257.63	5	51.52	0.0002*
Total error	1.90	4	0.47	
Total	259.52	9	28.83	
	K $^{\#}$ (Consistency coefficient)			
Source	Square sum	Degree of freedom	Mean square	P
Model	0.12	5	0.024	0.02*
Total error	0.009	4	0.002	
Total	0.13	9	0.014	
	n $^{\#}$ (Flow behaviour index)			
Source	Square sum	Degree of freedom	Mean square	P
Model	0.26	5	0.051	0.10
Total error	0.05	4	0.01	
Total	0.39	9	0.03	

*$p \leq 0.05$ - $^{\#}$Fitted by the quadratic model - All the measurements were carried out at 60°C.

Conclusion

All ternary mixtures studied in this work presented a change in rheological behaviour with an increase in temperature, and the majority of the formulations were shear-thinning fluids. The rheological parameters were well-represented by the Herschel-Bulkley model. With an increase in temperature, a decrease in τ_o and K and an increase in n were observed. Good fit models were developed for yield stress, the consistency coefficient, and the flow behaviour index.

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