RHEOLOGICAL BEHAVIOR OF MANGO JELLY WITH INCORPORATION OF ITS BY-PRODUCT

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ABSTRACT – Industrialization of mango, including the peel, can be an alternative to reduce losses of non-standard fruits fresh of market and to lessen the generation of solid organic waste. Rheological behavior of mango jelly prepared with pulp, sugar and different concentrations of mango peel powder was investigated in this work. Steady state tests were run at 25, 40 and 60 °C and dynamic state tests were run at 25 °C. At 25 °C, all steady rheological data were well fitted to Herschel-Bulkey model. However, at 40 and 60 °C, the samples with higher peel powder content were not fitted to any classical model. It was proposed an equation that relates the effect of concentration and temperature on apparent viscosity of the samples. Temperature dependence on the apparent viscosity followed Arrhenius relationship and the mango peel powder concentration followed an exponential model. Moreover, based on the results, all formulations were classified as weak gels.

1. INTRODUCTION

Mango (Mangifera indica L.) is a native fruit from South Asia that belongs to Anacardiaceae family and is among the tropical fruits of great worldwide demand. As most tropical fruits, mango is produced in large amounts over a short period of time and it deteriorates quickly due to its high perishability. Even with the employment of new technologies, one of the greatest problem the fruit industry must face refers to the significant amount of organic waste that is generated. Mango peel is a major by-product of mango processing industry and it constitutes about 15–20% of total weight of mango fruit. It is estimated that in mango processing for obtaining juices and pulps, 40% of agro industrial waste (peel and seed) are generated. Peel has been found to be a good source of polyphenols, carotenoids, dietary fiber, vitamin E and vitamin C, exhibiting antioxidant properties (Ajila et al., 2007a; Ajila et al., 2007b; Ajila and Rao, 2013) and peptides endowed with biological activities (Fasoli and Righetti, 2013).

The mango can be used to prepare slices and pieces in syrup, nectar, juices, candied sweets, cereals, wine, vinegar and even lesser-known products, such as "amchur" or "amchoor" and "chutney" (Manica et al., 2001). However, most of the production of mango derivatives corresponds to jams and jellies.
The content and type of the ingredients used in the preparation of jellies usually lead to a gel structure changes that are often measured by rheology. Rheological behavior of jam and jelly have been widely studied (Álvarez et al., 2006; Basu and Shivhare, 2010; Basu et al., 2013; Basu et al., 2011; Carbonell et al., 1991a, b). The authors have established that the rheological properties of food systems as jellies and jams are mainly affected by the amount and type of sugar added, proportion and kind of gelling agent, fruit pulp content, and temperature during the process. Further, to the best of our knowledge, no scientific information is available in the literature concerning the variation of rheological properties of mango jelly with peel powder in its composition. So, the aims of this work are: i) to produce jellies with different contents of mango peel powder; ii) to verify the influence of the powder on the flow and viscoelastic properties of the jellies; iii) to evaluate the effect of the temperature on the flow properties of the jellies, and iv) to determine the energy of activation of the samples.

2. MATERIAL AND METHODS

2.1 Obtaining the Mango Peel Powder

Mangoes (Keitt cultivate) were purchased at a local market (Porto Alegre, RS, Brazil). Mangoes were chosen at harvest maturity and the fruits that were green, spoiled, and rotten or attacked by insects and larvae were excluded. After, the selected fruits were sanitized in bath (10 ppm sodium hypochlorite water for 20 min). The fruits are, then, peeled and the pulp was removed using a sharp knife. The raw material was divided into two distinct parts: pulp and peel. The pulp was ground in a domestic blender and stored in polyethylene bags under freezing. The peel was dried at 50 °C for 72 h with circulating air (Solab, SL 102/110, Brazil). Next, the peels were crushed in an industrial blender and sieved (Mesh Tyler 100).

2.2 Preparation of Mango Jellies

The jellies were prepared according to the following steps: 200 g of pulp, with or without mango peel powder, and 100 g of commercial sucrose were transferred to a beaker of 1 L. The mango peel flour was added to jellies in different concentrations (0%, 3%, 5%, and 10 % relative to the initial amount of pulp, w/w). The mix was heated on a hot plate at 100 °C under magnetic stirring. The remaining sugar (100 g) was added when the mixture started boiling. Heating was stopped when the total soluble solids content of the jellies reached 65–66%Brix (measure using a refractometer - Carl Zeiss, 32-Gmodel, Vienna, Austria); at this stage, the pH of the jelly was adjusted using a pHmeter (Tecnal, TEC-3MP model, Piracicaba, Brazil) at 3.4 by adding commercial citric acid monohydrate (Baker et al., 2005). After, 50 g of the mixture was poured into sterilized glass containers and allowed to cool under ambient condition. During the cooking process, which was approximately 1 h and 15 min long, the jelly has reached an average temperature of 90 °C. At the end, the products were stocked at 7±1°C for 24 h prior to the analysis.
In the analysis of the results, the samples will be named in accordance with the percentage of the mango peel powder as J (0 %), J3 (3 %), J5 (5 %) and J10 (10%).

2.2 Rheological Measurements

Rheological measurements (steady and dynamic tests) were carried out in a rotational rheometer (Ares, TA Instruments, New Castle, USA), using plate-plate geometry (50 mm of diameter) with gap of 1.5 mm.

Steady state measurements: flow curves were obtained plotting the shear stress values against the shear rate values, which were increased from 0.5 to 200 s\(^{-1}\). Data from the curve were fitted to the Herschel-Bulkley model:

\[
\tau = \tau_0 + K\dot{\gamma}^n
\]  

(1)

where \(\tau\) is the shear stress, \(\tau_0\) is the initial shear stress, \(K\) is the consistence index, \(n\) is the flow index and \(\eta_T\) is the apparent viscosity measured at different shear rate values.

Determination of the activation energy \((E_a)\): the steady tests were run at 25, 40 and 60°C, and the activation energy \((E_a)\) was calculated in accordance with the equation 2:

\[
\ln \eta_T = \ln \eta_c + \frac{E_a}{RT}
\]  

(2)

where, \(\eta_T\) is the apparent viscosity at 12.5 s\(^{-1}\), 50 s\(^{-1}\) and 125 s\(^{-1}\), \(T\) is the temperature (K), R is universal gas constant (1.987 cal mol\(^{-1}\) K\(^{-1}\)) and \(\eta_T\) is an empirical constant. The chosen shear rate values are based on the industrial process such as agitation, pumping and mixture. The apparent viscosity was correlated to the peel concentration as follows:

\[
\ln \eta_T = \ln \eta_c + b_1C
\]  

(3)

where, \(\eta_T\) is the apparent viscosity at 12.5 s\(^{-1}\), 50 s\(^{-1}\) and 125 s\(^{-1}\); \(C\) is the peel concentration and \(\eta_c\) and \(b_1\) are empirical constants. The combined effect of the temperature and concentration can be described by Equation 4 (IBARZ et al., 1992a; IBARZ et al., 1992b):

\[
\ln \eta_T = \ln a + \frac{E_a}{RT} + b_2C
\]  

(4)

Dynamic state measurements: all dynamic measurements were run at 25 °C and performed in the linear viscoelastic region (LVR), which was determined for each sample by performing strain sweep tests at 1 rad\(\cdot s^{-1}\). Frequency sweeps were performed over the range of 0.1 – 400 rad\(\cdot s^{-1}\).
2.3 Statistical Analysis

Parameter estimation for the proposed models was accomplished by the least-square method, using the software Statistica 10.0 (Statsoft Inc., Tulsa, OK, USA).

3. RESULTS AND DISCUSSION

Table 1 presents the results of the fitting of the experimental data to Herschel-Bulkley model (Equation 1), the activation energy (\(E_a\)) values and also the frequency range where \(G'/G''\) is higher than 3.

Table 1- Effect of mango peel powder on rheological parameters of mango jellies.

| Sample | Rheological parameters | Frequency range (rads \(^{-1}\)) \(G'/G'' > 3\) |
|--------|------------------------|-----------------------------------------------|
|        | \(\tau_0\)  | \(K\)  | \(n\)  | \(R^2\) | \(E_a\) (Kcal/mol) | \(E_a(50)\) | \(E_a(75)\) | \(E_a(99)\) |
|        | 25 °C    |          |        |        |                  |          |          |             |
| J      | 43.85 ± 1.24 | 7.02 ± 0.55 | 0.626 ± 0.014 | 0.999 | 3.66 | 4.36 | 4.46 | 0.1-2.0 |
| J3     | 67.98 ± 2.05 | 10.98 ± 0.94 | 0.618 ± 0.016 | 0.998 | 4.84 | 5.34 | 5.39 | 0.1-1.58 |
| J5     | 70.54 ± 2.11 | 10.15 ± 0.90 | 0.641 ± 0.016 | 0.998 | 4.47 | 5.68 | 6.23 | 0.1-1.58 |
| J10    | 99.03 ± 2.74 | 12.35 ± 1.12 | 0.656 ± 0.017 | 0.998 | 6.05 | 7.07 | 7.39 | 0.1-0.30 |
|        | 40 °C    |          |        |        |                  |          |          |             |
| J      | 52.25 ± 1.18 | 3.05 ± 0.43 | 0.696 ± 0.026 | 0.997 |        |          |          |             |
| J3     | 69.61 ± 1.97 | 3.92 ± 0.69 | 0.706 ± 0.033 | 0.996 |        |          |          |             |
| J5     | 58.52 ± 7.93 | 11.32 ± 4.67 | 0.512 ± 0.075 | 0.973 |        |          |          |             |
| J10    | 75.57 ± 8.16 | 12.82 ± 4.67 | 0.529 ± 0.065 | 0.977 |        |          |          |             |
|        | 60 °C    |          |        |        |                  |          |          |             |
| J      | 35.40 ± 2.19 | 2.97 ± 1.05 | 0.599 ± 0.065 | 0.982 |        |          |          |             |
| J3     | 48.96 ± 3.42 | 2.39 ± 1.32 | 0.678 ± 0.103 | 0.962 |        |          |          |             |
| J5     | 42.48 ± 14.41 | 12.05 ± 10.95 | 0.384 ± 0.153 | 0.881 |        |          |          |             |
| J10    | 27.76 ± 41.34 | 31.27 ± 38.36 | 0.218 ± 0.163 | 0.846 |        |          |          |             |

*Codes: J: mango jellies without peel powder; J3: mango jellies with 3% (w/w) of peel powder; J5: mango jellies with 5% (w/w) of peel powder; J10: mango jellies with 10% (w/w) of peel powder.

As can be observed by the value of the coefficient of determination \(R^2\), at 25 °C, all data were well fitted to Herschel-Bulkley model, as well as the samples measured at 40 °C without and with 3% (w/w) of peel powder; at 60 °C only the samples without peel powder were well fitted to the model. The apparent viscosity showed shear-thinning behavior and decreased with increasing temperature. Maceiras et al. (2007) also reported similar pseudoplastic behavior for peach, plum, strawberry and raspberry purees. The jellies with 5 and 10% (w/w) of peel powder analyzed at 40 and 60 °C were not fitted to any rheological model and this fact will be discussed after.
At 25 °C, a significant increase (p < 0.05) of the \( \tau_0 \) parameter (from 43.85 to 99.03 Pa) with the increase of the peel content was observed. Additionally, the consistency index \( (n) \) and the flow behavior index \( (K) \) also increased from 7.02 to 12.35 Pa.s and from 0.626 to 0.656, respectively.

The data were well fitted to Equation 4 that shows the combined effect of the temperature and the peel powder concentration on apparent viscosity at 12.5 s\(^{-1}\) (Equation 5), 50 s\(^{-1}\) (Equation 6) and 125 s\(^{-1}\) (Equation 7). The model could explain 95.8 %, 96.1 % and 94.9 % of all variance in data, respectively.

\[
\ln \eta_{12.5} = -3.08 \pm 0.49 + \left(1496.91 \pm 152.29\right) \frac{1}{T} + (0.06 \pm 0.01)C \tag{5}
\]

\[
\ln \eta_{50} = -6.96 \pm 0.58 + \left(2403.42 \pm 183.99\right) \frac{1}{T} + (0.05 \pm 0.01)C \tag{6}
\]

\[
\ln \eta_{125} = -8.87 \pm 0.75 + \left(2826.22 \pm 236.60\right) \frac{1}{T} + (0.05 \pm 0.01)C \tag{7}
\]

It was verified that the apparent viscosity increased as increased the peel powder content and reduced as increased the temperature. It can be also observed from Table 1 that the greater shear rate and concentration of peel, the greater the energy of activation, indicating that apparent viscosity is more dependent on temperature in these samples (Steffe, 1996).

The results for energy of activation \( (E_a) \) were between 3.66 kcal.mol\(^{-1}\) and 7.39 kcal.mol\(^{-1}\); these values are similar to those reported for mango jam and other types of fruits jams: Basu and Shivhare (2010) found energy of activation between 2.76–10.48, kcal.mol\(^{-1}\) for mango jams with different amounts of sugar, pectin and pH values. Miguel et al. (2009) found energy of activation of 5.66 kcal.mol\(^{-1}\) for strawberry jam and Moura et al.(2011) obtained values that ranged from 13 to 15 kcal.mol\(^{-1}\) for strawberry and light guava jellies.

As mentioned before, the jellies analyzed at 40 and 60 °C with 5 and 10 % (w/w) of peel powder were not fitted to any rheological model. Moreover, these samples presented loops of shear stress (Figure 1b) that can be related to structural changes promoted by peel powder addiction. Unexpectedly, the presence of the peel powder can lead to weaker pectin network formation, increasing the instability of the food system and, consequently, influencing the rheological behavior of the samples. However, to better understanding these results, further studies are indicated which includes analysis of microscopy and physicochemical characterization of the peel powder.
Figure 1 - Steady-state rheogram of mango jellies with different amount of peel powder at 25 °C (a) and 60 °C (b).

Typical curves of storage ($G'$) and loss ($G''$) modulus of the mango sweet as a function of frequency are shown in Figure 2. Storage modulus values were higher than loss modulus values over the entire frequency range, indicating a typical gel-like system (Brummer, 2006). According to Lapasin et al. (1995), gels can be classified either as strong or weak on the basis of their $G'/G''$ ratio. The $G'/G''$ ratio of a true or strong gel, whose intermolecular junctions have a high binding energy, is higher than 3. In the case of the samples, this condition is achieved for jellies only at low frequency values (Table 1). Therefore, all samples were characterized as weak gels and were not differentiate as the viscoelastic parameters.

Figure 2 - Frequency sweeps of mango jellies with different amount of peel powder. (a) Storage ($G'$) and (b) loss moduli ($G''$).
4. CONCLUSION

The present work shows the rheological behavior of the jellies prepared with different contents of mango peel powder. The results show that the samples behaved as pseudoplastic fluids exhibiting yield stress. At 25 °C, the Herschel–Bulkley model described adequately the steady-state rheological behavior of jellies. The increase of mango peel content associated with the increase of temperature lead to a deviation of the expected flow behavior of the jellies that could not be fitted to any flow rheological model. Moreover, the apparent viscosity increased as increased the peel content and reduced as increased the temperature. Concerning the energy of activation ($E_a$), it was observed that it increases as the peel content increases. Additionally, it was found that the behavior of mango jellies at 25°C is typical of a weak gel-like structure.

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