Effect of high pressure homogenization (HPH) on the rheological properties of tomato juice: Viscoelastic properties and the Cox–Merz rule

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Article info
Article history:
Received 5 October 2011
Received in revised form 19 June 2012
Accepted 21 July 2012
Available online 3 August 2012

Keywords:
Food properties
High pressure homogenization
Rheology
Viscoelasticity
Viscosity

Abstract

High pressure homogenization (HPH) is a non-thermal technology which has been widely studied as a partial or total substitute for the thermal processing of food. Although microbial inactivation has been widely studied, there are only a few papers in the literature reporting on physicochemical changes in fruit products due to HPH, especially regarding their rheological properties. The present work evaluated the effect of HPH (up to 150 MPa) on the viscoelastic properties of tomato juice. HPH increased the tomato juice storage ($G'\text{)}$ and loss ($G''\text{)}$) moduli. The parameters $G'$ and $G''$ were modelled as a power function of the oscillatory frequency ($\omega$), and then evaluated as a function of homogenization pressure. It was observed that HPH processing improved tomato juice consistency more than it modified its nature/behaviour. The changes observed in the viscoelastic properties were attributed to disruption of the suspended particles during processing. Moreover, two modified Cox–Merz rules were used to correlate the products steady-state shear properties with viscoelasticity. The results obtained indicated that this process could be used to improve both product elastic and viscous behaviour, highlighting possible applications of the HPH process as a valuable tool to promote physical property changes in food products.

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1. Introduction

The rheological characterization of food is important for the design of unit operations, process optimization and high quality product assurance (Ibarz and Barbosa-Cánovas, 2003; Rao, 1999). From an engineering standpoint, the steady flow curve is the most valuable way to characterize the rheological behaviour of fluids (Steffe, 1996). However many phenomena cannot be described by the viscosity function alone and thus elastic behaviour must also be taken into consideration (Steffe, 1996). The viscoelastic properties are very useful in the design and prediction of product stability (Ibarz and Barbosa-Cánovas, 2003). Moreover, viscoelastic products may exhibit interesting behaviour such as the Weissenberg and Barus effects (Ibarz and Barbosa-Cánovas, 2003; Steffe, 1996). Thus the study and description of the viscoelastic properties of liquid foods is important for a better understand of their behaviour during processing, storage and consumption.

Tomato is one of the most popular and widely grown vegetables in the world. It is also one of the most important vegetables in the food industry, and widely included in the human diet. However, there are few reports on the viscoelastic characterization of tomato products, this being particularly true for the evaluation of the effect of each unit operation on the viscoelastic properties of tomato products. Although homogenization is a unit operation widely used in tomato processing, there are only a few papers related to the effect of high pressure homogenization (HPH) on tomato product rheology, especially on the viscoelastic properties.

High pressure homogenization (HPH) technology consists of pressurizing a fluid such that it flows quickly through a narrow gap valve, which further increases its velocity to a great extent, resulting in depressurization with consequent cavitation and high shear stress. Thus the particles, cells and macromolecules suspended in the fluid are subjected to high mechanical stress, becoming twisted and deformed. This technology has been studied by many authors as a non-thermal food preservation technique, especially for fruit products. The present work evaluated the effect of high pressure homogenization (HPH) on the viscoelastic properties of tomato juice.

2. Materials and methods

As described by Augusto et al. (2012b), a 4.5–6 Brix tomato juice was obtained by diluting a commercial 30–45 Brix pulp in distilled water. A commercial pulp was used for guarantee of standardiza-
The oscillatory frequency (Rao, 1999) and complex viscosity (Rao, 1999) are commonly used to describe the viscoelastic behaviour of food and dispersions. The shear stress value within the linear viscoelastic range of 0.01–100 Hz was used. The storage modulus (G') and loss modulus (G'\text{''}) were modelled as a power function of the oscillatory frequency (\(\gamma\)) (Eqs. (1) and (2)), as commonly used to describe the viscoelastic behaviour of food and dispersions (Rao, 1999).

\[ G' = k' \cdot \gamma^n \]  

(1)

\[ G'' = k'' \cdot \gamma^n \]  

(2)

Due to the non-destructive nature of small amplitude oscillatory measurements, it is possible to carry out multiple tests on the same sample under different test conditions (Dogan and Koki, 2007). Thus, after the frequency sweep period, a steady-state shear protocol was applied in order to evaluate the Cox–Merz rule. The Cox–Merz rule states that the apparent viscosity (\(\eta_a = \sigma/\gamma\)) at a specific shear rate (\(\dot{\gamma}\)) is equal to the complex viscosity (\(\eta''\)) at a specific oscillatory frequency (\(\omega\)), when \(\dot{\gamma} = \omega\) (Eq. (3); Rao, 1999). When this rule is valid, the rheological food properties can be obtained by either oscillatory or steady-state shear experiments (Gunasekaran and Ak, 2000). This is particularly useful due to the characteristics and limitations of each kind of experiment.

\[ \eta''(\omega) = \eta_a(\dot{\gamma})|_{\dot{\gamma}=\omega} \]  

(3)

The apparent viscosity of the product was evaluated using the steady-state shear protocol. Samples were sheared at a constant shear rate (300 s\(^{-1}\)) for 10 min in order to eliminate product thixotropy (Augusto et al., 2012b; Augusto et al., 2012c). Thus, a linear decreasing stepwise protocol (100 to 0.01 s\(^{-1}\)) was used in order to guarantee the steady-state shear condition (~5 min).

The parameters of each model were obtained by linear or non-linear regression using the software CurveExpert Professional (v.1.2.0, http://www.curveexpert.net, USA) with a significant probability level of 95%.

Moreover, the effect of homogenization pressure (\(P_h\)) on the parameters of Eqs. (1) and (2) was evaluated using the analysis of variance (ANOVA) and Tukey test at a 95% confidence level. The software STATISTICA 5.5 (StatSoft, Inc., USA) was used for this purpose.

3. Results and discussion

3.1. Viscoelastic properties

The native tomato juice linear viscoelastic region limit was set at 0.1 Pa, in accordance with the results of Augusto et al. (2011b). The limits of the other sample were close to 1.0 Pa. Thus a shear stress of 0.1 Pa was selected for the oscillatory frequency sweeps, since it could be used for all the samples.

Fig. 1 shows the effect of high pressure homogenization (0–150 MPa) on the tomato juice mechanical spectra. Although the oscillatory frequency sweeps were carried out in the range from 0.01 to 100 Hz, the linear viscoelastic region was limited by the frequency of ~25 Hz for all the samples. Thus Fig. 1 only shows the results obtained in the linear range, in accordance with that reported for tomato juice (Augusto et al., 2011b), tomato

### Nomenclature

- \(x\): magnitude index in power modified Cox–Merz rule (Eq. (5))
- \(\beta\): behaviour index in power modified Cox–Merz rule (Eq. (5))
- \(n\): magnitude index in linear modified Cox–Merz rule (Eq. (4))
- \(\dot{\gamma}\): shear rate (s\(^{-1}\))
- \(\eta_a\): apparent viscosity (= \(\sigma/\dot{\gamma}\)) (Pa s)
- \(\eta''\): complex viscosity (Pa s)
- \(\sigma\): shear stress (Pa)
- \(\sigma_0\): yield stress, Herschel–Bulkley model (Pa)
- \(\omega\): oscillatory frequency (Hz)
- \(A\): slope index in the linear model for evaluation of experimental values versus those obtained by models (Eq. (6))
- \(B\): intercept index in the linear model for evaluation of experimental values versus those obtained by models (Eq. (6))
- \(G'\): storage modulus (Pa)
- \(G''\): loss modulus (Pa)
- \(k'\) and \(k''\): consistency coefficients in the power law model of the viscoelastic properties (Eqs. (1) and (2))
- \(n'\) and \(n''\): behaviour index in the power law model of the viscoelastic properties (Eqs. (1) and (2))
- \(P_h\): homogenization pressure (MPa)
concentrates (Den Ouden and Van Vliet, 2002; Yoo and Rao, 1996; Rao and Cooley, 1992), tomato suspensions (Bayod and Tornberg, 2011) and ketchups (Yilmaz et al., 2011; Bayod et al., 2008), and Eqs. (1) and (2) were only evaluated in this frequency range.

The storage modulus ($G'$) was always higher than the loss modulus ($G''$) in the oscillatory frequency ($\omega$) range evaluated, for all the products. This indicates that the elastic properties of tomato juice are dominant, rather than the viscous ones, and that the products can be classified as weak gels (Rao, 1999). This behaviour is typically observed in suspensions with network-like structures, being characteristic of fruit products and similar to that reported for tomato and other vegetable products.

The dependence of $G'$ on the oscillatory frequency was greater than for $G''$, especially at high frequencies. Moreover, in a way similar to the behaviour of tomato concentrate (Bayod et al., 2008), at $\omega < 0.1$ Hz the tomato juice $G'$ was almost independent of the oscillatory frequency. According to Bayod et al. (2008), this is typical of highly structured materials, classifying the products between true gels (characterized by covalent cross-linked materials) and concentrated suspensions (characterized by entanglement networks).

As expected, the values for $G'$ and $G''$ showed a rising tendency with rising oscillatory frequency, the opposite behaviour of the complex viscosity ($\eta^*$). Moreover, as described by Bayod et al. (2008) for tomato concentrates, $G'$ increased slightly with increasing frequencies, whereas $G''$ remained constant at low frequencies and then increased at higher frequencies.

Thus, it was possible to model the storage and loss moduli as a power function of the oscillatory frequency (Eqs. (1) and (2)). The $R^2$ regression values were always higher than 0.95, with the exception of the 0 MPa $G''$ tomato juice behaviour. The loss modulus ($G''$) of the native sample showed low agreement with the power law model, with $R^2$ values close to 0.78. This was expected due to the nature of tomato juice. Fig. 2 shows the effect of high pressure

![Fig. 1. Tomato juice mechanical spectra: effect of HPH (0–150 MPa) on storage modulus ($G'$, $\sigma$), loss modulus ($G''$, $\bullet$) and complex viscosity ($\eta^*$, $\times$). Vertical bars represent the standard deviation for each value. (a) 0 MPa, (b) 25 MPa, (c) 50 MPa, (d) 100 MPa and (e) 150 MPa.](image-url)
homogenization on the parameters of Eqs. (1) and (2). The values obtained were in accordance with those described for other tomato and vegetable products (Table 1).

The values for \(n'\) were always higher than those for \(n''\) (Fig. 2), which demonstrates that the viscous behaviour of the tomato juice became more important at high frequencies. The effect of high pressure homogenization was greater for the magnitudes of \(G'\) and \(G''\) than for their shapes, the homogenization pressure (\(P_H\)) changing the values for \(k'\) and \(k''\) much more than those for \(n'\) and \(n''\). After homogenization, the value for \(n'\) of the tomato juice had increased by 24–53%, and that for \(n''\) by 37–43%, although the values for \(n'\) were always close to 0.1 and those for \(n''\) always between 0.2 and 0.3. After homogenization, the value for \(k'\) was 320% (25 MPa), 260% (50 and 100 MPa) and 196% (150 MPa) higher than in the original juice, and the value for \(k''\) had increased by 419% (25 MPa), 316% (50 MPa), 289% (100 MPa) and 211% (150 MPa).

This suggests that tomato juice behaviour is not greatly affected by the homogenization process (\(n', n''\)), although its consistency is \((k', k'')\), in accordance with the steady-state shear results described by Augusto et al. (2012b).

The parameters \(k', n'\) (Eq. (1)), \(k''\) and \(n''\) (Eq. (2)) first increased, and then decreased, with increasing homogenization pressure (\(P_H\)) (Fig. 2). This indicates that the main changes in tomato juice take place at “lower” \(P_H\) values (25–50 MPa), as observed by Augusto et al. (2012b). Moreover it also indicates that in this “lower” \(P_H\) range (25–50 MPa), the homogenization of tomato juice results in a strong internal structure, which is partially broken at high \(P_H\).

Augusto et al. (2012b) evaluated the suspended particles of tomato juice after high pressure homogenization (HPH). Not only was the mean diameter affected by HPH, but also the particle size distribution (PSD). The control juice (0 MPa) showed a monomodal distribution, with particle diameters ranging between ~100 and 1000 \(\mu\)m. When the juice was processed at 50 MPa, a broader distribution was observed, with particles ranging between ~10 and ~1000 \(\mu\)m. Finally, when the juice processed at 150 MPa was evaluated, a further reduction in the particle diameter and a narrow distribution (~10–300 \(\mu\)m) was observed. Moreover, the changes in particle diameter were less pronounced between 50 and 150 MPa than between 0 and 50 MPa. Therefore the effect of homogenization pressure (\(P_H\)) on the disruption of suspended particles followed an asymptotic behaviour, i.e., increasing \(P_H\) values showed less effect at higher \(P_H\) values. Similar behaviour was observed by Silva et al. (2010) for pineapple pulp homogenized at up to 70 MPa.

Thus, increasing \(P_H\) values result in smaller suspended particles, with greater surface area and consequently increased inter-particle interactions (Augusto et al., 2012b), which explains the higher values for \(G'\) and \(G''\) (\(k'\) and \(k''\)) of the homogenized juices when compared to the control (0 MPa).

Moreover, homogenization in the 25- to 50-MPa range results in a broader PSD (Augusto et al., 2012b) with a greater particle volume fraction (\(\phi\)), since the small particles fill the volume between the larger particles. Thus, greater inter-particle interaction is to be expected, which explains the higher \(k'\) and \(k''\) values observed under these process conditions.

Den Ouden and Van Vliet (2002) studied the effect of homogenization tomato concentrates at 17 MPa on their storage modulus (\(G'\)). After homogenization, the \(G'\) at 1 Hz had changed from ~50 to 80–90 Pa for the 5–Brix product. In the present work, the tomato juice at 1 Hz changed from 191 Pa (0 MPa) to 590 Pa (25 MPa), 415 Pa (50 MPa), 470 Pa (100 MPa) and 360 Pa (150 MPa).

Bengtsson and Tornberg (2011) studied the effect of homogenization at 9 MPa on the rheological properties of apple, tomato, potato and carrot fibre suspensions. The authors observed that with low degrees of homogenization, the \(G'\) increased 2.5 times in tomato, potato and carrot suspensions, when compared to the non-homogenized samples. For apple fibre suspensions, however, the \(G'\) remained constant. Moreover, the authors observed that the increase in \(G'\) due to the homogenization process was not as pronounced as for \(G'\), and that the increase in \(G'\) followed the increase in volume fraction obtained on homogenization. An increase in \(G'\) due to homogenization (up to three passes at 9 MPa) was also observed by Bayod and Tornberg (2011) for tomato suspensions.

<table>
<thead>
<tr>
<th>Product</th>
<th>(n')</th>
<th>(n'')</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tomato juice (HPH 0–150 MPa)</td>
<td>0.08–0.12</td>
<td>0.21–0.30</td>
<td>Present work</td>
</tr>
<tr>
<td>Tomato concentrates (21–34 °Brix)</td>
<td>0.08–0.24</td>
<td>0.11–0.25</td>
<td>Bayod et al. (2008), Yoo and Rao (1996), Rao and Cooley (1992)</td>
</tr>
<tr>
<td>Ketchups</td>
<td>0.10–0.18</td>
<td>0.24–0.42</td>
<td>Yilmaz et al. (2011), Bayod et al. (2008)</td>
</tr>
<tr>
<td>Potato puree</td>
<td>0.06–0.10</td>
<td>0.10–0.19</td>
<td>Alvarez et al. (2004)</td>
</tr>
<tr>
<td>Peach juice with fibres</td>
<td>0.22–0.24</td>
<td>0.33–0.40</td>
<td>Augusto et al. (2011a)</td>
</tr>
<tr>
<td>Vegetable-based baby foods</td>
<td>0.06–0.14</td>
<td>0.16–0.22</td>
<td>Ahmed and Ramaswamy (2006)</td>
</tr>
<tr>
<td>Siriguela pulp</td>
<td>0.14</td>
<td>0.27</td>
<td>Augusto et al. (2012a)</td>
</tr>
</tbody>
</table>
Lopez-Sanchez et al. (2011a) studied the effect of homogenization up to 60 MPa on the rheological properties of tomato, broccoli and carrot suspensions. The results obtained varied according to the product studied, highlighting the need for better understanding of the unit operations in food processing. While homogenization increased the yield stress ($\sigma_0$), apparent viscosity ($\eta_a$), and storage ($G'$) and loss ($G''$) moduli of the tomato suspension, the opposite behaviour was observed for the carrot and broccoli suspensions. The authors described the different tissue compositions and sensitivity to shear, and related the behaviour observed to the changes in product phase volume (which increased in tomato and decreased in carrot and broccoli).

Lopez-Sanchez et al. (2011b) studied the effect of homogenization up to 100 MPa on the rheological properties of tomato and carrot emulsions (emulsions of vegetable, water and olive oil). The carrot emulsion $G'$ values showed a small increase when homogenized at 10 MPa, which decreased when processed at 100 MPa. The product $G'$ was almost stable when homogenized at 10 MPa, but decreased when processed at 100 MPa. The tomato emulsions showed a different behaviour. Both their $G'$ and $G''$ were almost stable when homogenized at 10 MPa, but decreased when processed at 100 MPa. The authors observed that the tomato cell wall disrupted at lower homogenization pressures ($P_H$) when compared to the carrot.

The results obtained described the effect of high pressure homogenization (HPH) on the internal structure of tomato juice. They indicated that the process could be used to improve both the elastic and viscous behaviour of the product. Thus HPH can be used to increase the consistency of tomato juice, improving its sensory acceptance, reducing the need for hydrocolloids and reducing particle sedimentation or serum separation.

3.2. Applicability of the Cox–Merz Rule

As observed in Fig. 1, the Cox–Merz rule could not be used directly (Augusto et al., 2011b). As commonly observed in food products, the complex viscosity ($\eta^*$) magnitudes were always higher than the apparent viscosity ($\eta_a$) magnitudes (Fig. 3). The non-fitting of the Cox–Merz rule for complex dispersions is attributed to the presence of high-density entanglements or to the development of structure and intermolecular aggregation in solution (Da Silva and Rao, 1992).

The rheological oscillatory and steady-state shear rheological properties of foods are generally correlated by linear and power

Fig. 3. Tomato juice complex ($\eta^*$, ○) and apparent ($\eta_a$, ●) viscosities. Effect of HPH (0–150 MPa). (a) 0 MPa, (b) 25 MPa, (c) 50 MPa, (d) 100 MPa and (e) 150 MPa.
The regression of these data to a linear function (Eq. (6)) resulted in three parameters, that could be used to evaluate the description of the experimental values by the models, i.e., the linear slope ($A$; which must be as close as possible to the unity), the intercept ($B$; which must be as close as possible to zero) and the coefficient of determination ($R^2$; which must be as close as possible to the unity). Using Eq. (6), it can be seen that the models obtained describe the experimental values well (Table 3). Moreover, it was observed that the power model (Eq. (5)) fitted the experimental values better than the linear model (Eq. (4)).

$$
\eta^*_{\text{model}} = A \cdot \eta^*_\text{experimental} + B 
$$

(6)

The results obtained indicated that the tomato juice rheological properties could be obtained by either oscillatory or steady-state shear experiments, even after high pressure homogenization. Moreover, Table 4 shows that the values obtained were in accordance with those described by Augusto et al. (2011b) for tomato juice, as well as with those described for other fruit products such as ketchup, vegetable-based baby foods, potato puree and tamarind juice.

The parameters $\lambda$ (Eq. (4)) and $x$ and $\beta$ (Eq. (5)) showed similar behaviour in relation to the homogenization pressure ($P_h$), to the behaviour observed for the parameters $k'$, $n'$ (Eq. (1)), $k''$ and $n''$ (Eq. (2)). The parameters $\lambda$ and $x$ first increased and then decreased with increase in $P_h$, while parameter $\beta$ followed the opposite trend. However, in contrast with that observed for $k'$ and $k''$, and in accordance with that observed for $n'$ and $n''$, the changes in $\lambda$, $x$ and $\beta$ in relation to the homogenization pressure ($P_h$) were relatively small. The value for $x$ is related to the magnitude of the difference between the apparent ($\eta_a$) and complex ($\eta^*$) viscosities, and was the parameter that changed more (up to 40%). The value for $\beta$ is related to the differences in behaviour between the apparent ($\eta_a$) and complex ($\eta^*$) viscosities, and only changed 2%. The linear model only had one parameter, $\lambda$, which is related to both magnitude and behaviour differences and changed up to 28%, an intermediate value. Once again this indicates that high pressure homogenization improves tomato juice consistency more than it modifies its nature (internal structure).

The results obtained highlighted the possible applications of high pressure homogenization (HPH) as a valuable tool to promote physical properties changes in food products.

4. Conclusions

The present work evaluated the effect of high pressure homogenization (HPH) on the viscoelastic properties of tomato juice. HPH increased the values of the tomato juice storage ($G'$) and loss ($G''$) moduli. The products G' and G'' were modelled as a power function of the oscillatory frequency ($\omega$), of which the parameters were then evaluated as a function of the homogenization pressure ($P_h$). Moreover, it was observed that HPH processing improved tomato juice consistency more than it modified its nature (internal structure). The changes observed in the viscoelastic properties were attributed to disruption of suspended particles during processing. Moreover, two modified Cox–Merz rules were used to correlate the steady-state shear properties of the product to its viscoelasticity. The results obtained highlighted possible applications of high pressure homogenization (HPH) as a valuable tool to promote physical properties changes in food products.

Acknowledgment

The authors are grateful to the São Paulo Research Foundation (FAPESP) for funding Project Nos. 2010/05241-8 and 2010/05240-1.
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