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Mestre em Tecnologia de Alimentos

Efeito da Homogeneização à Alta Pressão (HAP) nas Propriedades Reológicas de Suco de Tomate

Tese apresentada à Faculdade de Engenharia de Alimentos da Universidade Estadual de Campinas para obtenção do título de Doutor em Tecnologia de Alimentos

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“Se vi mais longe,

foi porque estava sobre ombros de gigantes”

Isaac Newton

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e a minha ESPOSA,

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Pedro

Sumário

Efeito da Homogeneização à Alta Pressão (HAP) nas Propriedades Reológicas de Suco de Tomate

Resumo

A homogeneização a alta pressão (HAP) tem sido estudada por diversos autores como metodologia não térmica para a conservação de alimentos, especialmente produtos de frutas. Trabalhos realizados com esses produtos e testes industriais indicam aumento de consistência devido a HAP. No entanto, poucos trabalhos da literatura estudam alterações físico-químicas em produtos de frutas devido à HAP, especialmente em relação às características reológicas. A avaliação de tais alterações é essencial não só para o entendimento e dimensionamento do processo, mas também permite a utilização do método para provocar alterações intencionais e desejáveis em alimentos, como aumento de consistência. O presente trabalho estudou o efeito da homogeneização a alta pressão (HAP) nas características reológicas de suco de tomate. Na primeira parte do trabalho, avaliaram-se as propriedades reológicas dependentes do tempo, em estado estacionário e de viscoelasticidade linear de sucos não processados, determinando assim as técnicas e os modelos matemáticos mais adequados para utilização nas demais etapas do projeto. Em seguida avaliou-se o efeito da HAP nas características reológicas de um modelo de soro de suco de tomate. A HAP reduziu a viscosidade do modelo, sendo tal redução modelada como função da pressão de homogeneização (P_H). Avaliou-se então o efeito da HAP no suco. A HAP reduziu o tamanho das partículas em suspensão, assim como sua distribuição, promovendo maior interação entre partículas e entre partículas e o soro. Como consequência, resultou em aumento da consistência, tixotropía, comportamento viscoso e elástico dos produtos. O efeito da P_H se mostrou assintótico, sendo discutidas as razões para tal, modelando-se os parâmetros obtidos como função da P_H. Por fim, avaliou-se o efeito da HAP nas propriedades de deformação e relaxação do suco de tomate. Utilizando o modelo de Burger, identificaram-se os componentes estruturais do suco de tomate associados aos comportamentos reológicos. Dessa forma, o presente trabalho descreveu as mudanças estruturais associadas ao processo que afetam a reologia do produto. Conclui-se que a HAP é uma poderosa ferramenta para promoção de alterações físicas em produtos de frutas.

Palavras-chave:

Homogeneização a alta pressão (HAP), propriedades físicas, reologia, viscoelasticidade, viscosidade.

Effect of High Pressure Homogenization (HPH) on the Rheological Properties of Tomato Juice

Abstract

High pressure homogenization (HPH) has been widely studied as a non-thermal method for food preservation. Industrial assessments and scientific works have demonstrated the consistency increasing in those products due to HPH. However, just a few works in literature have studied the physico-chemical changes in fruit products due HPH processes. The evaluation of rheological changes due to HPH is important not only for process design, but also for using this technology in order to promote desirable changes in food products, such as improvement of its consistency. The present work studied the effect of high pressure homogenization (HPH) on the rheological properties of tomato juice. Firstly, it was evaluated the tomato juice time-dependent, steady-state shear and viscoelastic properties. This first part was carried out in order to evaluate the rheological methods and mathematical models to be used in the work. Then, it was evaluated the effect of HPH on the rheological properties of a tomato juice serum model. The HPH decreased the serum model viscosity, which was modelled as function of the homogenization pressure (P_H). The HPH effect on tomato juice was then evaluated. The HPH decreased the suspended particle dimensions and distribution, resulting in higher particle-particle and serum-particle interaction. As a result, it was observed an increasing in product consistency, thixotropy, viscous and elastic behaviour. The effect of P_H showed an asymptotic behaviour, which was described and modelled. Finally, it was evaluated the effect of HPH on tomato juice creep and recovery properties. The mechanical Burger model well explained the juice creep compliance, and its parameters were associated to the juice structural components. Therefore, the present work described the tomato juice structural and rheological changes due to HPH processing. It was concluded that

the HPH process is a valuable tool to promote physical properties changes in food products.

Keywords:

High pressure homogenization (HPH), physical properties, rheology, viscoelasticity, viscosity.

Lista de Figuras

Lista de Tabelas

Nomenclatura

Chapter 2

γ = shear rate [s^{-1}]

η = viscosity [Pa·s]

η_a = apparent viscosity (= σ / γ) [Pa·s]

η_0 = initial viscosity in Falguera-Ibarz model (Equation 2.6) [Pa·s]

η_∞ = equilibrium viscosity in Falguera-Ibarz model (Equation 2.6) [Pa·s]

σ = shear stress [Pa]

σ_0 = yield stress, Herschel-Bulkley's model (Equation 2.5) [Pa]

σ_0 = initial stress in Figoni-Shoemaker model (Equation 2.2) [Pa]

σ_e= equilibrium stress in Figoni-Shoemaker model (Equation 2.2) [Pa]

σ_e= equilibrium stress in Hahn-Ree-Eyring model (Equation 2.4) [Pa]

a = slope index in the linear model for evaluation of experimental values versus those obtained by models (Equation 2.1) [-]

b = intercept index in the linear model for evaluation of experimental values versus those obtained by models (Equation 2.1) [-]

A = structural parameter in Weltman model (Equation 2.3) [Pa]

A = structural parameter in Hahn-Ree-Eyring model (Equation 2.4) [Pa]

A_0 = Arrhenius's pre-exponential parameter model (Equation 2.7)

B = kinetic parameter in Weltman model (Equation 2.3) [$Pa \cdot s^{-1}$]

B = kinetic parameter in Hahn-Ree-Eyring model (Equation 2.4) [$Pa \cdot s^{-1}$]

Ea = activation energy in Arrhenius's model (Equation 2.7) [$J \cdot mol^{-1}$]

k = consistency coefficient, Herschel-Bulkley's model (Equation 2.5) [$Pa \cdot s^n$]

k = kinetic parameter in Figoni-Shoemaker model (Equation 2.2) [s^{-1}]

k = viscosity decay parameter in Falguera-Ibarz model (Equation 2.6) [-]

n = flow behavior index, Herschel-Bulkley's model (Equation 2.5) [-]

R = universal constant of ideal gases [= 8.314 $Pa \cdot m^3 \cdot mol^{-1} \cdot K^{-1}$]

t = time [s]

T = absolute temperature [K]

Chapter 3

$\alpha_1, \alpha_2, \beta_1, \beta_2$ = parameters of the modified Cox-Merz rules (Equations 3.2-3.5)

$\dot{\gamma}$ = shear rate [s^{-1}]

η_a = apparent viscosity (= σ / γ) [Pa·s]

η^* =complex viscosity [Pa·s]

σ = shear stress [Pa]

G' = storage modulus [Pa]

G'' = loss modulus [Pa]

Chapter 4

$\dot{\gamma}$ = shear rate [s^{-1}]

ϕ = particle volume fraction [-]

η = viscosity [Pa·s]

η_r = relative viscosity (Equation 4.4) [Pa·s]

[η] = intrinsic viscosity [Pa·s]

σ = shear stress [Pa]

σ_0 = yield stress, Herschel-Bulkley's model [Pa]

k = consistency coefficient, Herschel-Bulkley's model [$Pa \cdot s^n$]

n = flow behavior index, Herschel-Bulkley's model [-]

P_H = homogenization pressure [MPa]

Chapter 5

α = slope index of the linear model for the evaluation of the experimental values versus those obtained by models (Equation 5.8) [-]

β = intercept index of the linear model for the evaluation of the experimental values versus those obtained by models (Equation 5.8) [-]

$\dot{\gamma}$ = shear rate [s^{-1}]

ϕ = particle volume fraction [-]

ϕ_m = maximum packing fraction of solids [-]

η = viscosity [Pa·s]

η_a = apparent viscosity (= σ / γ) [Pa·s]

η_r = relative viscosity (Equation 5.9) [Pa·s]

η_0 = initial viscosity in the Falguera-Ibarz model (Equation 5.7) [Pa·s]

η_∞ = equilibrium viscosity in the Falguera-Ibarz model (Equation 5.7) [Pa·s]

[η] = intrinsic viscosity [Pa·s]

ρ = particle density [$kg \cdot m^{-3}$]

σ = shear stress [Pa]

σ_0 = yield stress, Herschel-Bulkley model (Equation 5.6) [Pa]

σ_0 = initial stress in the Figoni-Shoemaker model (Equation 5.4) [Pa]

σ_e= equilibrium stress in the Figoni-Shoemaker model (Equation 5.4) [Pa]

A = structural parameter in the Weltman model (Equation 5.5) [Pa]

A_{SF} = particle specific surface area (Equation 5.3) [$m^3 \cdot g^{-1}$]

B = kinetic parameter in the Weltman model (Equation 5.5) [$Pa \cdot s^{-1}$]

d = particle diameter [m]

D[4,3] = particle volume-based diameter (Equation 5.1) [m]

D[3,2] = particle area-based diameter (Equation 5.2) [m]

k = consistency coefficient, Herschel-Bulkley model (Equation 5.6) [$Pa{\cdot}s^n$]

k_B = Boltzman constant [= $1.38{\cdot}10^{-23}$ $N{\cdot}m{\cdot}K^{-1}$]

k_{FS} = kinetic parameter in the Figoni-Shoemaker model (Equation 5.4) [s^{-1}]

k_{FI} = viscosity decline parameter in the Falguera-Ibarz model (Equation 5.7) [-]

n = flow behavior index, Herschel-Bulkley model (Equation 5.5) [-]

Pe = Peclet number (Equation 5.12) [-]

P_H = homogenization pressure [MPa]

$\bar{r}_{particle}$ = mean suspended particle radius [m]

V = particle volume [m³]

t = time [s]

T = absolute temperature [K]

Chapter 6

α = magnitude index in power modified Cox-Merz Rule (Equation 6.5) [-]

β = behavior index in power modified Cox-Merz Rule (Equation 6.5) [-]

λ = magnitude index in linear modified Cox-Merz Rule (Equation 6.4) [-]

$\dot{\gamma}$ = shear rate [s^{-1}]

η_a = apparent viscosity (= σ / γ) [$Pa{\cdot}s$]

η^* = complex viscosity [$Pa{\cdot}s$]

σ = shear stress [Pa]

σ_0 = yield stress, Herschel-Bulkley model [Pa]

ω = oscillatory frequency [Hz]

A = slope index in the linear model for evaluation of experimental values versus those obtained by models (Equation 6.6) [-]

B = intercept index in the linear model for evaluation of experimental values versus those obtained by models (Equation 6.6) [-]

G' = storage modulus [Pa]

G'' = loss modulus [Pa]

k', k'' = consistency coefficients in the power law model of the viscoelastic properties (Equations 6.1 and 6.2) [$Pa{\cdot}s^{n'}$, $Pa{\cdot}s^{n''}$]

n', n'' = behaviour index in the power law model of the viscoelastic properties (Equations 6.1 and 6.2) [-]

P_H = homogenization pressure [MPa]

Chapter 7

γ = strain [-]

ϕ = particle volume fraction [-]

η = viscosity, associated to the Newtonian dashpot [$Pa{\cdot}s$]

η_0 = Newtonian flow viscosity, associated to the Maxwell dashpot [$Pa{\cdot}s$]

η_1 = retarded viscosity, associated to the Kelvin-Voigt dashpot [Pa·s]

η^* = complex viscosity [Pa·s]

σ = shear stress [Pa]

σ_0 = yield stress, Herschel-Bulkley's model [Pa]

B = proportional kinetic parameter in recovery model (Equation 7.3) [s^{-C}]

C = power kinetic parameter in recovery model (Equation 7.3) [-]

G = elastic modulus, associated to the Hookean spring [Pa]

G_0 = instantaneous elastic modulus, associated to the Maxwell spring [Pa]

G_1 = retarded elastic modulus, associated to the Kelvin-Voigt spring [Pa]

G' = storage modulus [Pa]

G'' = loss modulus [Pa]

J = compliance (Equation 7.1) [Pa^{-1}]

J_∞ = residual compliance corresponding to the permanent deformation of the Maxwell dashpot [Pa^{-1}]

J_{KV} = recovery compliance due to the Kelvin-Voigt element [Pa^{-1}]

k = consistency coefficient, Herschel-Bulkley's model [$Pa·s^n$]

n = flow behavior index, Herschel-Bulkley's model [-]

P_H = homogenization pressure [MPa]

t = time [s]

Capítulo 1: Introdução, Objetivos e Revisão Bibliográfica

1.1. Introdução

A crescente busca por alimentos mais seguros e de melhor qualidade nutricional e sensorial cria a necessidade de melhor entendimento dos processos envolvidos na produção dos mesmos.

A tecnologia de homogeneização a alta pressão (HAP) tem sido estudada por diversos autores como metodologia não térmica para a conservação de alimentos líquidos, especialmente produtos de frutas.

Embora diversos trabalhos apresentem a utilização da HAP para inativação microbiana e consequente aumento da estabilidade microbiológica dos produtos de frutas, poucos trabalhos avaliam as alterações físico-químicas nestes produtos devido à HAP, especialmente em relação as características reológicas.

A avaliação de tais alterações é essencial não só para o entendimento e dimensionamento do processo, mas também permite a utilização do método para provocar alterações intencionais e desejáveis em alimentos, como aumento de consistência e diminuição de separação de fases.

O tomate é um dos vegetais mais populares do mundo (NISHA et al. 2010). De fato, é um dos vegetais mais importantes para a indústria de alimentos, sendo seus produtos largamente consumidos e presentes na dieta humana (SÁNCHEZ et al., 2002).

Um dos parâmetros de maior importância sensorial e industrial em produtos de tomate é a consistência (AKBUDAK, 2010; AGUILÓ-AGUAYO, SOLIVA-FORTUNY, MARTÍN-BELLOSO, 2009; SÁNCHEZ et al., 2003; SÁNCHEZ et al., 2002; HAYES, SMITH, MORRIS, 1998; MIZRAHI, 1997; YOO, RAO, 1994; MOHR, 1987b, RAO, 1977). Dessa forma, o conhecimento do comportamento reológico desses produtos é importante não somente para dimensionamento de diversas operações unitárias como bombeamento, misturas e trocas de calor (IBARZ, BARBOSA-CÁNOVAS, 2003; RAO, 1999) como também para otimização de produtos e processos.

Embora diversos trabalhos tenham sido realizados para entendimento da influência das características da matéria prima e processo nas características reológicas de produtos de tomate, os resultados apresentados na literatura apresentam grande variação, tornando difícil uma descrição geral dos produtos (BAYOD et al., 2007). Grande parte dos trabalhos relaciona as características reológicas à medidas empíricas ou em um único ponto, isto é, uma única condição de taxa de deformação (γ). Bayod, Willers e Tornberg (2008) destacam a necessidade de realização de mais estudos sobre a influência de cada parâmetro do processo nas características reológicas de produtos de tomate.

A influência de diversos fatores no comportamento reológico de produtos de tomate tem sido estudada por diversos autores. Embora diversos trabalhos afirmem que a homogeneização aumenta a consistência de produtos de tomate (BAYOD et al., 2007; OUDEN, VLIET, 2002; OUDEN, VLIET, 1997; BERESOVSKY, KOPELMAN, MIZRAH, 1995; THAKUR, SINGH, HANDA, 1995; BECKER et al., 1987; FODA, MCCOLLUM, 1970; WHITTENBERG, NUTTING, 1958), não se encontra na literatura estudo detalhado do efeito das condições do processo de homogeneização nas características reológicas destes produtos. A maioria dos trabalhos realiza avaliações apenas antes e depois da realização do processo, e em apenas uma determinada condição definida empiricamente. Nenhum trabalho avalia de forma sistemática a influência do processo de homogeneização nas propriedades reológicas desses produtos.

Pérez-Conesa et al. (2009) recomendam a realização do processo de homogeneização para melhoria do valor nutricional de produtos de tomate devido ao aumento da extração de folatos (de interesse nutricional), enquanto Corbo et al. (2010) destacam a tecnologia como alternativa ao processamento de suco de tomate. Torna-se assim necessário o melhor entendimento dos parâmetros desse processo nas características do produto final.

Dessa forma, destaca-se a necessidade de realização de mais estudos de avaliação das alterações físico-químicas nos alimentos devido à homogeneização a alta pressão (HAP). A influência desse processo nas propriedades reológicas de alimentos deve ser melhor entendida, principalmente devido às evidências apresentadas em recentes trabalhos e utilização industrial do processo, permitindo assim sua utilização e melhor dimensionamento para o processamento de alimentos.

1.2. Objetivos

O presente trabalho teve por objetivo estudar o efeito da homogeneização a alta pressão (HAP) nas propriedades reológicas se suco de tomate.

Os objetivos específicos foram:

- Avaliar as propriedades reológicas dependentes do tempo e em cisalhamento em estado estacionário do suco de tomate, verificando os modelos mais adequados para descrever tais propriedades (Capítulo 2).
- Avaliar a viscoelasticidade do suco de tomate, assim como a aplicação da Regra de Cox-Merz (Capítulo 3).
- Avaliar o efeito da HAP nas propriedades reológicas de um modelo de soro de suco de tomate (Capítulo 4).
- Avaliar o efeito da HAP nas propriedades reológicas dependentes do tempo e em cisalhamento em estado estacionário do suco de tomate, modelando os parâmetros que descrevem tais propriedades como função da pressão de homogeneização (Capítulo 5).
- Avaliar o efeito da HAP nas propriedades viscoelásticas do suco de tomate, assim como na aplicação da Regra de Cox-Merz (Capítulo 6).
- Avaliar o efeito da HAP nas propriedades de deformação e relaxação (*creep and recovery*) do suco de tomate, utilizando modelos mecânicos para descrever o produto (Capítulo 7).

1.3. Revisão Bibliográfica

1.3.1. Homogeneização a alta pressão (HAP)

A tecnologia de homogeneização a alta pressão (HAP) consiste na pressurização de um fluido (em geral em pressões de até 350 MPa) e rápida passagem do mesmo por uma válvula com orifício estreito, resultando em grande aumento da velocidade de escoamento e despressurização, com consequente cavitação e alta tensão de cisalhamento. Dessa forma, as partículas, células e macromoléculas em suspensão no fluido são submetidas a alta tensão mecânica, sendo torcidas e deformadas (PINHO et al., 2011; INNINGS, FUCHS, TRÄGÅRDH, 2011; FLOURY et al., 2004). Essa tecnologia tem sido estudada por diversos autores como metodologia não térmica para a conservação de alimentos líquidos, especialmente produtos de frutas.

Diversos trabalhos avaliam a utilização da HAP na inativação microbiana e consequente aumento da estabilidade microbiológica dos produtos de frutas. O potencial da utilização de HAP em substituição total ou parcial ao processo térmico de sucos, combinado ou não com a utilização de refrigeração, é apresentado na literatura para sucos de tomate (CORBO et al., 2010), maçã (SUÁREZ-JACOBO et al., 2012; MARESCA, DONSÌ, FERRARI, 2011; DONSÌ et al., 2009; PATHANIBUL et al., 2009; SALDO et al., 2009), manga (TRIBST et al., 2011; TRIBST et al., 2009), açaí (ALIBERTI, 2009), laranja (CAMPOS, CRISTIANINI, 2007; TAHIRI et al., 2006), cenoura (PATRIGNANI et al., 2010; PATHANIBUL et al., 2009; PATRIGNANI et al., 2009) e damasco (PATRIGNANI et al., 2010; PATRIGNANI et al., 2009).

Poucos trabalhos, no entanto, estudaram alterações físico-químicas em produtos de frutas devido a HAP, especialmente em relação as características reológicas. A avaliação de tais alterações é essencial não só para o entendimento e dimensionamento do processo, mas também permite a utilização do método para provocar alterações intencionais e desejáveis em alimentos, como aumento de consistência e diminuição de separação de fases. Floury et al. (2004) e Floury et al. (2002) citam a HAP como uma importante ferramenta para modificações de polímeros, principalmente para aplicações em alimentos e farmacêuticas. Masson et al. (2011) e Lopez-Sanchez et al. (2011) destacam o potencial da utilização da HAP como tecnologia para alteração de propriedades físicas de alimentos, reduzindo a utilização de aditivos.

Lacroix et al. (2005) avaliaram a influência da HAP na estabilidade da opalescência de suco de laranja. Após tratamento a 170 MPa, o suco apresentou estabilidade de 4 dias a 30ºC (condição para vida de prateleira acelerada), contra 2 dias apresentado pelo não processado. Tal resultado também foi influenciado pelo pH do suco e prévio tratamento térmico. Os produtos processados por HAP apresentaram características sensoriais mais próximas às naturais. Resultados semelhantes são descritos por Welti-Chanes, Ochoa-Velasco e Guerrero-Beltrán (2009), com suco de laranja processado por HAP (50 - 250 MPa) permanecendo turvo por 12 dias a 4ºC, contra apenas seis horas do suco não processado. Embora sem mensurar, ambos os trabalhos relatam a redução do tamanho das partículas em suspensão, citando como fundamental no aumento da estabilidade do suco. As características reológicas dos sucos processados por HAP não foram avaliadas. Sentandreu et al. (2011) estudaram o efeito da homogeneização à 20 MPa na estabilidade de suco de laranja, observando redução do tamanho das partículas em suspensão e aumento da estabilidade de turbidez.

Donsì et al. (2009) observaram a redução do tamanho das partículas em suspensão para suco de maçã processados a 200 MPa. De forma semelhante ao observado para suco de laranja (SENTANDREU et al., 2011), a distribuição do tamanho das partículas (PSD) passou da faixa de 100−1.000 μm iniciais para 10-100 μm. Entretanto, os sucos foram classificados como fluidos Newtonianos, com viscosidade menor quando processados por HAP. Calligaris et al. (2012) também observaram pequena redução na viscosidade aparente de suco de banana processado por HAP.

Patrignani et al. (2010 e 2009) observaram aumento da viscosidade aparente (medida por viscosímetro *falling ball*) de suco de damasco com o processamento por HAP (100 MPa, até oito ciclos). Os autores discutem que tais alterações se devem, provavelmente, a alterações estruturais das pectinas, porém não avaliando o efeito da HAP na distribuição do tamanho de partículas (PSD).

Não observaram alterações na viscosidade aparente de suco de cenoura processado de forma semelhante. Sinchaipanit e Kerr (2007) observaram aumento na viscosidade aparente (medida em capilares) do suco e soro de cenoura após homogeneização a baixas pressões (0,7-1,4 MPa), assim como menor sedimentação do suco. Após processo as partículas em suspensão apresentaram redução de tamanho, tanto médio quanto na distribuição (de 10-1000 μm, com média 339 μm; para 5-500 μm, com média 82 μm). Segundo os autores, o rompimento de células resulta em liberação de pectinas da lamela média para o soro.

Pickardt, Dongowski e Kunzek (2004) observaram separação das células de cenoura homogeneizadas em três ciclos a 6-10 MPa, e rompimento com consequente presença de fragmentos celulares em processos de 9-12 ciclos a 30 MPa. As suspensões de cenoura homogeneizadas (12 ciclos a 35 MPa) apresentaram menor tensão de cisalhamento inicial (σ_0) e modulo de armazenamento (G') do que os produtos não homogeneizados. Entretanto, os autores atribuem tais características à menor capacidade de rehidratação dos produtos homogeneizados.

Tribst (2008) observou aumento da viscosidade aparente (medida por viscosímetro rotacional Brookfield a 30 rpm) de néctar de manga após processo de HAP (até 300 MPa). Os néctares despolpados tratados a 100 MPa e 250 MPa apresentaram viscosidades aparentes de 2142 cP e 2852 cP, respectivamente, enquanto o néctar não processado por HAP apresentou viscosidade aparente de 242 cP. O aumento de consistência foi tão grande que o produto teve que ser despolpado e tratado com enzimas pécticas para permitir o processamento.

Lopez-Sanchez et al. (2011) avaliaram o efeito da HAP nas características de emulsões elaborados com polpas diluídas de tomate ou cenoura e azeite de oliva, em pressões de homogeneização de até 100 MPa. Os autores observaram que o comportamento reológico e microestrutural das polpas de cenoura e tomate apresentaram alterações diferentes em relação à HAP. As células de cenoura se mostraram mais resistentes às tensões envolvidas, se alongando em pressões de até 10 MPa e se rompendo a partir destas, enquanto as células de tomate apresentaram rompimento mesmo em processos a 10 MPa. O módulo de armazenamento (G') de ambos os produtos foi reduzido em processos acima de 10 MPa. Em processos de até 10 MPa, não houve alteração do módulo de armazenamento (G') nos produtos de tomate, havendo aumento do mesmo para os de cenoura. Enquanto o processamento por HAP resultou em aumento da tensão de cisalhamento inicial (σ_0) para cenouras, este teve efeito oposto em tomates. Os autores observam que as diferentes estruturas celulares dos diferentes tipos de vegetais implicam em possível comportamento distinto em relação ao processamento por HAP.

O trabalho de Silva et al. (2010) é o que descreve com mais detalhes a influência do processo de HAP nas características reológicas de produtos de frutas. Os autores avaliaram o comportamento da curva de escoamento de polpas de abacaxi submetidas ao processo de HAP. As polpas foram processadas em pressões de homogeneização de até 70 MPa, sendo avaliados os efeitos do processo na curva de escoamento (características reológicas em cisalhamento em regime estacionário), PSD e perfil de sedimentação ao longo de 10 dias. Os autores observaram redução no tamanho das partículas em suspensão, tanto por microscopia óptica quanto através da análise de PSD. Tanto a distribuição do tamanho das partículas (distribuição mais centrada) quanto o tamanho médio das mesmas foi reduzido. Segundo os autores, embora as características morfológicas das partículas não tenham se alterado devido ao processo, as partículas menores resultantes formam uma nova estrutura. As características reológicas de fluxo do produto foram modeladas segundo o modelo de Ostwald de Waele (lei da potência), com índice de comportamento do fluido (n) aumentando e o índice de consistência (k) e viscosidade aparente (μ_a) diminuindo com o processamento. As maiores alterações foram observadas em pressões de homogeneização de até 30-40 MPa, com pouca variação à partir desse nível. Os sucos processados em pressões de homogeneização de até 40 MPa apresentaram maior estabilidade à sedimentação, enquanto pressões de processamento maiores não preveniram a separação de fases. Os autores observaram que, seguindo a Lei de Stokes, as menores partículas em suspensão decorrentes de maiores pressões de homogeneização deveriam ter velocidade de precipitação menor (ao contrário do observado). Observaram também que ao reduzir o tamanho das partículas em suspensão, aumenta-se também a interação entre elas devido a Forças de Van der Waals. Os autores sugerem que a sedimentação dos sucos processados acima de 40 MPa pode ser decorrente da formação de agregados de partículas (embora não tenham observado tal formação utilizando microscopia óptica).

Entretanto, o não aumento de estabilidade observado por Silva et al. (2010) pode ser decorrente da redução da consistência do soro (meio dispersante), seguindo a Lei de Stokes e a redução de consistência em soluções de polissacarídeos processadas por HAP, observadas por Wang et al. (2011, goma de linhaça), Harte e Venegas (2010, goma xantana e κ-carragena), Floury et al. (2002, carboxi metil celulose), Corredig e Wicker (2001, pectinas) e Lagoueyte e Paquin (1998, goma xantana).

Dessa forma, destaca-se a necessidade de realização de mais estudos de avaliação das alterações físico-químicas nos alimentos devido à homogeneização a alta pressão (HAP). A influência desse processo nas propriedades reológicas de alimentos deve ser melhor entendida, principalmente devido às evidências apresentadas em recentes trabalhos e utilização industrial do processo, permitindo assim sua utilização e melhor dimensionamento para o processo de alimentos.

1.3.2. Características reológicas de produtos de tomate

Grande parte da produção mundial de tomates é utilizada como ingredientes de diversos produtos alimentícios (SÁNCHEZ et al., 2002). O Brasil é o maior produtor de tomate industrial da América do Sul, sendo sua produção quase que totalmente voltada para o mercado interno (MELO, VILELA, 2005). A produção de tomate industrial do Estado de São Paulo se destaca por representar 42% em valor da produção brasileira, de cerca de 375 mil toneladas anuais (IBGE, 2009). Os principais derivados de tomate obtidos no país são o extrato concentrado e o molho de tomate (MELO, VILELA, 2005), extensivamente utilizados na indústria de alimentos como produto final ao consumidor ou matéria prima de diversos outros produtos.

Os produtos de tomate são compostos de células íntegras e pedaços de células do pericarpo (HAYES, SMITH, MORRIS, 1998) dispersas em um meio coloidal (soro) (TANGLERTPAIBUL, RAO, 1987b). Além de água, são formados por açúcares, ácidos orgânicos, proteínas, minerais, pectinas e outros polissacarídeos (sólidos solúveis; cerca de 87% dos sólidos totais); proteínas e paredes celulares com celulose e pectina (sólidos insolúveis; cerca de 13% dos sólidos totais) (WHITTENBERG, NUTTING, 1958). Possuem pH em geral entre 4,2 e 4,6 (HAYES, SMITH, MORRIS, 1998).

Um dos parâmetros de maior importância sensorial e industrial em produtos de tomate é a consistência (AKBUDAK, 2010; AGUILÓ-AGUAYO, SOLIVA-FORTUNY, MARTÍN-BELLOSO, 2009; SÁNCHEZ et al., 2003; SÁNCHEZ et al., 2002; HAYES, SMITH, MORRIS, 1998; MIZRAHI, 1997; YOO, RAO, 1994; MOHR, 1987b, RAO, 1977), sendo um dos principais objetivos na produção desses derivados garantir características reológicas que prolonguem pelo maior tempo possível a suspensão de sólidos (NOOMHORM, TANSAKUL, 1992). Sánchez et al. (2003) e Chou e Kokini (1987) observaram que a obtenção de derivados de tomate com maior consistência resulta em produtos finais mais baratos. Akbudak (2010) destaca que o controle das operações unitárias envolvidas no processo pode garantir propriedades otimizadas. Observa-se também que o conhecimento do comportamento reológico é importante para o dimensionamento de diversas operações unitárias como bombeamento, misturas e trocas de calor (SHARMA et al., 1996; VITALI, RAO, 1982; RAO, 1977). Entender os fatores que afetam essas características é primordial para obtenção de produto com maior aceitabilidade (MIZRAHI, 1997).

A influência de diversos fatores no comportamento reológico de produtos de tomate tem sido estudado por diversos autores, tais como temperatura (YILMAZ et al., 2011; DAK, VERMA, JAAFFREY, 2008; BAYOD et al., 2007; RAO, COOLEY, LIAO, 1999; RAO, BOURNE, COOLEY, 1981), concentração (DAK, VERMA, JAAFFREY, 2008; OUDEN, VLIET, 2002; YOO, RAO, 1996; BERESOVSKY, KOPELMAN, MIZRAH, 1995; YOO, RAO, 1994; RAO, COOLEY, 1992; TANGLERTPAIBUL, RAO, 1987b; RAO, BOURNE, COOLEY, 1981), composição (SHARMA et al., 1996; MOHR, 1987a; FODA, MCCOLLUM, 1970; WHITTENBERG, NUTTING, 1957; WHITTENBERG, NUTTING, 1958), pH (BERESOVSKY, KOPELMAN, MIZRAH, 1995; BECKER et al., 1972; TAKADA, NELSON, 1983), variedade (AKBUDAK, 2010; SÁNCHEZ et al., 2002; THAKUR, SINGH, HANDA, 1995; RAO, BOURNE, COOLEY, 1981), maturação (AKBUDAK, 2010), temperatura e método de trituração (KAUR et al., 2007; SÁNCHEZ et al., 2003; SÁNCHEZ et al., 2002; HAND et al., 1955), método de concentração (TANGLERTPAIBUL, RAO, 1987a), despolpador (SÁNCHEZ et al., 2003; SÁNCHEZ et al., 2002; OUDEN, VLIET, 1997; YOO, RAO, 1996; NOOMHORM, TANSAKUL, 1992; TANGLERTPAIBUL, RAO, 1987a; HAND et al., 1955), tamanho e distribuição de partículas (BAYOD et al., 2007; OUDEN, VLIET, 1997; YOO, RAO, 1994; TANGLERTPAIBUL, RAO, 1987a) e homogeneização (BAYOD, TORNBERG, 2011; OUDEN, VLIET, 2002; OUDEN, VLIET, 1997; THAKUR, SINGH, HANDA, 1995; WHITTENBERG, NUTTING, 1958; HAND et al., 1955).

Embora diversos trabalhos tenham sido realizados para entendimento da influência das características da matéria prima e do processo nas características reológicas de produtos de tomate, os resultados apresentados na literatura apresentam grande variação, tornando difícil uma descrição geral dos produtos (BAYOD et al., 2007). Grande parte dos trabalhos relaciona as características reológicas a medidas em um único ponto (TANGLERTPAIBUL, RAO, 1987a), isto é, uma única condição de taxa de deformação (γ) (como, por exemplo, os recentes trabalhos de Aguiló-Aguayo, Soliva-Fortuny e Martín-Belloso, 2009 e Hsu, 2008). Bayod, Willers e Tornberg (2008) destacam a necessidade de realização de mais estudos sobre a influência de cada parâmetro do processo nas características reológicas de produtos de tomate, enquanto Beresovsky, Kopelman e Mizrah (1995) destacam a importância do melhor entendimento da influência da composição e frações nessas características. Valencia et al. (2004) e Sánchez et al. (2002) observaram que existem poucos trabalhos na literatura com caracterização viscoelástica linear de produtos de tomate. Yoo e Rao (1996) destacam a importância da realização de testes de fluência para a caracterização reológica desses materiais. Bayod et al. (2007) e Hayes, Smith e Morris (1998) destacam a necessidade de realização de mais estudos em relação a dependência do tempo das características reológicas desses produtos, tanto pela escassez de trabalhos na área quanto pela falta de dados conclusivos.

A consistência de produtos de tomate depende tanto de sua composição química quando de sua estrutura física (WHITTENBERG, NUTTING, 1957). As propriedades reológicas de produtos de tomate são altamente dependentes da polpa em suspensão, relacionada com os sólidos insolúveis (WIS), (VALENCIA et al., 2004; SÁNCHEZ et al., 2003; VALENCIA et al., 2003; HAYES, SMITH, MORRIS, 1998; BERESOVSKY, KOPELMAN, MIZRAH, 1995; MOHR, 1987a; FODA, MCCOLLUM, 1970; WHITTENBERG, NUTTING, 1958) enquanto o soro contribui pouco para a consistência do produto final (VALENCIA et al., 2004; VALENCIA et al., 2003; BERESOVSKY, KOPELMAN, MIZRAH, 1995; FODA, MCCOLLUM, 1970). É influenciada primeiramente pela composição e estrutura de suas paredes celulares (WHITTENBERG, NUTTING, 1958), cuja camada externa é formada por fibras de celulose entrelaçadas com pectinas (THAKUR, SINGH, HANDA, 1995; WHITTENBERG, NUTTING, 1957). A pectina insolúvel ligada às fibras de celulose contribui significativamente para que as paredes celulares sejam eletricamente carregadas, mantendo-as assim em suspensão (WHITTENBERG, NUTTING, 1958) e, consequentemente, contribuindo predominantemente para a consistência desses produtos (WHITTENBERG, NUTTING, 1957). As pectinas são provenientes da parede celular dos tomates, especialmente da lamela média, onde mantém unidas as células. Durante o amadurecimento das frutas ou devido à ruptura dos tecidos no processamento, parte das pectinas se mantém nas paredes celulares, enquanto parte se desprende, ficando dispersas no soro (MOHR, 1987a).

Tanglertpaibul e Rao (1987b) observaram que o efeito da adição de polpa em concentrados de tomate é maior quão mais concentrado for o soro. Tal observação sugere uma interação entre os componentes do soro e a polpa dispersa. Beresovsky, Kopelman e Mizrah (1995) mostraram que tanto as pectinas da polpa em suspensão (maior importância) quanto as dispersas no soro (importância apenas em produtos diluídos) influenciam a consistência dos produtos. Segundo os autores, a interação entre proteínas (carregadas positivamente) e pectinas (carregadas negativamente) da polpa em suspensão e pectinas do soro definem a interação das partículas e consequentemente o comportamento reológico dos derivados de tomate. Por tal razão, a consistência desses produtos é influenciada pelo pH, sendo o máximo observado perto de pH 4,5 (BERESOVSKY, KOPELMAN, MIZRAH, 1995; TAKADA , NELSON, 1983).

O aumento da concentração dos sólidos dispersos, assim como a redução do tamanho dessas partículas resulta em aumento na consistência dos produtos (OUDEN, VLIET, 1997; YOO, RAO, 1994; TANGLERTPAIBUL, RAO, 1987a).

Os produtos de tomate apresentam comportamento seguindo modelo de Herschel-Bulkley (HB; $\sigma = \sigma_0 + k.\gamma^n$) (FARAHNAKY et al., 2010; MCCARTHY, MCCARTHY, 2009; SHARMA et al., 1996; RAO, BOURNE, COOLEY, 1981; CHARM, 1963), uma vez que seguem o modelo de Ostwald de Waele, isto é, lei da potência (DAK, VERMA, JAAFFREY, 2008; SAHIN, OZDEMIR, 2004; RAO, COOLEY, LIAO, 1999; YOO, RAO, 1994; RAO, COOLEY, 1992; TANGLERTPAIBUL, RAO, 1987a) e apresentam tensão de cisalhamento inicial (σ_0) (YOO, RAO, 1994; RAO, COOLEY, 1992; TANGLERTPAIBUL, RAO, 1987a). O soro de concentrados de tomate possui comportamento pseudoplástico (BAYOD, WILLERS, TORNBERG, 2008; TANGLERTPAIBUL, RAO, 1987b) próximo do Newtoniano (RAO, COOLEY, 1992; TANGLERTPAIBUL, RAO, 1987b).

Yoo e Rao (1994) modelaram o índice de consistência do fluido (k) como função potência da concentração de polpa, enquanto Dak, Verma e Jaaffrey (2008) o modelaram como função exponencial da concentração. Rao, Bourne e Cooley (1981) observam que o valor de k pode ser modelado tanto por uma função exponencial como potência da concentração, e que aparentemente a função potência é mais adequada ao se considerar grande faixa de concentração. Yoo e Rao (1994) observam que seu valor diminui com o aumento do tamanho das partículas em suspensão.

O índice de comportamento do fluido (n) apresenta pouca variação em relação à temperatura, concentração ou método de concentração (TANGLERTPAIBUL, RAO, 1987a; RAO, BOURNE, COOLEY, 1981), indicando que os perfis de velocidade no escoamento tubular de produtos de tomate são pouco variáveis (RAO, BOURNE, COOLEY, 1981). Seu valor aumenta com o aumento do tamanho das partículas em suspensão (YOO, RAO, 1994).

A tensão de cisalhamento inicial (σ_0) foi modelada como função potência (BAYOD et al., 2007) ou exponencial (SHARMA et al., 1996) da concentração de sólidos insolúveis (WIS), como função potência da concentração e do inverso do tamanho das partículas em suspensão (YOO, RAO, 1994) e como função exponencial com o quadrado da concentração (RAO, BOURNE, COOLEY, 1981).

Entretanto, devido a maior simplicidade, a maioria dos trabalhos realiza modelagem da viscosidade aparente ($\eta_a = \sigma / \gamma$) em função das características dos produtos de tomate. Tanglertpaibul e Rao (1987a) modelaram a viscosidade aparente de derivados de tomate como função potência da concentração de sólidos totais, enquanto para Valencia et al. (2003) tal propriedade é função linear do conteúdo de sólidos insolúveis e potência do tamanho das partículas em suspensão. Tanglertpaibul e Rao (1987b) modelaram a viscosidade aparente como uma função potência do conteúdo de polpa e linear da viscosidade aparente do soro. Esta, por sua vez, foi modelada como uma função potência do conteúdo de pectina, uma vez que a influência da concentração de sólidos solúveis no soro é muito baixa. Yoo e Rao (1994) modelaram a viscosidade aparente como função exponencial em relação ao conteúdo de polpa, ou combinação linear da viscosidade aparente do soro e polinômio do conteúdo e inverso do tamanho da polpa. A relação da viscosidade aparente com a temperatura foi modelada através da Equação de Arrhenius (RAO, COOLEY, LIAO, 1999), podendo conter termo de função potência de concentração (RAO, BOURNE, COOLEY, 1981).

Em relação às suas características viscoelásticas, os produtos de tomate se comportam como géis fracos, apresentando módulo de armazenamento maior que o de dissipação (G’ > G’’) (YILMAZ et al., 2011; LOPEZ-SANCHEZ et al.; 2011; BAYOD, WILLERS, TORNBERG, 2008; TIZIANI, VODOVOTZ, 2005b; OUDEN, VLIET, 2002; VALENCIA et al., 2004; SÁNCHEZ et al., 2002; MIZRAHI, 1997; YOO, RAO, 1996; RAO, COOLEY, 1992). Na aplicação de baixas tensões o sistema se deforma elasticamente com determinada rigidez; ao se aplicar uma tensão acima de σ_0 o fluido se deforma continuamente, como um fluido viscoso (BAYOD et al., 2007).

Os parâmetros viscoelásticos dos produtos de tomate (G’ e G’’) foram modelados por Yoo e Rao (1996) e Rao e Cooley (1992) como função potência da frequência de oscilação (ω). Yoo e Rao (1996) modelam a resposta de produtos de tomate ao teste de fluência (*creep compliance*) através de modelo mecânico com associações entre molas (elemento sólido ideal, que obedece a Lei de Hooke) e amortecedores (elemento fluido ideal, que obedece a Lei de Newton). Os produtos concentrados de tomate puderam ser bem descritos por modelo de Maxwell generalizado de seis elementos, com um parâmetro puramente elástico, um puramente viscoso e dois corpos Kelvin-Voigt associados.

Os produtos de tomate não seguem diretamente a Regra de Cox-Merz (YILMAZ et al., 2011; RAO, COOLEY, 1992). A Regra de Cox-Merz conjectura sobreposição das curvas de viscosidade aparente e complexa em condição de taxa de deformação e frequência de oscilação iguais ($\eta_a(\gamma) = \eta^*(\omega)\ |_{\gamma=\omega}$ – Rao, 2005), possibilitando assim a estimativa de valores de propriedades em cisalhamento estacionário à partir de experimentos de cisalhamento dinâmico e vice-versa (RAO, 1999; RAO, COOLEY, 1992). Embora a regra tenha sido confirmada experimentalmente para diversas dispersões e soluções de polímeros (GUNASEKARAN, AK, 2000), em sistemas complexos como alimentos em geral é necessária sua modificação através de uma função linear ($\eta_a(\gamma) = \eta^*(\alpha\cdot\omega)\ |_{\gamma=\omega}$) ou potência ($k\cdot\eta_a^{\alpha}(\gamma) = \eta^*(\omega)\ |_{\gamma=\omega}$) (RAO, 2005; GUNASEKARAN, AK, 2000; RAO, COOLEY, 1992).

A maioria dos trabalhos consideram as características reológicas de produtos de tomate independentes do tempo, embora Bayod et al. (2007), Tiziani e Vodovotz (2005a), Tiziani e Vodovotz (2005b), Vercet et al. (2002) e Mizrahi (1997) apresentam comportamentos dependentes do tempo (tixotrópico e reopéctico). Tal dependência se deve às mudanças estruturais no produto devido ao cisalhamento (RAMOS, IBARZ, 1998), isto é, destruição da estrutura interna durante a deformação (CEPEDA, VILLARÁN, IBARZ, 1999). Dessa forma, a caracterização reológica dependente do tempo é de extrema importância para o entendimento das alterações que ocorrem no produto devido ao processamento. Entretanto, Bayod et al. (2007) e Hayes, Smith e Morris (1998) observam que tal caracterização é rara na literatura para produtos de tomate.

A maioria dos estudos realiza avaliações pouco objetivas da dependência do tempo das características reológicas. Bayod et al. (2007), Tiziani e Vodovotz

(2005a) e Vercet et al. (2002) observaram a redução da viscosidade aparente de produtos de tomate ao longo do tempo. Tiziani e Vodovotz (2005a e2005b) e Vercet et al. (2002) observaram apenas qualitativamente a área de histerese nos ciclos de aumento e redução da taxa de deformação. Trabalhos mais amplos foram feitos por Mizrahi (1997). Mizrahi (1997) modelou tal dependência, observando queda da viscosidade aparente de tomates com o tempo seguindo uma cinética de primeira ordem.

A modelagem matemática de propriedades reológicas é essencial para o dimensionamento de processos e produtos. Embora diversos trabalhos ajustem os dados obtidos em determinada condição em modelos de escoamento, poucos realizam modelagem das propriedades reológicas de produtos de tomate em relação aos parâmetros do produto e processo. Nenhum trabalho avalia de forma sistemática a influência do processo de homogeneização nas propriedades reológicas desses produtos. Observa-se, portanto, a necessidade de melhor entendimento da influência dos parâmetros de processo nas propriedades reológicas de produtos de tomate.

1.3.3. Efeito da homogeneização nas características reológicas de produtos de tomate

A ação de tensões decorrentes de solicitações mecânicas possuem duas consequências no comportamento reológico de produtos de tomate: quando em níveis menores, como em agitações e processo de concentração em evaporadores, observa-se redução de consistência, provavelmente devido a quebra de agregados e menor interação entre partículas; quando em níveis maiores, como em processos de homogeneização, observa-se aumento da consistência (BERESOVSKY, KOPELMAN, MIZRAH, 1995).

A homogeneização aumenta a consistência de produtos de tomate (COLLE et al., 2011; BAYOD et al., 2007; OUDEN, VLIET, 2002; OUDEN, VLIET, 1997; BERESOVSKY, KOPELMAN, MIZRAH, 1995; THAKUR, SINGH, HANDA, 1995; BECKER et al., 1987; FODA, MCCOLLUM, 1970; WHITTENBERG, NUTTING,

1958) e o valor de tensão de cisalhamento inicial (σ_0) (BAYOD, WILLERS, TORNBERG, 2008; OUDEN, VLIET, 1997), pouco afetando as características viscoelásticas (OUDEN, VLIET, 2002).

A separação de soro ocorre mais rapidamente em suspensões não homogeneizadas do que em homogeneizadas (OUDEN, VLIET, 2002; THAKUR, SINGH, HANDA, 1995), uma vez que as células quebradas possuem dificuldade em se compactar (HAYES, SMITH, MORRIS, 1998). De fato, Hayes, Smith e Morris (1998) recomendam o processo de homogeneização em pressões de 6-10 MPa e temperatura de 66ºC como método de redução da separação de soro em produtos de tomate. Observa-se que a separação de soro é um atributo sensorial bastante negativo para derivados de tomate, como o ketchup por exemplo.

As diferenças no comportamento reológico dos produtos devido à homogeneização podem ser atribuídos a diversos fatores como a fração volumétrica de sólidos (ϕ), tipo, tamanho, características geométricas, número, orientação e deformabilidade das partículas em suspensão (BAYOD et al., 2007).

Enquanto as suspensões não homogeneizadas são formadas por células inteiras e material celular disperso, com forma quase esférica; após homogeneização as suspensões são formadas por material celular deformado, com tendência à formação de agregados fibrosos (BAYOD et al., 2007; HAYES, SMITH, MORRIS, 1998; WHITTENBERG, NUTTING, 1958). Bayod, Willers e Tornberg (2008) e Ouden e Vliet (1997) observaram também que as diferentes frações do tomate apresentam diferentes susceptibilidades à quebra durante o processo de homogeneização.

A redução do tamanho das partículas resulta em maior quantidade de partículas em um mesmo volume, com consequente menor distância entre elas e maior interação (YOO, RAO, 1994), além de maior área de superfície devido à fragmentação celular, contribuindo para o aumento da consistência (WHITTENBERG, NUTTING, 1958). Partículas de polpa em suspensão assimétricas ou com superfície mais rugosa apresentam maior resistência ao escoamento e consistência (HAYES, SMITH, MORRIS, 1998; OUDEN, VLIET, 1997). Becker et al. (1987) observaram ligação direta entre a proporção de células quebradas devido à redução do pH e ao aumento da consistência em produtos de tomate. Análise reológica desenvolvida por Yoo e Rao (1994) demonstra que as partículas em suspensão em concentrados de tomate possuem formato irregular e/ou superfícies rugosas, o que em parte explica o aumento da consistência de produtos homogeneizados.

Bayod e Tornberg (2011) estudaram a microestrutura de suspensões de tomate homogeneizadas a 9 MPa, observando aumento da área das superfícies das partículas e fração volumétrica e redução do tamanho das partículas em suspensão. Bayod et al. (2007) observaram redução do tamanho das partículas em suspensão e consequente aumento na consistência de concentrados de tomate devido a homogeneização à 9 MPa. Os autores observaram que a tensão de cisalhamento inicial (σ_0) também aumentou com a homogeneização. Entretanto, a relação de σ_0 com a concentração de sólidos insolúveis (WIS) passou de uma função potência de 2,5 para 2,0 depois do processo, o que indica menor dependência da composição.

Thakur, Singh e Handa (1995) estudaram o efeito da homogeneização (até 40 MPa) na consistência de sucos de tomates, porém analisando o comportamento reológico apenas por método empírico (utilização de pipeta de Libby). A consistência de sucos de tomate aumentou com o aumento da pressão de homogeneização até cerca de 20 MPa, mantendo-se então constante até 40 MPa. Maiores temperaturas de homogeneização resultam em menor consistência do produto, não tendo efeito sobre a consistência do soro. Sucos processados por trituração a quente apresentaram maior aumento de consistência em relação aos triturados a frio, indicando que as pectinas possuem importância nesse comportamento. No entanto, segundo os autores, a homogeneização não afeta a consistência do soro (embora não apresentem os dados). Observa-se que, devido à limitação do método empírico utilizado por Thakur, Singh e Handa (1995), não se pode afirmar que as características reológicas desses produtos não variam em processos entre 20 MPa e 40 MPa.

Floury et al. (2002) avaliaram as modificações reológicas de suspensões de metilcelulose submetidas ao processo de HAP (até 350 MPa). As soluções apresentaram redução do comportamento pseudoplástico e índice de consistência com o aumento das pressões utilizadas, sendo as principais alterações observadas em pressões de até 150 MPa. Resultado semelhante foi obtido na avaliação da viscosidade intrínseca das suspensões, indicando a quebra de ligações covalentes nas cadeias dos polímeros, confirmada por cromatografia de exclusão por tamanho. Os autores observaram que as forças mecânicas decorrentes da passagem do fluido pressurizado pela válvula de homogeneização resultam na quebra das ligações covalentes, e consequente redução da consistência de suas suspensões. Resultados semelhantes foram observados por Lagoueyte e Paquin (1998) para goma xantana.

À partir dos resultados obtidos por Wang et al. (2011), Harte e Venegas (2010), Floury et al. (2002), Corredig e Wicker (2001) e Lagoueyte e Paquin (1998), é de se esperar que a consistência do soro de tomate seja reduzida com o processo de homogeneização, embora nenhum trabalho realize tal avaliação. O balanço entre as alterações estruturais e de consistência do processo na polpa e no soro irão caracterizar a influência do processo no produto final.

1.3.4. Considerações finais

Embora diversos trabalhos afirmem que a homogeneização aumenta a consistência de produtos de tomate (COLLE et al., 2011; BAYOD et al., 2007; OUDEN, VLIET, 2002; OUDEN, VLIET, 1997; BERESOVSKY, KOPELMAN, MIZRAH, 1995; THAKUR, SINGH, HANDA, 1995; BECKER et al., 1987; FODA, MCCOLLUM, 1970; WHITTENBERG, NUTTING, 1958), não se encontra na literatura estudo detalhado do efeito das condições do processo de homogeneização nas características reológicas de produtos de tomate.

A maioria dos trabalhos citados realiza avaliação apenas antes e depois da realização do processo em apenas uma determinada condição, definida empiricamente. O trabalho de Thakur, Singh e Handa (1995), embora avalie o efeito da pressão de homogeneização (até 40 MPa), realiza avaliação apenas com medidas empíricas de consistência, não elucidando a verdadeira influência desse processo no comportamento reológico desses produtos. O trabalho de Bayod et al. (2007) utiliza pressões de até 9 MPa, enquanto o de Bayod, Willers e Tornberg (2008) não cita as condições do processo. Ouden e Vliet (2002) e Ouden e Vliet

(1997) apenas comparam produtos homogeneizados (8 MPa e 20 MPa) e não homogeneizados, quanto a tensão de cisalhamento inicial (σ_0) e viscosidade aparente. A influência das condições de processo, em especial temperatura de processo e pressão de homogeneização, não está completamente elucidada. Destaca-se assim a importância do presente trabalho avaliar e modelar a influência desses fatores nas características reológicas de produtos de tomate.

1.4. Referências

AGUILÓ-AGUAYO, I.; SOLIVA-FORTUNY, R.; MARTÍN-BELLOSO, O. Changes in viscosity and pectolytic enzymes of tomato and strawberry juices processed by high-intensity pulsed electric fields. **International Journal of Food Science and Technology**, v.44, p.2268-2277, 2009.

AKBUDAK, B. Effects of harvest time on the quality attributes of processed and non-processes tomato varieties. **International Journal of Food Science and Technology**, v.45, p.334-343, 2010.

ALIBERTI, N. C. M. **Influência da Homogeneização a Alta Pressão Sobre a Retenção de Antocianinas Presentes na Polpa de Açaí (*Euterpe oleraceae* Mart.).** Tese (Doutorado em Engenharia) - Universidade de São Paulo, 2009.

BAYOD, E.; MÅNSSON, P.; INNINGS, F.; BERGENSTÅHL, B.; TORNBERG, E. Low shear rheology of concentrated tomato products. Effect of particle size and time. **Food Biophysics**, v.2, p.146-157, 2007.

BAYOD, E.; TORNBERG, E. Microstructure of highly concentrated tomato suspensions on homogenization and subsequent shearing. **Food Research International**, v.44, p.755-764, 2011.

BAYOD, E.; WILLERS, E. P.; TORNBERG, E. Rheological and structural characterization of tomato paste and its influence on the quality of ketchup. **LWT - Food Science and Technology**, v.41, p.1289-1300, 2008.

BECKER, R.; MIERS, J. C.; NUTTING, M. D.; DIETRICH, W. C.; WAGNER, J. R. Consistency of tomato products: 7, effect of acidification on cell walls and cell breakage. **Journal of Food Science**, v.37, n.1, p.118-125, 1972.

BERESOVSKY, N.; KOPELMAN, I. J.; MIZRAH, S. The role of pulp interparticle interaction in determining tomato juice viscosity. **Journal of Food Processing and Preservation**, v.19, n.2, p.133-146, 1995.

CALLIGARIS, S.; FOSCHIA, M.; BASTOLOMEOLI, I.; MAIFRENI, M.; MANZOCCO, L. Study on the applicability of high-pressure homogenization for the production of banana juices. **LWT – Food Science and Technology**, v.45, p.117-121, 2012.

CAMPOS, F ; CRISTIANINI, M . Inactivation of *Saccharomyces cerevisiae* and *Lactobacillus plantarum* in orange juice using ultra high-pressure homogenization. **Innovative Food Science & Emerging Technologies**, v.8, n.2, p. 226-229, 2007.

CEPEDA, E.; VILLARÁN, M. C.; IBARZ, A. Rheological properties of cloudy and clarified juice of *Malus flurzbunda* as a function of concentration and temperature. **Journal of Texture Studies**, v.30, p.481-491, 1999.

CHARM, S. E. The direct determination of shear stress-shear rate behavior of foods in the presence of a yield stress. **Journal of Food Science**, v.28, n.1, p.107-113, 1963.

CHOU, T. D.; KOKINI, J. L. Rheological properties and conformation of tomato paste pectins, citrus and apple pectins. **Journal of Food Science**, v.52, n.6, p.1658-1664, 1987.

COLLE, I. J. P.; ANDRYS, A.; GRUNDELIUS, A.; LEMMENS, L.; LÖFGREN, A.; BUGGENHOUT, S. V.; LOEY, A. V.; HENDRICKX, M. Effect of pilot-scale aseptic processing on tomato soup quality parameters. **Journal of Food Science**, v.76, n.5, p.C714-C723, 2011.

CORBO, M. R.; BEVILACQUA, A.; CAMPANIELLO, D.; CICCARONE, C.; SINIGAGLIA, M. Use of high pressure homogenization as a mean to control the growth of foodborne moulds in tomato juice. **Food Control**, v.21, p.1507-1511, 2010.

CORREDIG, M.; WICKER, L. Changes in the molecular weight distribution of three commercial pectins after valve homogenization. **Food Hydrocolloids**, v.15, p.17-23, 2001.

DAK, M.; VERMA, R. C.; JAAFFREY, S. N. A. Rheological properties of tomato concentrate. **International Journal of Food Engineering**, v.4, n.7, article 11, 2008.

DONSÌ, F.; ESPOSITO, L.; LENZA, E.; SENATORE, B.; FERRARI, G. Production of self-stable Annurca apple juice with pulp by high pressure homogenization. **International Journal of Food Engineering**, v.5, n.4, article 12, 2009.

FARAHNAKY, A.; MAJDINASAB, M.; MAJZOOBI, M.; MESBAHI, G. A comparative study of physicochemical and rheological properties of iranian tomato pastes. **International Journal of Food Engineering**, v.6, n.1, article 5, 2010.

FLOURY, J.; BELLETTRE, J. ; LEGRAND, J.; DESRUMAUX, A. Analysis of a new type of high pressure homogeniser. A study of the flow pattern. **Chemical Engineering Science**, v.59, p.843-853, 2004.

FLOURY, J.; DESRUMAUX, A.; AXELOS, M. A.V.; LEGRAND, J. Degradation of methylcellulose during ultra-high pressure homogenisation. **Food Hidrocolloids**, v.16, p.47-53, 2002.

FODA, Y. M.; MCCOLLUM, J. P. Viscosity as affected by various constituents of tomato juice. **Journal of Food Science**, v.35, p.333-338, 1970.

GUNASEKARAN, S.; AK, M. M. Dynamic oscillatory shear testing of foods – selected applications. **Trends in Food Science and Technology**, v.11, p.115-127, 2000.

HAND, D. B.; MOYER, J. C.; RANSFORD, J. R.; HENING, J. C.; WHITTENBERG, R. T. Effect of processing conditions on the viscosity of tomato juice. **Food Technology**, v.9, n.5, p.228-235, 1955.

HARTE, F.; VENEGAS, R. A model for viscosity reduction in polysaccharides subjected to high-pressure homogenization. **Journal of Texture Studies**, v.41, p.49–61, 2010.

HAYES, W. A.; SMITH, P. G.; MORRIS, A. E. J. The production and quality of tomato concentrates. **Critical Reviews in Food Science and Nutrition**, v. 38, n.7, p.537-564, 1998.

HSU, K. C. Evaluation of processing qualities of tomato juice induced by thermal and pressure processing. **LWT - Food Science and Technology**, v.41, p.450-459, 2008.

IBARZ, A.; BARBOSA-CÁNOVAS, G. V. **Unit Operations in Food Engineering**. Boca Raton: CRC Press, 2003.

INNINGS, F.; FUCHS, L.; TRÄGÅRDH, C. Theoretical and experimental analyses of drop deformation and break-up in a scale model of a high-pressure homogenizer. **Journal of Food Engineering**, v.103, p.21-28, 2011.

INSTITUTO BRASILEIRO DE GEOGRAFIA E ESTATÍSTICA (IBGE). **Censo Agropecuário 2006**. Rio de Janeiro: IBGE, 2009.

KAUR, C.; GEORGE, B.; DEEPA, N.; JAGGI, S.; KAPOOR, H. C. Viscosity and quality of tomato juice as affected by processing methods. **Journal of Food Quality**, v.30, p.864-877, 2007.

LACROIX, N.; FLISS, I.; MAKHLOUE, J. Inactivation of pectin methylesterase and stabilization of opalescence in orange juice by dynamic high pressure. **Food Research International**, v.38, p.569-76, 2005.

LAGOUEYTE, N.; PAQUIN, P. Effects of microfluidization on the functional properties of xanthan gum. **Food Hydrocolloids**, v.12, p.365-371, 1998.

LOPEZ-SANCHEZ, P.; SVELANDER, C.; BIALEK, L.; SCHUMM, S.; LANGTON, M. Rheology and microstructure of carrot and tomato emulsions as a result of high-pressure homogenization conditions. **Journal of Food Science**, v.76, n.1, p.E130-E140, 2011.

MARESCA, P.; DONSÌ, F.; FERRARI, G. Application of a multi-pass high-pressure homogenization treatment for the pasteurization of fruit juices. **Journal of Food Engineering**, v.104, p.364-372, 2011.

MASSON, L. M. P.; ROSENTHAL, A.; CALADO, V. M. A.; DELIZA, R.; TASHIMA, L. Effect of ultra-high pressure homogenization on viscosity and shear stress of fermented dairy beverage. **LWT - Food Science and Technology**, v.44, p.495-501, 2011.

MCCARTHY, K. L.; MCCARTHY, M. J. Relationship between in-line viscosity and Bostwick measurement during ketchup production. **Journal of Food Science**, v.74, n.6, p.E291-E297, 2009.

MELO, P. C. T.; VILELA, N. J. Desafios e perspectivas para a cadeia brasileira do tomate para processamento industrial. **Horticultura Brasileira***,* v.23, n.1, p.154-157, 2005.

MIZRAHI, S. Irreversible shear thinning and thickening of tomato juice. **Journal of Food Process and Preservation**, v.21, p.267-277, 1997.

MOHR, W. P. Tomato fruit properties affecting consistency of concentrated product. **Canadian Journal of Plant Science**, v.67, p.881-890, 1987a.

MOHR, W. P. Measuring consistency of tomato thin pulp and puree. **Canadian Journal of Plant Science**, v.67, p.919-921, 1987b.

NISHA, P.; SINGHAL, R. S.; PANDIT, A. B. Kinetic modelling of colour degradation in tomato puree (*Lycopersicon esculentum* L.). **Food and Bioprocess Technology**, *in press*, 2010. DOI:10.1007/s11947-009-0300-1.

NOOMHORM, A.; TANSAKUL, A. Effect of pulper-finisher operation on quality of tomato juice and tomato puree. **Journal of Food Process Engineering**, v.15, n.4, p.229-239, 1992.

OUDEN, F. W. C. Den; VLIET, T. Van. Particle size distribution in tomato concentrate and effects on rheological properties. **Journal of Food Science**, v.62, n.3, p.565-567, 1997.

OUDEN, F. W. C. Den; VLIET, T. Van. Effect of concentration on the rheology and serum separation of tomato suspensions. **Journal of Texture Studies**, v.33, p.91-104, 2002.

PATHANIBUL, P.; TAYLOR, T. M.; DAVIDSON, P. M.; HARTE, F. Inactivation of *Escherichia coli* and *Listeria innocua* in apple and carrot juices using high pressure homogenization and nisin. **International Journal of Food Microbiology**, v.129, p.316-320, 2009.

PATRIGNANI, F.; VANNINI, L.; KAMDEM, S. L. S.; LANCIOTTI, R.; GUERZONI, M. E. Effect of high pressure homogenization on *Saccharomyces cerevisiae* inactivation and physic-chemical features in apricot and carrot juices. **International Journal of Food Microbiology**, v.136, p.26-31, 2009.

PATRIGNANI, F.; VANNINI, L.; KAMDEM, S. L. S.; LANCIOTTI, R.; GUERZONI, M. E. Potentialites of high pressure homogenization to inactivate *Zygosaccharomyces bailii* in fruit juices. **Journal of Food Science**, v.75, n.2, p.M116-M120, 2010.

PÉREZ-CONESA, D.; GARCÍA-ALONSO, J.; GARCÍA-VALVERDE, V.; INIESTA, M. D.; JACOB, K.; SÁNCHEZ-SILES, L. M.; ROS, G.; PERIAGO, M. J. Changes in bioactive compounds and antioxidant activity during homogenization and thermal processing of tomato puree. **Innovative Food Science and Emerging Technologies**, v.10, p.179-188, 2009.

PICKARDT, C.; DONGOWSKI, G.; KUNZEK, H. The influence of mechanical and enzymatic disintegration of carrots on the structure and properties of cell wall materials. **European Food Research and Technology**, v.219, p.229-239, 2004.

PINHO, C. R. G.; FRANCHI, M. A.; AUGUSTO, P. E. D.; CRISTIANINI, M. Avaliação do escoamento de leite desnatado durante homogeneização a alta pressão (HAP) por meio de fluidodinâmica computacional (CFD). **Brazilian Journal of Food Technology**, v.14, n.3, p.232-240, 2011.

RAMOS, A. M.; IBARZ, A. Thixotropy of orange concentrate and quince puree. **Journal of Texture Studies**, v.29, p.313-324, 1998.

RAO, M. A. Rheology of liquid foods – a review. **Journal of Texture Studies**, v.8, p.135-168, 1977.

RAO, M. A. Flow and Functional Models for Rheological Properties of Fluid Foods. In: RAO, M. A. **Rheology of Fluid and Semisolid Foods: Principles and Applications**. Gaithersburg: Aspen Publishers, 1999.

RAO, M. A. Rheological Properties of Fluid Foods. In: RAO, M. A.; RIZVI, S. S. H.; DATTA, A. K. **Engineering Properties of Foods**. Boca Raton: CRC Press, 3rd ed., 2005.

RAO, M. A.; BOURNE, M. C.; COOLEY, H. J. Flow properties of tomato concentrates. **Journal of Texture Studies**, v.12, n.4, p.521-538, 1981.

RAO, M. A.; COOLEY, H. J. Rheological behavior of tomato pastes in steady and dynamic shear. **Journal of Texture Studies**, v.23, p.415-425, 1992.

RAO, M. A.; COOLEY, H. J.; LIAO, H. J. High temperature rheology of tomato puree and starch dispersion with a direct-drive viscometer. **Journal of Food Process Engineering**, v.22, p.29-40, 1999.

SAHIN, H.; OZDEMIR, F. Effect of some hydrocolloids on the rheological properties of different formulated ketchups. **Food Hydrocolloids**, v.18, p.1015-1022, 2004.

SALDO, J.; SUÁREZ-JACOBO, Á.; GERVILLA, R.; GUAMIS, B.; ROIG-SAGUÉS, A. X. Use of ultra-high-pressure homogenization to preserve apple juice without heat damage. **High Pressure Research**, v.29, n.1, p.52-56, 2009.

SÁNCHEZ, M. C.; VALENCIA, C.; CIRUELOS, LATORRE, A.; GALLEGOS, C. Rheological properties of tomato paste: influence of the addition of tomato slurry. **Journal of Food Science**, v.68, n.2, p.551-554, 2003.

SÁNCHEZ, M. C.; VALENCIA, C.; GALLEGOS, C.; CIRUELOS, A.; LATORRE, A. Influence of processing on the rheological properties of tomato paste. **Journal of the Science of Food and Agriculture**, v.82, p.990-997, 2002.

SENTANDREU, E.; GURREA, M. C.; BETORET, N.; NAVARRO, J. L. Changes in orange juice characteristics due to homogenization and centrifugation. **Journal of Food Engineering**, v.105, p.241-245, 2011.

SHARMA, S. K.; LEMAGUER, M.; LIPTAY, A.; POYSA, V. Effect of composition on the rheological properties of tomato thin pulp. **Food Research International**, v.29, n.2, p.175-179, 1996.

SILVA, V. M.; SATO, A. C. K.; BARBOSA, G.; DACANAL, G.; CIRO-VELÁSQUEZ, H. J.; CUNHA, R. L. The effect of homogenisation on the stability of pineapple pulp. **International Journal of Food Science and Technology**, v.45, n.10, p.2127-2133, 2010.

SINCHAIPANIT, P.; KERR, W. L. Effect of reducing pulp-particles on the physical properties of carrot juice. **ASEAN Food Journal**, v.14, n.3, p.205-214, 2007.

SUÁREZ-JACOBO, Á.; SALDO, J.; RUFER, C. E.; GUAMIS, B.; ROIG-SAGUÉS, A. X.; GERVILLA, R. Aseptically packaged UHPH-treated apple juice: safety and quality parameters during storage. **Journal of Food Engineering**, v.109, p.291-300, 2012.

TAHIRI, I.; MAKHLOUF, J.; PAQUIN, P.; FLISS, I. Inactivation of food spoilage bacteria and *Escherichia coli* O157:H7 in phosphate buffer and orange juice using dynamic high pressure. **Food Research International**, v.39, p.98-105, 2006.

TAKADA, N.; NELSON, P. E. Pectin-protein interaction in tomato products. **Journal of Food Science**, v.48, n.5, p.1408-1411, 1983.

TANGLERTPAIBUL, T.; RAO, M. A. Rheological properties of tomato concentrates as affected by particle size and methods of concentration. **Journal of Food Science**, v.52, n.1, p.141-145, 1987a.

TANGLERTPAIBUL, T.; RAO, M. A. Flow properties of tomato concentrates: effect of serum viscosity and pulp content. **Journal of Food Science**, v.52, n.2, p.318-321, 1987b.

THAKUR, B. R.; SINGH, R. K.; HANDA, A. K. Effect of homogenization pressure on consistency of tomato juice. **Journal of Food Quality**, v.18, n.389-396, 1995.

TIZIANI, S.; VODOVOTZ, Y. Rheological characterization of a novel functional food: tomato juice with soy germ. **Journal of Agricultural and Food Chemistry**, v.53, p7267-7273, 2005a.

TIZIANI, S.; VODOVOTZ, Y. Rheological effects of soy protein addition to tomato juice. **Food Hydrocolloids**, v.19, n.1, p.45-52, 2005b.

TRIBST, A. A. L. **Efeito do Processamento por Alta Pressão Dinâmica Combinado com Tratamento térmico Brando na Inativação de *Aspergillus Niger* em Néctar de Manga.** Dissertação (Mestrado em Tecnologia de Alimentos) - Universidade Estadual de Campinas, 2008.

TRIBST, A. A. L.; FRANCHI, M. A.; CRISTIANINI, M. MASSAGUER, P. R. Inactivation of *Aspergillus niger* in mango nectar by high-pressure homogenization combined with heat shock. **Journal of Food Science**, v.74, n.9, p.M509-M514, 2009.

TRIBST, A. A. L.; FRANCHI, M. A.; CRISTIANINI, M. MASSAGUER, P. R. Quality of mango nectar processed by high-pressure homogenization with optimized heat treatment. **Journal of Food Science**, v.76, n.2, p.M106-M110, 2011.

VALENCIA, C.; SÁNCHEZ, M. C.; CIRUELOS, A.; GALLEGOS, C. Influence of tomato paste processing on the linear viscoelasticity of tomato ketchup. **Food Science and Technology International**, v.10, n.2, p.95-100, 2004.

VALENCIA, C.; SÁNCHEZ, M. C.; CIRUELOS, A.; LATORRE, A.; MADIEDO, J. M.; GALLEGOS, C. Non-linear viscoelasticity modeling of tomato paste products. **Food Research International**, v.36, p.911-919, 2003.

VERCET, A.; SÁNCHEZ, C.; BURGOS, J.; MONTAÑÉS, L.; BUESA, P. L. The effects of manothermosonication on tomato pectic enzymes and tomato paste rheological properties. **Journal of Food Engineering**, v.53, p.273-278, 2002.

VITALI, A. A.; RAO, M. A. Flow behavior of guava puree as a function of temperature and concentration. **Journal of Texture Studies**, v.13, n.3, p.275-289, 1982.

Wang, Y.; Dong, L.; Wang, L. J.; Xue, J. (2011). Effects of high pressure homogenization on rheological properties of flaxseed gum. **Carbohydrate Polymers**, v.83, p.489–494, 2011.

WELTI-CHANES, J.; OCHOA-VELASCO, C.E.; GUERRERO-BELTRÁN, J. Á. High pressure homogenization of orange juice to inactivate pectinmethylesterase. **Innovative Food Science & Emerging Technologies**, v.10, p.457-462, 2009.

WHITTENBERG, R. T.; NUTTING, G. C. Effect of tomato cell structures on consistency of tomato juice. **Food Technology**, v.11, p.19-22, 1957.

WHITTENBERG, R. T.; NUTTING, G. C. High viscosity of cell wall suspensions prepared from tomato juice. **Food Technology**, v.12, p.420-422, 1958.

YILMAZ, M. T.; KARAMAN, S.; CANKURT, H.; KAYACIER, A.; SAGDIC, O. Steady and dynamic oscillatory shear rheological properties of ketchup-processed cheese mixtures: effect of temperature and concentration. **Journal of Food Engineering**, v.103, p.197-210, 2011.

YOO, B.; RAO, M. A. Effect of unimodal particle size and pulp content on rheological properties of tomato puree. **Journal of Texture Studies**, v.25, n.4, p.421-436, 1994.

YOO, B.; RAO, M. A. Creep and dynamic rheological behavior of tomato concentrates: effect of concentration and finisher screen size. **Journal of Texture Studies**, v.27, n.4, p.451-459, 1996.

Chapter 2: Rheological Behavior of Tomato Juice: Steady-State Shear and Time-Dependent Modeling

This chapter was developed at University of Lleida, and is currently in press as:
AUGUSTO, P. E. D.; FALGUERA, V.; CRISTIANINI, M.; IBARZ, A. Rheological behavior of tomato juice: steady-state shear and time-dependent modeling. **Food and Bioprocess Technology**, *in press*, 2010.
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Abstract

Introduction The present work has evaluated the time dependent and steady-state shear rheological properties of tomato juice.

Materials and Methods Three models were compared for describing the shear stress decay during shearing (Figoni–Shoemaker, Weltman, and Hahn–Ree–Eyring), and the parameters of each model were empirically related with the shear rate.

Result The three evaluated models, as well as their modification as function of shear rate, described well the experimental data of tomato thixotropy. The Herschel– Bulkley and Falguera–Ibarz models have shown to be very adequate to describe the data from steady-state shear. The obtained data are potentially useful for future studies on food properties and process design.

Keywords:

Food Properties, modeling, rheology, thixotropy, tomato Juice.

Comportamento Reológico de Suco de Tomate: Modelamento das Propriedades de Cisalhamento em Estado Estacionário e Dependentes do Tempo

Resumo

Introdução O presente trabalho avaliou as propriedades reológicas dependentes do tempo e em cisalhamento em estado estacionário do suco de tomate.

Material e Métodos Comparou-se três modelos (Figoni–Shoemaker, Weltman, e Hahn–Ree–Eyring) para descrição do decaimento da tensão de cisalhamento durante deformação, sendo os parâmetros de cada modelo relacionados empiricamente com a taxa de deformação.

Resultados Os três modelos avaliados, assim como suas modificações como função da taxa de deformação, descreveram bem os dados experimentais de tixotropia do suco de tomate. Os modelos de Herschel–Bulkley e Falguera–Ibarz se mostraram adequados para descrever os dados de cisalhamento em estado estacionário. Os dados obtidos são bastante úteis para futuros estudos de propriedades de alimentos e desenvolvimento de processos.

Palavras-chave:

Modelagem, propriedades dos alimentos, reologia, suco de tomate, tixotropia.

2.1. Introduction

Tomato is one of the most popular and widely grown vegetables in the world (Nisha et al., 2010). In fact, tomato is one of the most important vegetables for the food industry. Its products consumption is large and widely included in human diet. The rheological characterization of tomato products is important not only for unit operations design, but also for optimization process and high quality products assurance.

In fact, many studies have been published regarding the rheological characterization of tomato products. However, data presented in literature are very variable (Bayod et al., 2007) and concentrated only in steady-state shear stress measurements. Many studies have just considered one-condition measurement (just apparent viscosity evaluation) or empiric methods of evaluation (as the Bostwick consistometer).

Time dependence is related to the structural change due to shear (Ramos and Ibarz, 1998), i.e., the destruction of internal structure during flow (Cepeda et al., 1999). Consequently, time dependent rheological characterization is extremely important for understanding the products changes that occur during the process. However, these characterizations are rare in the literature for tomato products (Bayod et al., 2007. Hayes et al., 1998).

Mizrahi (1997) has modeled the apparent viscosity reduction with time subjecting the product to constant shear rate. The apparent viscosity decay was well modeled by a first-order kinetic (i.e., $d\eta_a / dt = -k \cdot t$). However, other studies have carried out little objective evaluations. Bayod et al. (2007), Tiziani and Vodovotz (2005a) and Vercet et al. (2002) observed a reduction in apparent viscosity of tomato products over time, obtained in an experiment of constant shear stress or shear rate. Tiziani and Vodovotz (2005a and 2005b) and Vercet et al. (2002) observed only qualitatively the hysteresis area in the cycle of increase and decrease of the shear rate.

Thus, it is a lack of information concerning the time-dependent rheological properties of tomato juice, as well as its modeling as function of shear rate.

Moreover, although the Herschel-Bulkley has been widely used for modeling tomato products steady-state shear properties, a recently proposed rheological model (Falguera and Ibarz, 2010) has not yet been evaluated for tomato products.

This work has evaluated the time-dependent rheological properties of tomato juice, comparing three models for describing the shear stress decay during shearing (Figoni-Shoemaker, Weltman and Hahn-Ree-Eyring). Moreover, the steady-state shear behavior of the tomato juice was evaluated by comparing two models (Herschel-Bulkley and Falguera-Ibarz).

2.2. Materials and Methods

A commercial tomato juice produced in Spain was used in order to guarantee the standardization and repeatability. The product is salt aditionated and is aseptically packaged after thermal process. Its soluble solids content were determinated by using a refractometer, while its total solid content was measured by drying the samples in a vacuum oven at 70ºC (five replicates).

The rheological evaluation was carried out with new samples, with no mechanical history. Thus, samples were placed in the rheometer and kept at rest for 10 min before start shearing.

Rheological measurements were carried out in a Haake RS 80 rheometer with controlled stress (σ), using a Couette geometry (concentric cylinder; Haake Z40-DIN). The cup and bob radius ratio was 1.0847 (bob radius = 20.000 ± 0.004 mm). Temperature was maintained constant by using a water-bath (Phoenix ThermoHaake C25P) with deviation lower than ±0.3°C.

The experiments were carried out in three replicates, and the regressions were done for each replicate. The parameters of each model were obtained by non-linear regression using the software Stat-Graphics Plus v. 5.1 (Statistical Graphics Corp), and using a significant probability level of 95%.

The goodness of the models was evaluated by plotting the values of shear stress obtained by models (σ_{model}) as function of the experimental values

($\sigma_{experimental}$). The regression of those data to a linear function (Equation 2.1) results in three parameters that that can be used to evaluated the description of the experimental values by the models, i.e., the linear inclination (a; that must be as close as possible to the unit), the intercept (b; that must be as close as possible to zero) and the coefficient of determination (R^2; that must be as close as possible to the unit).

$$\sigma_{model} = a \cdot \sigma_{experimental} + b \qquad \text{(Equation 2.1)}$$

2.2.1. Time-dependent shear modeling

After rest, the samples were sheared at constant shear rate (γ, at 50, 100, 250, 400 and 500 s^{-1}) for 1000 s, while the shear stress were measured. Temperature was maintained constant at 25ºC.

The shear stress decay was evaluated by three models, widely used for describing the thixotropy in foods (Ibarz and Barbosa-Cánovas, 2003). The evaluated models were the Figoni and Shoemaker (Figoni and Shoemaker, 1983: Equation 2.2), Weltman (Weltman, 1943; Equation 2.3) and Hahn, Ree and Eyring (Hahn et al., 1959; Equation 2.4). The kinetic parameters were obtained by non-linear regression using the software Stat-Graphics Plus v. 5.1 (Statistical Graphics Corp) using a significant probability level of 95%, and then evaluated as function of shear rate.

$$\sigma = \sigma_e + (\sigma_0 - \sigma_e) \cdot \exp(-k \cdot t) \qquad \text{(Equation 2.2)}$$

$$\sigma = A - B \cdot \ln t \qquad \text{(Equation 2.3)}$$

$$\ln(\sigma - \sigma_e) = A - B \cdot t \qquad \text{(Equation 2.4)}$$

2.2.2. Steady-State Shear Modeling

Once the product time dependent behavior was determined, i.e., its characteristics to flow, the steady-state shear behavior was evaluated in the temperature range of 0ºC to 80ºC. Samples were sheared at 250 s^{-1} for 250 s, predetermined condition for the elimination of product thixotropy. The shear stress data were evaluated in the shear rate range of 0.01 s^{-1} to 500 s^{-1}, and thus modeled using the Herschel-Bulkley model (Equation 2.5). The Herschel-Bulkley model comprises the Newton, Bingham and Ostwald-de-Waele (power law) models, and is being widely used for describing the rheological properties of food products.

$$\sigma = \sigma_0 + k \cdot \gamma^n \qquad \text{(Equation 2.5)}$$

The tomato juice flow behavior was also evaluated by using another rheological model, recently proposed by Falguera and Ibarz (2010). In the Falguera-Ibarz model, the variation of the apparent viscosity ($\eta_a = \sigma / \gamma$) with the shear rate is described by a power decay from an initial value (η_0) to a equilibrium one (η_∞) (Equation 2.6).

$$\eta_a = \eta_\infty + (\eta_0 - \eta_\infty) \cdot \gamma^{(-k)} \qquad \text{(Equation 2.6)}$$

2.3. Results and Discussion

The tomato juice soluble solids content were 5.4±0.2ºBrix, with 5.96±0.02% (w/w) of total solids (mean of five replicates ± standard deviation).

2.3.1. Time-Dependent Shear Modeling

Figure 2.1 shows the shear stress decay of samples when sheared during 1000 s. It can be seen that tomato juice shows a thixotropic behavior in the shear rate range of 50 s^{-1} to 500 s^{-1}. In the original product, the internal structure formed by the insoluble pulp dispersed in the serum has a higher resistance to deformation, resulting in a higher shear stress. When shearing is carried out, this structure is broken, as one may notice by the stress decay. For the five shear rates evaluated it takes 250-500 s for stress stabilization.

Table 2.1 shows the mean values for the parameters of the models of Figoni and Shoemaker, Weltman and Hahn, Ree and Eyring, respectively. The value of R^2 was always higher than 90% in each replicates.

In Figoni and Shoemaker model the parameter σ_e is the equilibrium shear stress, i.e., its value after time of shearing enough to complete the break of the product internal structure. The parameter σ_0 is the initial shear stress, i.e., in the beginning of shearing, while k is related with its stress decay during time. As expected, due to the pseudoplastic nature of tomato juice, the parameters of Figoni and Shoemaker model have shown a tendency to increase with shear rate (Figure 2.2).

In Weltman model, the parameter A is related with the initial shear stress, while B is related with its stress decay. The parameter A has shown a tendency to increase with shear rate as expected due to the juice pseudoplastic behavior, while B has shown a tendency to vary closed to a mean value (Figure 2.3).

In Hahn, Ree and Eyring model, the parameter σ_e is the same as in Figoni and Shoemaker model, and B is the same as k. The initial shear stress is giving by the parameter A. While the parameters σ_e and B have shown a tendency to increase due shear rate, A has varied closed to a mean value (Figures 2.4 and 2.5).

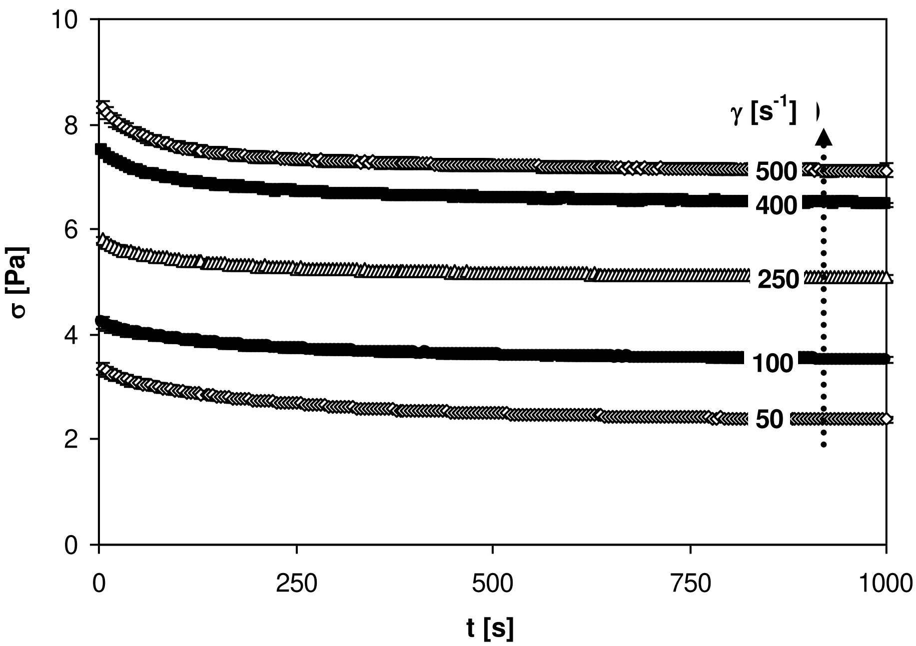

Figure 2.1. Tomato juice stress decay during shearing at 50, 100, 250, 400 and 500 s^{-1} for 1000 s. Mean of three replicates at 25ºC; vertical bars represent the standard deviation in each value.

The obtained values are in accordance with those described in the literature for fruit products, in special the parameters related with the stress decay with shearing (k in Figoni and Shoemaker model; B in Weltman and Hahn, Ree and Eyring models).

Table 2.1. Values for the parameters of Figoni and Shoemaker, Weltman and Hahn, Ree and Eyring models (mean of three replicates ± standard deviation).

γ [s^{-1}]	**Figoni & Shoemaker** $\sigma = \sigma_e + (\sigma_0 - \sigma_e) \cdot \exp(-k \cdot t)$		
	σ_e **[Pa]**	σ_0 **[Pa]**	***k*** **[s^{-1}]**
50	2.39 ± 0.10	3.26 ± 0.10	0.0043 ± 0.0002
100	3.52 ± 0.10	4.15 ± 0.10	0.0046 ± 0.0002
250	5.12 ± 0.08	5.70 ± 0.09	0.0052 ± 0.0002
400	6.55 ± 0.03	7.36 ± 0.02	0.0059 ± 0.0002
500	7.17 ± 0.10	8.17 ± 0.10	0.0077 ± 0.00015
γ [s^{-1}]	**Weltman** $\sigma = A - B \cdot \ln t$		
	A **[Pa]**	***B*** **[Pa·s^{-1}]**	
50	3.93 ± 0.12	0.228 ± 0.012	
100	4.62 ± 0.18	0.163 ± 0.027	
250	6.10 ± 0.09	0.148 ± 0.008	
400	7.87 ± 0.01	0.200 ± 0.004	
500	8.64 ± 0.10	0.227 ± 0.001	
γ [s^{-1}]	**Hahn, Ree & Eyring** $\ln(\sigma - \sigma_e) = A - B \cdot t$		
	σ_e **[Pa]**	***A*** **[Pa]**	***B*** **[Pa·s^{-1}]**
50	2.39 ± 0.05	-0.139 ± 0.052	0.0044 ± 0.0002
100	3.52 ± 0.16	-0.466 ± 0.162	0.0047 ± 0.0002
250	5.12 ± 0.04	-0.560 ± 0.035	0.0052 ± 0.0001
400	6.55 ± 0.03	-0.203 ± 0.029	0.0060 ± 0.0002
500	7.16 ± 0.01	-0.003 ± 0.005	0.0074 ± 0.0001

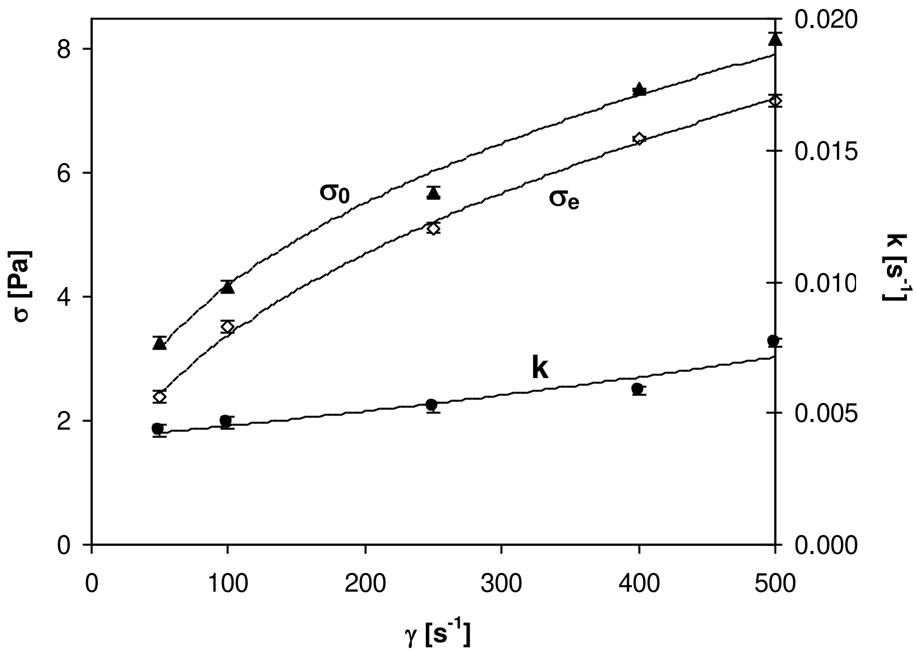

Figure 2.2. Parameters of Figoni and Shoemaker model as function of shear rate. Vertical bars are the standard deviation in each mark, and the continuous lines are the empirical regressions of Table 2.3.

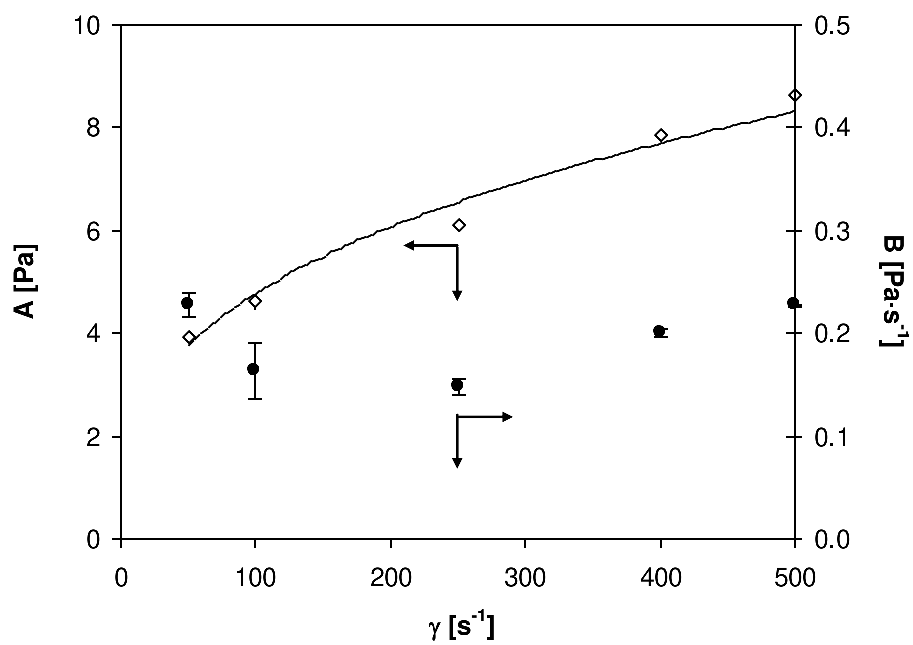

Figure 2.3. Parameters of Weltman model as function of shear rate. Vertical bars are the standard deviation in each mark, and the continuous lines are the empirical regressions of Table 2.3.

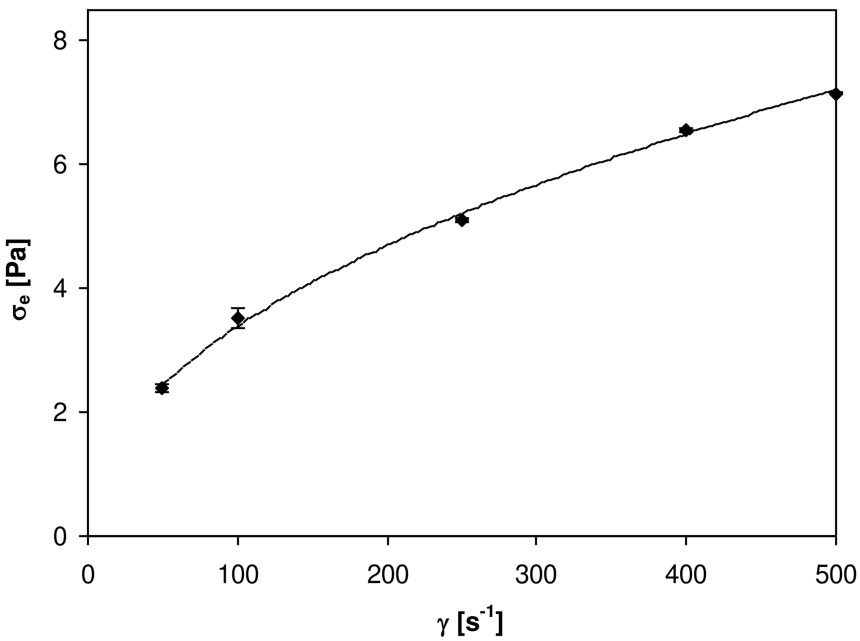

Figure 2.4. Parameter σ_e of Hahn, Ree and Eyring model as function of shear rate. Vertical bars are the standard deviation in each mark, and the continuous lines are the empirical regressions of Table 2.3.

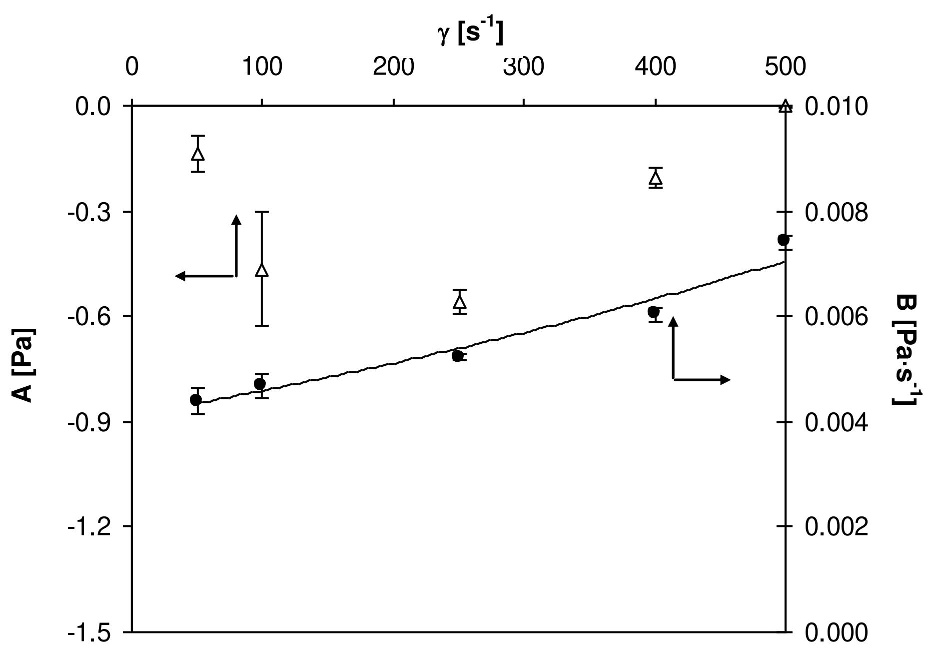

Figure 2.5. Parameters A and B of Hahn, Ree and Eyring model as function of shear rate. Vertical bars are the standard deviation in each mark, and the continuous lines are the empirical regressions of Table 2.3.

The k value of Figoni and Shoemaker model in gilaboru juice at 43ºBrix vary from 0.0027 s^{-1} to 0.0031 s^{-1} in the shear rate range of 50-150 s^{-1} (Altan, Kus and Kaya, 2005). In the same conditions, the value of B (Weltman model) vary from 0.89 $Pa \cdot s^{-1}$ to 1.17 $Pa \cdot s^{-1}$. Abu-Jdayil et al. (2004) has used the Weltman model for modeling the time dependent rheological behavior of tomato paste (5.7% solids). The B value vary from 10^{-14} - 0.0187 $Pa \cdot s^{-1}$ in the shear rate range of 2.2-79 s^{-1}. Basu et al. (2007) has modeled the shear stress decay of pineapple jams using the Hahn, Ree and Eyring model. The value of B vary from 0.0024 to 0.0094 $Pa \cdot s^{-1}$ in the shear rate range of 10-100 s^{-1}. Similar results were observed by Ravi and Bhattacharya (2006) for chickpea flour dispersions. The B value of Hahn, Ree and Eyring model vary 0.0044 to 0.0059 $Pa \cdot s^{-1}$ in the shear rate range of 5-200 s^{-1}.

The experimental data were well described by the three evaluated models, as can be seen by the regression to the Equation 2.1. The values of a and R^2 were always higher than 0.99, while the values of b were always lower than 0.03 (Table 2.2). Those models were successfully used in the characterization of concentrated mandarin juice (Falguera et al., 2010), gilaboru juice (Altan, Kus and Kaya, 2005), *Malus floribunda* juice (Cepeda et al., 1999), tomato paste (Abu-Jdayil et al., 2004), pineapple jam (Basu et al., 2007), chickpea flour dispersions (Ravi and Bhattacharya, 2006), quince puree (Ramos and Ibarz, 1998), peach and plum pulps (Lozano and Ibarz, 1994) and ketchup, mustard and baby food (Choi and Yoo, 2004).

Those parameters were then empirically modeled as function of shear rate, with the exception of the parameters A in Weltman model and B in Hahn, Ree and Eyring model, whose values were assumed to be the average of the obtained values. The modeling was obtained with high values of R^2, as demonstrated in Table 2.3.

Table 2.2. Values for the parameters a, b and R2 for the regression of the experimental values versus those obtained by the evaluated models: $\sigma_{model} = a \cdot \sigma_{experimental} + b$

Original Models (Equations 2.2-2.4)	**a**	**b**	**R^2**
Figoni and Shoemaker	0.996	0.026	0.998
Weltman	0.997	0.019	0.998
Hahn, Ree and Eyring	0.995	0.027	0.998
Modified Models - f (γ) (Table 2.3)	**a**	**b**	**R^2**
Figoni and Shoemaker	0.997	0.030	0.995
Weltman	0.964	0.182	0.995
Hahn, Ree and Eyring	1.000	0.023	0.996

Table 2.3. Parameters of Figoni and Shoemaker, Weltman and Hahn, Ree and Eyring models as function of shear rate (tomato juice at 25ºC, 50 $s^{-1} < \gamma < 500\ s^{-1}$).

Model	**Parameter**	**f (γ)**	**R^2**
Figoni and Shoemaker $\sigma = \sigma_e + (\sigma_0 - \sigma_e) \cdot \exp(-k \cdot t)$	σ_e [Pa]	$0.389 \cdot \gamma^{0.470}$	0.997
	σ_0 [Pa]	$0.678 \cdot \gamma^{0.396}$	0.992
	k [s^{-1}]	$0.004 \cdot e^{0.0011 \cdot \gamma}$	0.935
Weltman $\sigma = A - B \cdot \ln(t)$	A [Pa]	$0.981 \cdot \gamma^{0.344}$	0.978
	B [$Pa \cdot s^{-1}$]	0.193	mean value
Hahn, Ree and Eyring $\ln(\sigma - \sigma_e) = A - B \cdot t$	σ_e [Pa]	$0.390 \cdot \gamma^{0.470}$	0.997
	A [Pa]	-0.274	mean value
	B [$Pa \cdot s^{-1}$]	$0.004 \cdot e^{0.0011 \cdot \gamma}$	0.964

It is important to observe that, as expected, the expressions for the parameters σ_e and k in Figoni and Shoemaker model were the same as the parameters σ_e and B in Hahn, Ree and Eyring model. It is expected that both models are essentially similar, with the same mathematical expression (if the exponential function is applied in both sides of the Hahn, Ree and Eyring model).

The obtained expressions were then evaluated, as earlier described, by using Equation 2.1. The parameters of the regression for the modified models whose parameters are function of shear rate are presented in Table 2.2. As one may see, the modified Figoni and Shoemaker, Weltman and Hahn, Ree and Eyring models, i.e., the models with parameters as the function of shear rate, described well the experimental data.

Although the three models can be well used to describe the time dependent behavior of tomato juice rheology, the modified Hahn, Ree and Eyring model has shown a slight better description of experimental data, followed by the modified Weltman and the Figoni and Shoemaker model.

2.3.2. Steady-State Shear Modeling

Figure 2.6 shows the flow curves (shear stress as the function of shear rate) of the tomato juice in the evaluated temperature range, as well as the apparent viscosity associated with each shear rate.

The values for the parameters of the Herschel-Bulkley model are shown in Table 2.4. As an alternative to the Herschel-Bulkley model, the apparent viscosity of the tomato juice was evaluated by the Falguera-Ibarz model, whose parameters are shown in Table 2.4. The value of R^2 was always higher than 99% in each replicates.

It is possible to observe that the tomato juice showed a small, but representative yield stress (σ_0; Herschel-Bulkley model). The yield stress is the minimum shear stress required to initiate the product flow, being related to the internal structure of the material that must be broken (Genovese and Rao, 2005; Tabilo-Munizaga and Barbosa-Cánovas, 2005). At stress below the yield stress, the material deforms elastically, behaving like an elastic solid; above the yield stress it starts flowing, behaving like a viscous liquid (Bayod et al., 2007). The presence of a yield stress is a typical characteristic of multiphase materials (Sun and Gunasekaran, 2009), as the tomato juice, formed by a dispersion of insoluble material (cellular walls and its materials) in a water-solution (serum, containing sugars, minerals, proteins and soluble polysaccharides). Moreover, as expected, the tomato juice showed a shear-thinning behavior, with the flow behavior index (n) always lower than 1.

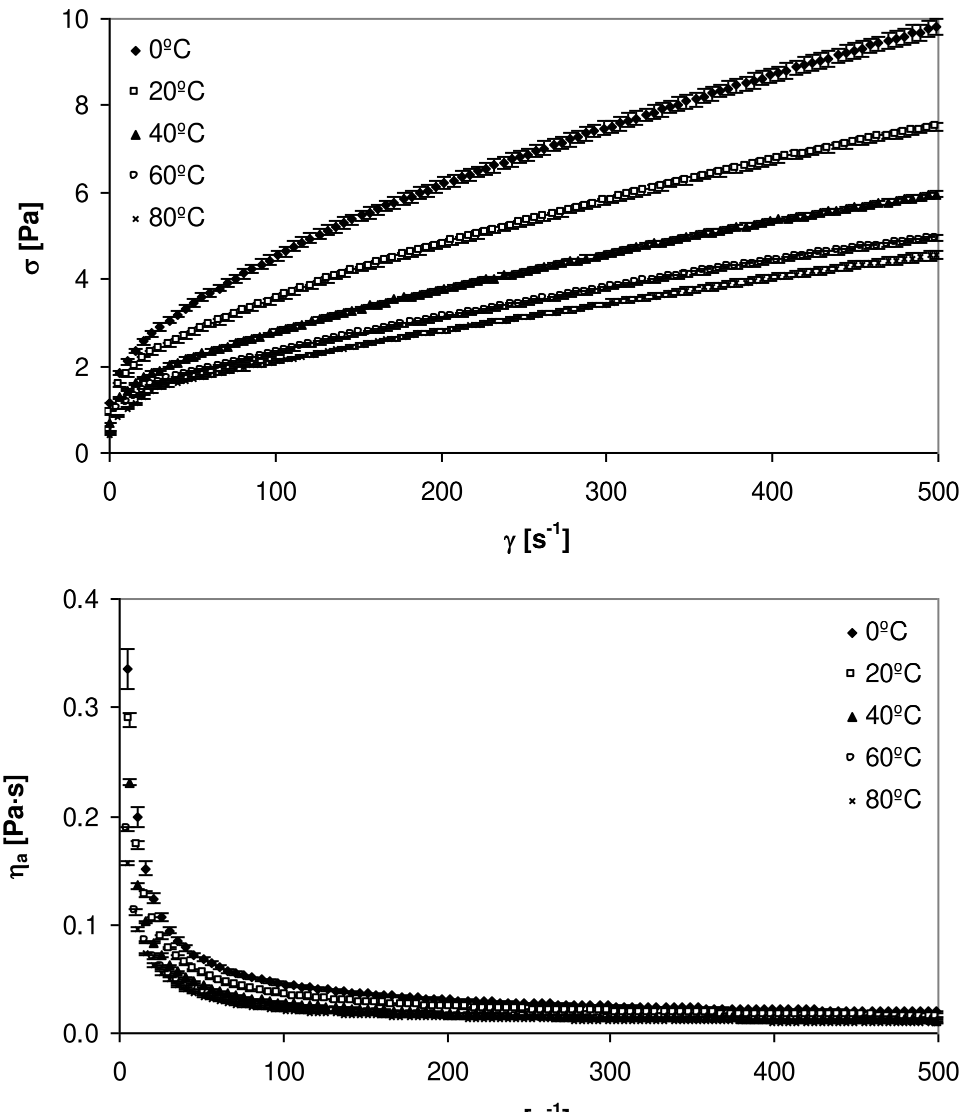

Figure 2.6. Flow curves (σ x γ) and apparent viscosity (η_a x γ) of tomato juice at 0ºC, 20ºC, 40ºC, 60ºC and 80ºC.Mean of three replicates; vertical bars represent the standard deviation in each value.

Table 2.4. Values for the parameters of Herschel-Bulkley and Falguera-Ibarz models (mean of three replicates ± standard deviation)

Herschel-Bulkley: $\sigma = \sigma_0 + k \cdot \gamma^{(n)}$			
T [ºC]	**σ_0 [Pa]**	**k [Pa·s^n]**	**n**
0	0.93 ± 0.03	0.27 ± 0.00	0.56 ± 0.00
20	0.94 ± 0.05	0.19 ± 0.01	0.56 ± 0.02
40	0.73± 0.02	0.16 ± 0.00	0.56 ± 0.00
60	0.56 ± 0.02	0.14 ± 0.00	0.56 ± 0.00
80	0.48 ± 0.04	0.13 ± 0.01	0.58 ± 0.07
Falguera-Ibarz: $\eta_a = \eta_\infty + (\eta_0 - \eta_\infty) \cdot \gamma^{(-k)}$			
T [ºC]	**η_∞ [Pa·s]**	**η_0 [Pa·s]**	**k**
0	0.011 ± 0.001	1.207 ± 0.050	0.774 ± 0.004
20	0.008 ± 0.000	1.114 ± 0.039	0.807 ± 0.005
40	0.006 ± 0.000	0.894 ± 0.015	0.807 ± 0.008
60	0.004 ± 0.000	0.668 ± 0.009	0.772 ± 0.010
80	0.003 ± 0.000	0.519 ± 0.007	0.719 ± 0.006

The obtained values of yield stress (σ_0), flow behavior index (n) and consistency index (k) are closed to those described in the literature for fruit products as açaí and jabuticaba pulps and carrot and blackberry juices (Table 2.5).

The flow behavior index (n) is assumed to be relatively constant with temperature (Rao 1999), as illustrated in Table 2.4. It enables the utilization of a constant value equal to the average in the evaluated temperature range (0.563). The yield stress and consistency index (k) decay with temperature were modeled according to Arrhenius model (Equation 2.7, where each parameter A is modeled by a pre-exponential factor – A_0, and the activation energy – Ea; R is the constant of the ideal gases and T is the absolute temperature, i.e., in K). The parameters of Herschel-Bulkley model as function of temperature are shown in Table 6. The regressions R^2 were higher than 0.90.

Table 2.5. Values for the parameters of Herschel-Bulkley for fruit products.

Product	T [ºC]	σ_0 [Pa]	k [Pa·s^n]	n	Reference
Tomato juice	20	0.94	0.19	0.56	Present work
Carrot juice	20	0.478	0.031	0.648	Vandresen et al. (2009)
Blackberry juice	20	0.29	1.12	0.44	Haminiuk et al. (2006)
Jabuticaba pulp	25	1.55	0.477	0.599	Sato and Cunha (2009)
Açai pulp	25	4.35	0.17	0.78	Tonon et al. (2009)

As expected, the values of the initial (η_0) and equilibrium (η_∞) apparent viscosity decay with temperature in the Falguera-Ibarz model. The value of k tends to show a small variation close to a mean value. As suggested by Falguera and Ibarz (2010), the apparent viscosity of the tomato juice was modeled according to Arrhenius model. The pre-exponential parameter (A_0) and the activation energy (Ea) where evaluated as power and logaritmic function of shear rate (Table 2.6). The regressions R^2 were higher than 0.98. As demonstrated in Table 2.7, the obtained activation energies are closed to those reported for fruit products.

$$A = A_0 \exp\left(\frac{Ea}{R \cdot T}\right) \qquad \text{(Equation 2.7)}$$

The experimental data were well described by the two evaluated models, as one may notice by values of a and R^2 were always higher than 0.96, while the values of b were always lower than 0.2 (Table 2.8). The results have demonstrated that both models can be successfully used for describing the flow behavior of tomato juice.

Table 2.6. Values for the parameters of Arrhenius equation in the Herschel-Bulkley and Falguera-Ibarz model (mean of three replicates ± standard deviation)

Herschel-Bulkley: $\sigma = \sigma_0 + k \cdot \gamma^{(n)}$			
Parameter	**A_0**	**Ea [J.mol^{-1}]**	**R^2**
σ_0 (Pa)	0.042	7274.8	0.907
k (Pa·s^n)	0.010	7353.3	0.955
n	0.56		mean value
Falguera-Ibarz: $\eta_a = \eta_\infty + (\eta_0 - \eta_\infty) \cdot \gamma^{(-k)}$			
Parameter	**A_0**	**Ea [J.mol^{-1}]**	**R^2**
$\eta_a = f(\gamma)$ 50 s^{-1}<γ<500 s^{-1}	$0.0556 \cdot \gamma^{-0.7846}$	$677.3 \cdot \ln(\gamma) + 4521.8$	0.999 (A_0) 0.981 (Ea)

Table 2.7. Activation energy (Ea) of the Arrhenius model ($A = A_0 \cdot \exp(Ea / R \cdot T)$) for the consistency index (k) and apparent viscosity (η_a) in fruit products

Product	$Ea_{(k)}$ [J·mol^{-1}]	$Ea_{(\eta a)}$ [J·mol^{-1}]	Reference
Tomato juice	7353.3	7389.9 – 8798.5 (10 – 500 s^{-1})	Present work
Acerola juice	-	7482 – 14630 (100 s^{-1})	Silva et al. (2005)
Tomato paste	8600 – 13000	-	Dak et al. (2008)
Reconstituted tomato concentrates	7360-3630	-	Barbana and El-Omri (*in press*)
Jabuticaba pulp	13000	9446.8 (100 s^{-1})	Sato and Cunha (2007)
Açai pulp	-	6210 (100 s^{-1})	Tonon et al. (2009)

Table 2.8. Values for the parameters a, b and R^2 for the regression of the experimental values versus those obtained by the models as function of temperature: $\sigma_{model} = a \cdot \sigma_{experimental} + b$; $\eta_{model} = a \cdot \eta_{experimental} + b$

Model	a	b	R^2
Herschel-Bulkley	0.965	0.195	0.993
Falguera-Ibarz	0.976	0.001	0.994

2.4. Conclusions

The present work has evaluated the time-dependent rheological properties of a commercial tomato juice. Three models were used to describe the shear stress decay during shearing (Figoni and Shoemaker, Weltman and Hahn, Ree and Eyring). The parameters of each model were empirically related with the shear rate. Then, the steady-state shear behavior of the product was evaluated by using the Herschel-Bulkley and Falguera-Ibarz models. The tomato juice was characterized as a thixotropic fluid, with pseudoplastic behavior with yield stress. Its rheological properties were closed to those previously reported in the literature for other fruit products. All evaluated models described well the experimental values, contributing to the studies of physical properties of foods and process design.

2.5. Acknowledgments

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2.6. Nomenclature

γ = shear rate [s^{-1}]

η = viscosity [Pa·s]

η_a = apparent viscosity (= σ / γ) [Pa·s]

η_0 = initial viscosity in Falguera-Ibarz model (Equation 2.6) [Pa·s]

η_∞ = equilibrium viscosity in Falguera-Ibarz model (Equation 2.6) [Pa·s]

σ = shear stress [Pa]

σ_0 = yield stress, Herschel-Bulkley's model (Equation 2.5) [Pa]

σ_0 = initial stress in Figoni-Shoemaker model (Equation 2.2) [Pa]

σ_e= equilibrium stress in Figoni-Shoemaker model (Equation 2.2) [Pa]

σ_e= equilibrium stress in Hahn-Ree-Eyring model (Equation 2.4) [Pa]

a = slope index in the linear model for evaluation of experimental values versus those obtained by models (Equation 2.1) [-]

b = intercept index in the linear model for evaluation of experimental values versus those obtained by models (Equation 2.1) [-]

A = structural parameter in Weltman model (Equation 2.3) [Pa]

A = structural parameter in Hahn-Ree-Eyring model (Equation 2.4) [Pa]

A_0 = Arrhenius's pre-exponential parameter model (Equation 2.7)

B = kinetic parameter in Weltman model (Equation 2.3) [$Pa \cdot s^{-1}$]

B = kinetic parameter in Hahn-Ree-Eyring model (Equation 2.4) [$Pa \cdot s^{-1}$]

Ea = activation energy in Arrhenius's model (Equation 2.7) [$J \cdot mol^{-1}$]

k = consistency coefficient, Herschel-Bulkley's model (Equation 2.5) [$Pa \cdot s^n$]

k = kinetic parameter in Figoni-Shoemaker model (Equation 2.2) [s^{-1}]

k = viscosity decay parameter in Falguera-Ibarz model (Equation 2.6) [-]

n = flow behavior index, Herschel-Bulkley's model (Equation 2.5) [-]

R = universal constant of ideal gases [= 8.314 $Pa \cdot m^3 \cdot mol^{-1} \cdot K^{-1}$]

t = time [s]

T = absolute temperature [K]

2.7. References

Abu-Jdayil, B.; Banat, F.; Jumah, R.; Al-Asheh, S.; Hammad, S. A. (2004). comparative study of rheological characteristics of tomato paste and tomato powder solutions. **International Journal of Food Properties**, 7(3), 483-497.

Altan, A.; Kus, S.; Kaya, A. (2005). Rheological behaviour and time dependent characterization of gilaboru juice (*Viburnum opulus L.)*. **Food Science and Technology International**, 11(2), 129-137.

Basu, S.; Shivharey, U.S.; Raghavan, G.S.V. (2007). Time dependent rheological characteristics of pineapple jam. **International Journal of Food Engineering**, 3(3), article 1.

Bayod, E.; Mansson, P.; Innings, F.; Bergenstahl, B.; Tornberg, E. (2007). Low shear rheology of concentrated tomato products. Effect of particle size and time. **Food Biophysics**, 2,146-157.

Barbana, C.; El-Omri, A. (2010). Viscometric behavior of reconstituted tomato concentrate. **Food and Bioprocess Technology**, *in press,* DOI: 10.1007/s11947-009-0270-3.

Cepeda, E.; Villarán, M. C.; Ibarz, A. (1999). Rheological properties of cloudy and clarified juice of *Malus floribunda* as a function of concentration and temperature. **Journal of Texture Studies**, 30, 481-491.

Choi, Y. H.; Yoo, B. (2004). Characterization of time-dependent flow properties of food suspensions. **International Journal of Food Science and Technology**, 39, 801–805.

Dak, M.; Verma, R. C.; Jaaffrey, S. N. A. (2008). Rheological properties of tomato concentrate. **International Journal of Food Engineering**, 4(7), article 11.

Falguera, V.; Ibarz, A. (2010). A new model to describe flow behaviour of concentrated orange juice. **Food Biophysics**, 5,114–119.

Falguera,V.; Vélez-Ruiz, J. F.; Alins, V.; Ibarz, A. (2010). Rheological behaviour of concentrated mandarin juice at low temperatures. **International Journal of Food Science and Technology**, 45, 2194-2200.

Figoni, P. I.; Shoemaker, C. F. (1983). Characterization of time dependent flow properties of mayonnaise under steady shear. **Journal of Texture Studies**, 14, 431–442.

Genovese, D. B.; Rao, M. A. (2005). Components of vane yield stress of structured food dispersions. **Journal of Food Science**, 70(8), E498-E504.

Hahn, S. J.; Ree, T.; Eyring, H. (1959). Flow mechanism of thixotropic substances. **Industrial and Engineering Chemistry**, 51, 856-857.

Haminiuk, C. W. I.; Sierakowski, M. R.; Izidoro, D. R.; Masson, M. L. (2006). Rheological characterization of blackberry pulp. **Brazilian Journal of Food Technology**, v.9, n.4, p.291-296.

Hayes, W. A.; Smith, P. G.; Morris, A. E. J. (1998). The production and quality of tomato concentrates. **Critical Reviews in Food Science and Nutrition**, 38(7), 537-564.

Ibarz, A.; Barbosa-Cánovas, G. V. (2003). **Unit Operations in Food Engineering**. Boca Raton: CRC Press.

Lozano, J. E.; Ibarz, A. (1994). Thixotropic behavior of concentrated fruit pulps. **LWT-Food Science and Technology**, 27, 16-18.

Mizrahi, S. (1997). Irreversible shear thinning and thickening of tomato juice. **Journal of Food Process and Preservation**, 21, 267-277.

Nisha, P.; Singhal, R. S.; Pandit, A. B. (2010). Kinetic modelling of colour degradation in tomato puree (*Lycopersicon esculentum* L.). **Food and Bioprocess Technology**, *in press,* DOI: 10.1007/s11947-009-0300-1.

Ramos, A. M.; Ibarz, A. (1998). Thixotropy of orange concentrate and quince puree. **Journal of Texture Studies**, 29, 313-324.

Rao, M.A. (1999). Flow and functional models for rheological properties of fluid foods. In: RAO, M.A. (Ed.). **Rheology of Fluid and Semisolid Foods: Principles and Applications.**, Gaithersburg: Aspen Publishers.

Ravi, R.; Bhattacharya, S. (2006). The time-dependent rheological characteristics of a chickpea flour dispersion as a function of temperature and shear rate. **International Journal of Food Science and Technology,** 41, 751-756.

Sato, A. C. K.; Cunha, R. L. (2007). Influence of temperature on the rheological behavior of jaboticaba pulp. **Ciência e Tecnologia de Alimentos**, 27(4), 890-896.

Sato, A. C. K.; Cunha, R. L. (2009). Effect of particle size on rheological properties of jaboticaba pulp. **Journal of Food Engineering,** 91, 566–570.

Silva, F.C.; Guimaraes, D. H. P.; Gasparetto, C.A. (2005). Rheology of acerola juice: effects of concentration and temperature. **Ciência Tecnologia de Alimentos**, v.25, n.1, p. 121-126. (in portuguese)

Sun, A.; Gunasekaran, S. (2009). Yield stress in foods: measurements and applications. **International Journal of Food Properties**, 12, 70-101.

Tabilo-Munizaga, G.; Barbosa-Cánovas, G. V. (2005). Rheology for the food industry. **Journal of Food Engineering**, 67, 147-156.

Tiziani, S.; Vodovotz, Y. (2005a). Rheological characterization of a novel functional food: tomato juice with soy germ. **Journal of Agricultural and Food Chemistry**, 53, 7267-7273.

Tiziani, S.; Vodovotz, Y. (2005b). Rheological effects of soy protein addition to tomato juice. **Food Hydrocolloids**, 19(1), 45-52.

Tonon, R.V.; Alexandre, D.; Hubinger, M. D.: Cunha, R. L. (2009). Steady and dynamic shear rheological properties of açai pulp (*Euterpe oleraceae* Mart.). **Journal of Food Engineering,** 92, 425–431.

Vandresen, S., Quadri, M. G. N., Souza, J. A. R.., Hotza, D. (2009). Temperature effect on the rheological behavior of carrot juices. **Journal of Food Engineering**, 92, 269-274.

Vercet, A.; Sánchez, C.; Burgos, J.; Montañés, L.; Buesa, P. L. (2002). The effects of manothermosonication on tomato pectic enzymes and tomato paste rheological properties. **Journal of Food Engineering**, 53, 273-278.

Weltman, R. N. Breakdown of thixotropic structure as function of time. (1943). **Journal of Applied Physics**, 14, 343-350.

Chapter 3: Viscoelastic Properties of Tomato Juice: Applicability of the Cox-Merz Rule

This chapter was developed at University of Lleida, and is currently in press as:
AUGUSTO, P. E. D.; FALGUERA, V.; CRISTIANINI, M.; IBARZ, A. Viscoelastic Properties of Tomato Juice: Applicability of the Cox-Merz Rule. **Food and Bioprocess Technology**, *in press*, 2011.
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Abstract

Tomato is one of the most important vegetables for the food industry. Rheological characterization of food is important for products, equipments and unit operations design and evaluation. It is necessary for process optimization and high quality products assurance. However, the works in literature present variable data, and some rheological characterization, as viscoelastic properties, are still scarce. The present work has evaluated the viscoelastic properties of tomato juice, as well as the applicability of the Cox-Merz rule. Tomato juice has shown dominant elastic properties rather than the viscous ones, and could be classified as a weak gel (storage modulus higher then loss modulus). Moreover, due to the low pulp content, it has shown low viscoelastic behavior, with small dependency of oscillatory of the storage modulus. The rheological oscillatory and steady-state shear rheological properties of tomato juice was then correlated by two linear modifications on the Cox-Merz rule. The obtained values are in agreement with those described in the literature for other food products. The obtained data are potentially useful for future studies on food properties and process design.

Keywords:

Cox-Merz rule, food properties, rheology, viscoelastic properties.

Propriedades Viscoelásticas de Suco de Tomate: Aplicação da Regra de Cox-Merz

Resumo

O tomate é um dos vegetais mais importantes para a indústria de alimentos. A caracterização reológica de alimentos é essencial para o dimensionamento e avaliação de produtos, equipamentos e operações unitárias, sendo necessário para obtenção de produtos de qualidade e processos otimizados. Entretanto, os trabalhos da literatura apresentam dados com grande variabilidade, inclusive com poucos estudos de algumas caracterizações reológicas, como as propriedades viscoelásticas. O presente trabalho avaliou as propriedades viscoelásticas de suco de tomate, assim como a aplicabilidade da regra de Cox-Merz. O suco de tomate apresentou propriedades elásticas dominantes em relação às viscosas, sendo classificado como um gel fraco (módulo de armazenamento maior do que o viscoso). Devido ao baixo teor de polpa, apresentou baixo comportamento viscoelástico, com módulo de armazenamento apresentado baixa dependência da frequência de oscilação. As características reológicas em cisalhamento em estado estacionário e oscilatório foram correlacionadas utilizando-se duas modificações lineares da regra de Cox-Merz. Os dados obtidos se mostraram compatíveis com os apresentados na literatura por outros produtos alimentícios, sendo úteis para futuros trabalhos na área de propriedades de alimentos e dimensionamento de processos.

Palavras-chave:

Propriedades dos alimentos, propriedades viscoelásticas, reologia, regra de Cox-Merz.

3.1. Introduction

Tomato is one of the most popular and widely grown vegetables in the world (Nisha et al. 2010). In fact, tomato is one of the most important vegetables for the food industry, and its products consumption is large and widely included in human diet. The rheological characterization of tomato products is important not only for unit operations design, but for process optimization and high quality products assurance.

In fact, many works have been published regarding tomato products rheological characterization. However, data presented in literature are very variable (Bayod et al. 2007) and concentrated only in steady state shear stress measurements. Many works just considered one-condition measurement (just apparent viscosity evaluation) or empiric methods evaluation (as the Bostwick consistometer). Moreover, it is important to notice that viscoelastic characterization of tomato products are still scarce (Sánchez et al. 2002; Valencia et al. 2004).

The viscoelastic properties are important to understand and predict the physical-chemical stability of food dispersions, as fruit juices. The Cox-Merz rule states that the apparent viscosity ($\eta_a = \sigma / \dot{\gamma}$) at a specific shear rate ($\dot{\gamma}$) is equal to the complex viscosity (η^*) at a specific oscillatory frequency (ω), when $\dot{\gamma} = \omega$ (Equation 3.1; Rao, 2005).

$$\eta_a(\dot{\gamma}) = \eta^*(\omega)\big|_{\dot{\gamma}=\omega} \qquad \text{(Equation 3.1)}$$

When its rule is valid, the rheological food properties can be determined by even oscillatory or steady-state shear experiments (Gunasekaran and Ak, 2000). It is particularly useful due to the characteristics and limitations in each kind of experiment.

The steady-state shear experiments have limitations related to slippage and migration of sample constituents (Gunasekaran and Ak, 2000), which is particularly truth in some food products as fruit juices. Moreover, in these experiments, the sample internal structure is broken, limiting the understanding of product behavior in low shear situations, as in particle sedimentation. Dynamic rheological experiments can then be used for characterize those products.

Dynamic rheological tests are generally conducted by small amplitude oscillatory measurements that are nondestructive experiments (Rao, 2005; Dogan and Kokini, 2007). Thus, it is possible to conduct multiple tests on the same sample under different test conditions (Dogan and Kokini, 2007). However, small amplitude oscillatory measurements have the limitation of not being appropriate in practical processing situations due to the low rates and strain at which the test is applied (Dogan and Kokini, 2007; Steffe, 1996). For this characterization, steady-state shear experiments must be conducted (Gunasekaran and Ak, 2000).

Thus, it is extremely interesting to establish a correlation between the steady-state shear and dynamic oscillatory experiments, using the Cox-Merz rule.

The present work has evaluated the viscoelastic properties of tomato juice, as well as the applicability of the Cox-Merz rule.

3.2. Materials and Methods

A commercial tomato juice was used for guaranty of standardization and repeatability. Its soluble solids content were determined by using a digital refractometer (Atago RX-1000, Atago Co., Ltd., Tokyo,Japan), while its total solid content was measured by drying the samples in a vacuum oven at 70 ºC (five replicates). Its time-dependent and steady-state rheological behavior was previously evaluated by Augusto et al. (2010).

Rheological measurements were carried out in a Haake RS 80 rheometer with controlled stress (σ), using a Couette geometry (concentric cylinder; Haake Z40-DIN). The cup and bob radius ratio was 1.0847 (bob radius = 20.000 ± 0.004 mm). Temperature was maintained constant at 25 ºC by using a water-bath (Phoenix ThermoHaake C25P) with deviation lower than ±0.3 °C. The experiments were carried out in three replicates.

3.2.1. Steady-State Shear Behavior

The steady-state shear behavior was evaluated for testing the Cox-Merz rule. Samples were sheared at 250 s^{-1} for 250 s, predetermined condition for elimination of product thixotropy (Augusto et al., 2010). The shear stress data were then evaluated in the shear rate range of 0.01 s^{-1} to 10 s^{-1}.

3.2.2. Viscoelastic Properties

The rheological evaluation was carried out with new samples, which were placed in the rheometer and kept at rest for 10 min before start shearing.

Oscillatory stress sweeps between 0.01 and 10 Pa were performed at a frequency of 1 Hz to determine the linear viscoelastic range. Then, frequency sweep measurements were carried out to at a fixed shear stress value within the linear viscoelastic range, in the range of 0.01 to 10 Hz. The storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) were thus obtained as function of frequency (ω).

3.3. Results and Discussion

The tomato juice soluble solids content were 5.4±0.2ºBrix, with 5.96±0.02% (w/w) of total solids (mean of five replicates ± standard deviation). The shear stress of 0.1 Pa was selected for the oscillatory frequency sweeps (Figure 3.1), as it limits the product linear viscoelastic region.

As can be seen in Figure 3.1, tomato juice has shown low viscoelastic behavior, as storage modulus (G') dependency of oscillatory frequency was very small. It is expected due to the low concentration of pulp in suspension. Values of G' were always higher than those of G'', which indicates that tomato juice has dominant elastic properties rather than the viscous ones. Thus, the product can be classified as a weak gel (Rao, 1999). This behavior is typically observed in suspensions with network-like structure, being characteristic for fruit products. It is similar to those reported for peach puree (Massa et al. 2010), açai pulp (Tonon et al. 2009), jabuticaba pulp (Sato and Cunha, 2009), umbu pulp (Pereira et al. 2008), baby foods (Ahmed and Ramaswamy, 2006; Ramamoorthi et al. 2009), potato puree (Alvarez et al. 2004), peach juice with fibers (Augusto et al. 2011) and tomato concentrates (Bayod et al. 2008; Valencia et al. 2002; Yoo and Rao, 1996).

When the applicability of the Cox-Merz rule was evaluated, it was not possible to use it straight (Figure 3.2). As commonly observed in food products, the complex viscosity (η^*) magnitudes were always higher than the apparent viscosity (η_a) magnitudes. Although the Cox-Merz rule has been confirmed experimentally for several polymers dispersions and solutions, in complex systems as food products it is generally necessary to modify the original rule (Gunasekaran and Ak, 2000; Rao, 2005). The non-fitting of the Cox-Merz rule for complex dispersions is attributed to structural decay due to the extensive strain applied (Ahmed and Ramaswamy, 2006), presence of high-density entanglements or to the development of structure and intermolecular aggregation in solution (Da Silva and Rao, 1992). Thus, the rheological properties of the tomato juice differ from those of the polymer solutions and are more similar to those of the structured systems (Ahmed and Ramaswamy, 2006).

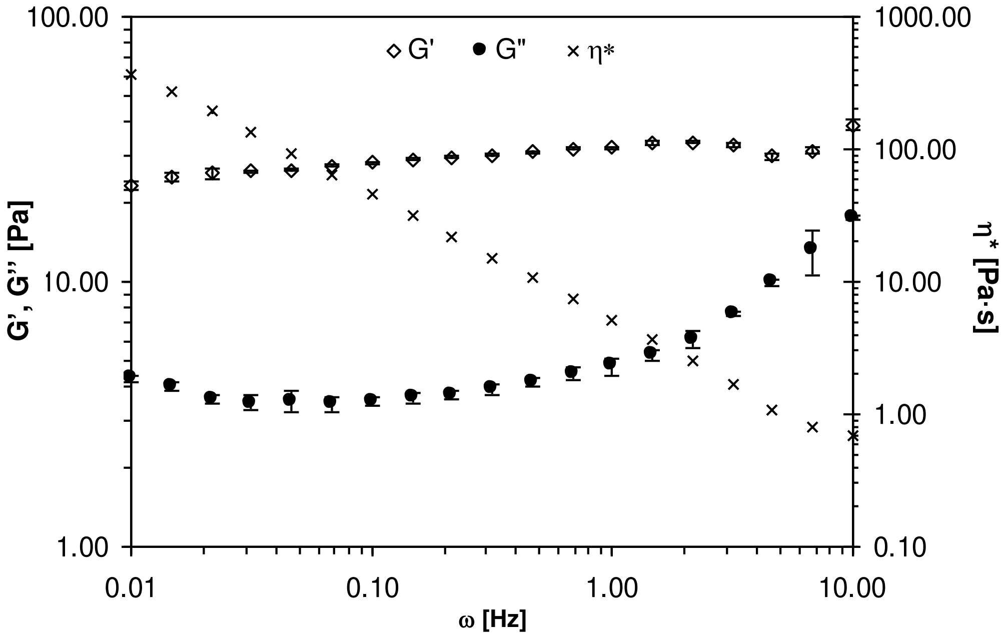

Figure 3.1. Oscillatory frequency sweeps at 0.1 Pa. Mean of three replicates at 25 °C; vertical bars represent the standard deviation in each value.

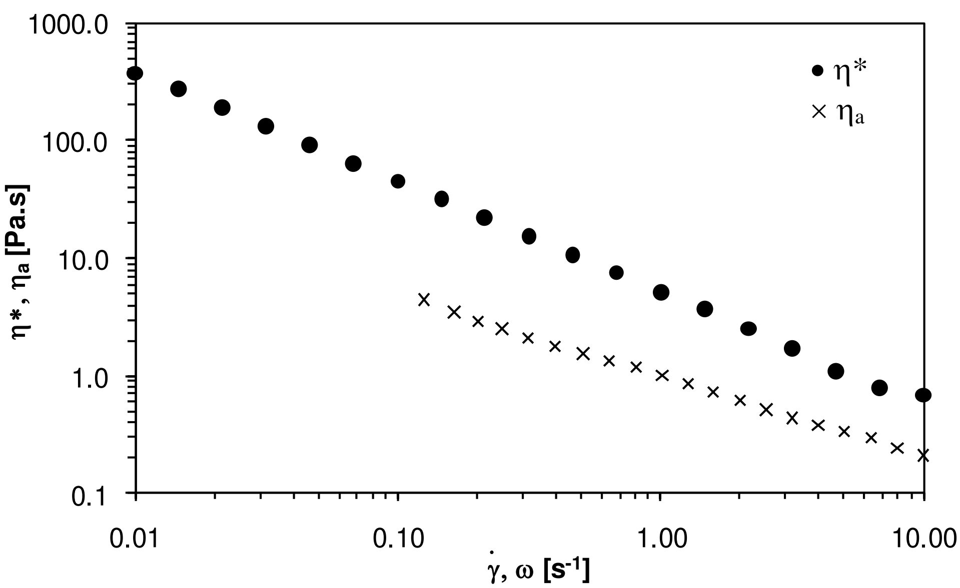

Figure 3.2. Apparent (× η_a) and complex (• η^*) viscosities as function of shear rate and oscillatory frequency

The rheological oscillatory and steady-state shear rheological properties of foods is generally correlated by linear modifications on the Cox-Merz rule (Gunasekaran and Ak, 2000; Rao, 2005). Figure 3.3 shows the four possible ways to applying linear modifications on the Cox-Merz rule, i.e., applying horizontal (α_1 in Equation 3.2; α_2 in Equation 3.3) or vertical (β_1 in Equation 3.4; β_2 in Equation 3.5) shift factors for correlating the apparent (η_a) and complex (η^*) viscosities.

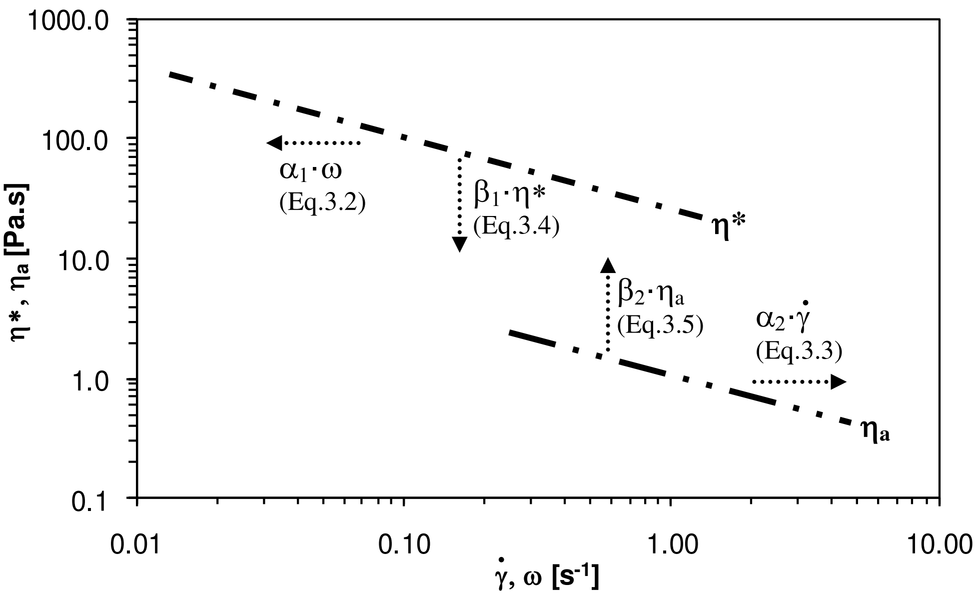

Figure 3.3. Apparent (η_a) and complex (η^*) viscosities as function of shear rate and oscillatory frequency: the four possible linear modifications of the Cox-Merz rule.

$$\eta_a(\dot{\gamma}) = \eta^*(\alpha_1 \cdot \omega)\Big|_{\dot{\gamma}=\omega} \quad \text{(Equation 3.2)}$$

$$\eta_a(\alpha_2 \cdot \dot{\gamma}) = \eta^*(\omega)\Big|_{\dot{\gamma}=\omega} \quad \text{(Equation 3.3)}$$

$$\eta_a(\dot{\gamma}) = \beta_1 \cdot \eta^*(\omega)\Big|_{\dot{\gamma}=\omega} \quad \text{(Equation 3.4)}$$

$$\beta_2 \cdot \eta_a(\dot{\gamma}) = \eta^*(\omega)\Big|_{\dot{\gamma}=\omega} \quad \text{(Equation 3.5)}$$

From those possible correlations, it is described in the literature the use of the factors α_1 (Equation 3.2) and β_1 (Equation 3.4) for the description of the rheological properties of foods (Ahmed and Ramaswamy, 2006; Alvarez et al. 2004; Canet et al. 2005; Kin and Yoo, 2006; Rao and Cooley, 1992).

Thus, an optimization procedure was established in order to determine the coefficients α_1 (Equation 3.2) and β_1 (Equation 3.4). It consists in estimate an initial value for the coefficient and procedure with the linear regression. The value of the coefficient of determination (R^2) is then calculated. The coefficient value is changed and the same procedure is carried out. The R^2 values are compared, and the process is repeated until the maximum value to the R^2 is obtained (Figure 3.4). The R^2 maximum value, thus, express the best fit of α_1 and β_1 to the Equation 3.2 and 3.4.

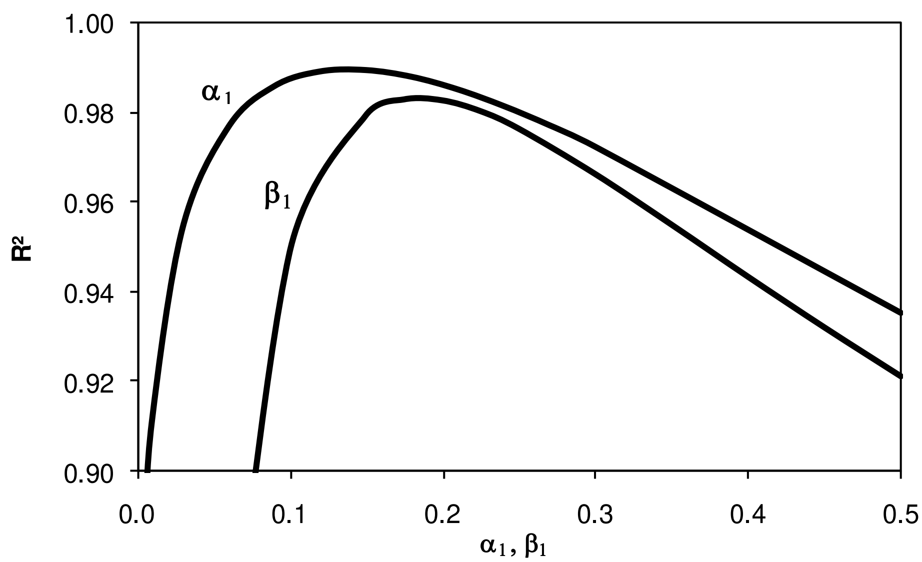

Figure 3.4. Optimization procedure for determining the parameters of the linear modified Cox-Merz rules (Equations 3.2 and 3.4)

By using this algorithm, it was possible to determine the values of α_1 and β_1 (Table 3.1), describing data with R^2 higher than 0.98 (Figure 3.5). It can be seen that the obtained values are in agreement with those described in the literature for tomato paste (Rao and Cooley, 1992), potato puree (Alvarez et al. 2011; Alvarez et al. 2004; Canet et al. 2005), rice starch – xantan gum mixtures (Kin and Yoo, 2006) and sweet potato baby food (Ahmed and Ramaswamy, 2006) (Table 3.1). It shows that the rheological properties of tomato juice can be determined by even oscillatory or steady-state shear experiments.

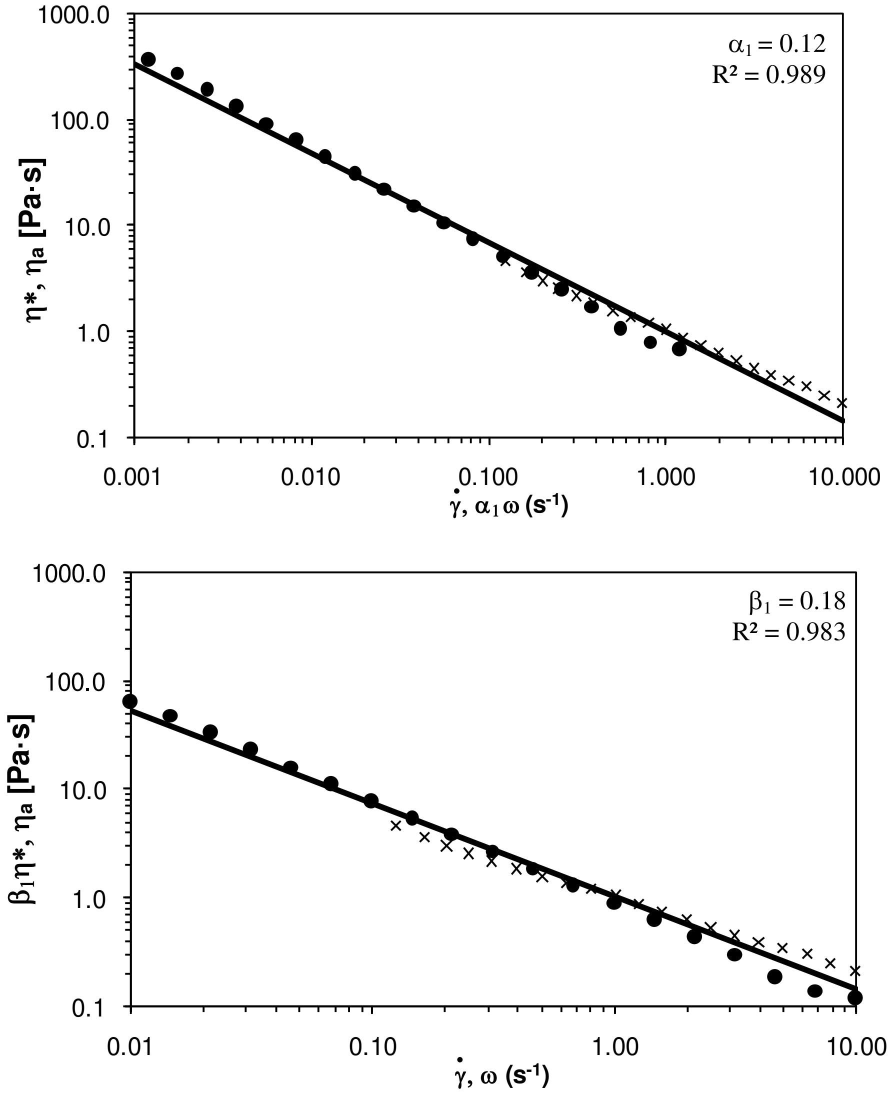

Figure 3.5. Apparent (× η_a) and complex (• η^*) viscosities as function of shear rate and oscillatory frequency: applicability of the linear modified Cox-Merz rules (Equations 3.2 and 3.4)

Table 3.1. Values for the parameters of the linear modified Cox-Merz rules (Equations 3.2 and 3.4) for food products.

Product	α_1	β_1	Reference
Tomato juice (5.4ºBrix, 25 ºC)	0.12	0.18	Present work
Tomato paste (26-30ºBrix, 40 ºC)	0.0029-0.029	-	Rao and Cooley (1992)
Potato puree (18.5-20.5% solids, 25 ºC)	0.008-0.020	-	Canet et al. (2005) Alvarez et al. (2004)
Potato puree (55 ºC) with pectin, xanthan gum, κ-carrageenan and/or sodium caseinate.	0.009-0.021	-	Alvarez et al. (2011)
Rice starch – xantan gum mixtures (25 ºC)	0.307-0.478	-	Kin and Yoo (2006)
Sweet potato baby food (11.2ºBrix, 20 ºC)	-	0.14	Ahmed and Ramaswamy (2006)

From an engineering standpoint, the steady flow curve is the most valuable way to characterize the rheological behavior of fluids. However, many phenomena cannot be described by the viscosity function alone and elastic behavior must be taken into consideration (Steffe, 1996).

The microstructure of a product can be correlated with its rheological behavior; the viscoelastic properties are very useful in the design and prediction of the stability of stored samples (Ibarz and Barbosa-Cánovas, 2003). Moreover, viscoelastic products may exhibit some interesting behavior as the Weissenberg and the Barus effects (Ibarz and Barbosa-Cánovas, 2003; Steffe, 1996).

Thus, the study and description of the viscoelastic properties of liquid foods are important for better understand the observed behavior during processing, storing and consumption, even for fluids as the tomato juice here studied.

It is interesting to observe that the studied tomato juice has thixotropic behavior (Augusto et al., 2010), and that its flow behavior can only be measured after a pre-shearing period. Thus, the relations to the modified Cox-Merz rule here obtained are potentially useful for rheological studies, once the complex viscosity (η^*) can be directly measured without the pre-shearing period.

The obtained results have methodological and scientific applications and the observed properties can be used for describing some important behavior in fruit juice stability as pulp sedimentation. Therefore, the results of the present work can be useful for future studies on food properties, rheology and product and process design.

3.4. Conclusions

The present work has evaluated the viscoelastic properties of tomato juice and the applicability of the Cox-Merz rule. Product has shown a weak gel behavior, with storage modulus higher than loss modulus in the evaluated frequency. Two linear modified Cox-Merz rules could describe the rheological properties of tomato juice. The obtained data are potentially useful for future studies on food properties and process design.

3.5. Acknowledgments

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3.6. Nomenclature

α_1, α_2, β_1, β_2 = parameters of the modified Cox-Merz rules (Equations 3.2-3.5)

$\dot{\gamma}$ = shear rate [s^{-1}]

η_a = apparent viscosity (= σ / γ) [Pa·s]

η^* =complex viscosity [Pa·s]

σ = shear stress [Pa]

G' = storage modulus [Pa]

G'' = loss modulus [Pa]

3.7. References

Ahmed, J., & Ramaswamy, H. S. (2006). Viscoelastic and thermal characteristics of vegetable puree-based baby foods. **Journal of Food Process Engineering**, 29, 219–233.

Alvarez, M. D., Fernández, C., & Canet, W. (2004). Rheological behaviour of fresh and frozen potato puree in steady and dynamic shear at different temperatures. **European Food Research Technology**, 218, 544-553.

Alvarez, M. D., Fernández, C., & Canet, W. (2011). Effect of cryoprotectant mixtures on rheological properties of fresh and frozen/thawed mashed potatoes. **Journal of Food Process Engineering**, 34, 224–250.

Augusto, P. E. D., Falguera, V., Cristianini, M., & Ibarz, A. (2010). Rheological behavior of tomato juice: steady-state shear and time-dependent modeling. **Food and Bioprocess Technology**, in press, DOI: 10.1007/s11947-010-0472-8.

Augusto, P. E. D., Falguera, V., Cristianini, M., & Ibarz, A. (2011). Influence of fibre addition on the rheological properties of peach juice**. International Journal of Food Science and Technology**, 46, 1086-1092.

Bayod, E., Månsson, P., Innings, F., Bergenståhl, B., & Tornberg, E. (2007). Low shear rheology of concentrated tomato products. Effect of particle size and time. **Food Biophysics**, v.2, p.146-157.

Bayod, E., Willers, E. P., & Tornberg, E. (2008). Rheological and structural characterization of tomato paste and its influence on the quality of ketchup. **LWT - Food Science and Technology**, 41, 1289-1300.

Canet, W., Alvarez, M. D., Fernández, C., & Luna, P. (2005). Comparisons of methods for measuring yield stresses in potato puree: effect of temperature and freezing. **Journal of Food Engineering**, 68, 143-153.

Da Silva, J. A. L., & Rao, M. A. (1992). Viscoelastic Properties of Food Hydrocolloid Dispersions. In: Rao, M. A., Steffe, J. F. **Viscoelastic Properties of Foods**. London: Elsevier Science Publishers Ltd.

Dogan, H.; Kokini, J. L. (2007). Rheological Properties of Foods. In: Heldman, D. R.; Lund, D. B. (Ed.). **Handbook of Food Engineering**, 2nd ed. Boca Raton: Taylor & Francis Group.

Gunasekaran, S., & Ak, M. M. (2000). Dynamic oscillatory shear testing of foods – selected applications. **Trends in Food Science and Technology**, 11, 115-127.

Ibarz, A., & Barbosa-Cánovas, G. V. (2003). **Unit Operations in Food Engineering**. Boca Raton: CRC.

Kin, C., & Yoo, B. (2006). Rheological properties of rice starch-xanthan gum mixtures. **Journal of Food Engineering**, 72, 120-128.

Massa, A., González, C., Maestro, A., Labanda, J., & Ibarz, A. (2010). Rheological characterization of peach purees. **Journal of Texture Studies**, 41, 532–548.

Nisha, P., Singhal, R. S., & Pandit, A. B. (2010). Kinetic modelling of colour degradation in tomato puree (Lycopersicon esculentum L.). **Food and Bioprocess Technology**. in press, DOI: 10.1007/s11947-009-0300-1.

Pereira, E. A., Brandão, E. M., Borges, S. V., & Maia, M. C. A. (2008). Influence of concentration on the steady and oscillatory shear behavior of umbu pulp. **Revista Brasileira de Engenharia Agrícola e Ambiental**, 12, 1, 87–90.

Ramamoorthi, L., Lee, Y., & Brewer, S. (2009). Effect of food matrix and heat treatment on the rheological properties of salmon-based baby food**. Journal of Food Engineering**, 95, 432–437.

Rao, M. A. (2005). Rheological Properties of Fluid Foods. In: Rao, M. A., Rizvi, S. S. H., & Datta, A. K. **Engineering Properties of Foods**. Boca Raton: CRC Press, 3rd ed..

Rao, M.A. (1999). Flow and functional models for rheological properties of fluid foods. In: Rao, M.A. (Ed.). **Rheology of Fluid and Semisolid Foods: Principles and Applications**. Gaithersburg: Aspen Publishers.

Rao, M. A., & Cooley, H. J. (1992). Rheological behavior of tomato pastes in steady and dynamic shear. **Journal of Texture Studies**, v.23, p.415-425.

Sánchez, M. C., Valencia, C., Gallegos, C., Ciruelos, A., & Latorre, A. (2002). Influence of processing on the rheological properties of tomato paste. **Journal of the Science of Food and Agriculture**, v.82, p.990-997.

Sato, A. C. K., & Cunha, R. L. (2009). Effect of particle size on rheological properties of jaboticaba pulp. **Journal of Food Engineering**, v.91, p.566–570.

Steffe, J.F. (1996). **Rheological Methods in Food Process Engineering**, 2nd ed. East Lansing: Freeman Press

Tonon, R.V., Alexandre, D., Hubinger, M. D., & Cunha, R. L. (2009). Steady and dynamic shear rheological properties of açai pulp (Euterpe oleraceae Mart.). **Journal of Food Engineering**, v.92, p.425–431.

Valencia, C., Sánchez, M. C., Ciruelos, A., Latorre, A., Franco, J. M., & Gallegos, C. (2002). Linear viscoelasticity of tomato sauce products: influence of previous tomato paste processing. **European Food Research Technology**, 214, 394–399.

Valencia, C., Sánchez, M. C., Ciruelos, A., & Gallegos, C. (2004). Influence of tomato paste processing on the linear viscoelasticity of tomato ketchup. **Food Science and Technology International**, v.10, n.2, p.95-100.

Yoo, B., & Rao, M. A. (1996). Creep and dynamic rheological behavior of tomato concentrates: effect of concentration and finisher screen size. **Journal of Texture Studies**, 27, 451-459 .

Chapter 4: Effect of High Pressure Homogenization (HPH) on the Rheological Properties of a Fruit Juice Serum Model

This chapter was developed at University of Campinas, and is currently under review as:

AUGUSTO, P. E. D.; IBARZ, A.; CRISTIANINI, M. Effect of High Pressure Homogenization (HPH) on the Rheological Properties of a Fruit Juice Serum Model.

Abstract

High pressure homogenization (HPH) is a non-thermal technology that has been widely studied as a partial or total substitute for thermal food processing. The present work evaluated the effect of HPH on the rheological properties of a fruit juice serum model, designed to be similar to tomato juice serum. Product viscosity decreased due to the increase in homogenization pressure, and could be modelled well using two functions (power-sigmoidal and exponential; R^2>0.98). The serum model processed at 200 MPa showed a viscosity decrease of 20% when compared to the original. Since fruit juice rheology is defined by the interactions occurring between the dispersed phase (suspended particles) and the solution (serum), the expected fruit juice behaviour was then discussed.

Keywords:

Food properties, high pressure homogenization, rheology, viscosity.

Efeito da Homogeneização a Alta Pressão (HAP) nas Propriedades Reológicas de um Modelo de Soro de Suco de Fruta

Resumo

A homogeneização a alta pressão (HAP) tem sido estudada como tecnologia substituta parcial ou total do processamento térmico de alimentos. O presente trabalho avaliou o efeito da HAP nas propriedades reológicas de um modelo de soro de suco de fruta, dimensionado para simular o soro de suco de tomate. A viscosidade do produto diminuiu com o aumento da pressão de homogeneização, sendo modelada utilizando duas funções matemáticas (potência-sigmoidal e exponencial; $R^2>0,98$). A redução da viscosidade no modelo de soro processado a 200 MPa foi de 20%. Como as propriedades reológicas de sucos de frutas são definidas pelas interações entre a fase dispersa (partículas suspensas) e a dispersante (soro), discutiu-se o comportamento esperado para o suco de fruta.

Palavras-chave:

Homogeneização a alta pressão, propriedades dos alimentos, reologia, viscosidade.

4.1. Introduction

High pressure homogenization (HPH) technology has been studied by many authors as a non-thermal food preservation technique, especially for fruit products. The use of HPH as a partial or total substitute for thermal food processing has been previously proposed for tomato (Corbo et al., 2010), apple (Donsì et al., 2009; Pathanibul et al., 2009; Saldo et al., 2009), mango (Tribst et al., 2011; Tribst et al., 2009), açaí (Aliberti, 2009), orange (Campos and Cristianini, 2007; Tahiri et al., 2006), carrot (Patrignani et al., 2010; Pathanibul et al., 2009; Patrignani et al., 2009) and apricot (Patrignani et al., 2010; Patrignani et al., 2009) juices. However, there is a lack of information in the literature regarding changes in the rheological properties of fruit products due to HPH processing.

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). The study of the influence of processing on the rheological properties of food is thus essential for an efficient product and process design.

Fruit juices are composed of an insoluble phase (the pulp) dispersed in a viscous solution (the serum). The dispersed phase, or pulp, is constituted of fruit tissue cells and their fragments, cell walls and insoluble polymer clusters and chains. The serum is an aqueous solution of soluble polysaccharides, sugars, salts and acids. The fruit juice rheological properties are thus defined by the interactions within each phase and between them.

The effect of HPH on the rheological properties of fruit juices will thus be a function of the balance between the structural changes in the pulp and serum. Therefore an evaluation of the effects of processing on the serum phase is important for a better understand of the effect of HPH on the juice rheological properties. However, no such work was found in the literature describing the effect of HPH on the rheological properties of fruit juice serum.

The use of model foods for process studies enables one to carry out simple, cost-effective and continuous experiments, without significantly changing the products (Berto et al., 2003). Moreover, the main benefit of using model food systems in scientific studies is the experimental reproducibility, which minimizes the effects of inherent variations in food characteristics (Augusto et al., 2011b).

Tomato is one of the most popular and widely grown vegetables in the world (Nisha et al. 2010). In fact, tomato is one of the most important vegetables in the food industry, and is widely consumed and included in the human diet (Augusto et al., 2010).

Tomato serum generally has a soluble solids content equivalent to 4-6ºBrix, with approximately 0.2-0.3% of pectin and a pH value of 3.8-4.5 (Augusto et al., 2010; Dak et al., 2008; Hsu, 2008; Tanglertpaibul and Rao, 1987; Takada and Nelson, 1983). A citric pectin solution was previously used by Takada and Nelson (1983) to evaluate tomato serum.

The degree of esterification (DE) of tomato pectin is a function of the process adopted, especially the blanching method used (hot or cold break), and the pectin DE of hot break tomato pulp is approximately 58-62% (Den Ouden and Van Vliet, 2002; Chou and Kokini, 1987).

Therefore, due to its industrial importance, tomato juice serum was chosen for evaluation in this work, and the serum model was designed to be similar to this product. Thus the present work evaluated the effect of high pressure homogenization (HPH) on the rheological properties of a fruit juice serum model, designed to be similar to tomato juice serum.

4.2. Material and Methods

4.2.1. Fruit Juice Serum Model

The fruit juice serum model evaluated here was composed of 5% (w/w) glucose and 0.3% (w/w) 58-62% DE pectin (citric pectin; Grindsted Pectin XSS100, Danisco) in distilled and deionized water (Milli-Q, Millipore, São Paulo, Brazil). The solution pH was adjusted to 4.2 using 0.1N NaOH.

The glucose and pectin were dispersed in water vigorously agitated at 1,000 rpm using a mechanical stirrer (Fisatrom 713D, São Paulo, Brazil). Then, it was allowed to rest overnight at 5ºC for complete hydration and release of air bubbles.

4.2.2. High Pressure Homogenization (HPH) Process

HPH processes were carried out using a high pressure homogenizer (Panda Plus, GEA Niro Soavi, Italy), with nominal maximum pressure operation up to 200 MPa. Samples were introduced into the equipment at 10ºC by suction, and quickly cooled using an ice bath just after the homogenization valve. The maximum temperature reached was 37°C (sample processed at 200 MPa, just before the ice bath).

The serum model was processed at 0, 25, 50, 75, 100, 150 and 200 MPa. The processed samples were refrigerated (5ºC) and their rheological properties evaluated on the same day.

4.2.3. Rheological Properties

Rheological measurements were carried out with a controlled stress (σ) rheometer (AR2000ex, TA Instruments, USA), with cone-plate geometry (2º, 60 mm of diameter). The temperature was maintained constant at 25ºC by a Peltier system.

The steady-state shear experiments were carried out in the shear rate ($\dot{\gamma}$) range of 0.1 s^{-1} to 100 s^{-1}. Samples were submitted to shear at 300 s^{-1} for 5 min to avoid thixotropy (data not shown). Product flow behaviour was modelled using the best fit with the Newton, Bingham, Ostwald-de-Waele (power law) and Herschel-Bulkley models.

The experiments were carried out with three replicates of freshly prepared samples, and the regression calculated for each replicate. The parameters for each model were obtained by linear or non-linear regression using the software CurveExpert Professional v.1.0.1, and a significant probability level of 95%.

4.3. Results and Discussions

Figure 4.1 shows the flow curves (σ versus $\dot{\gamma}$) for the fruit juice serum model homogenised at 0, 25, 50, 75, 100, 150 and 200 MPa. As expected, the serum model showed Newtonian behaviour ($R^2>0.99$), with a viscosity (η) close to the values reported for tomato serum (Table 4.1). Moreover, the serum model viscosity was close to that of other vegetable juices such as carrot, red raspberry, blueberry, pineapple and pomegranate juices, and clarified cashew, grape, peach, orange, cherry, pomegranate and *M. floribunda* juices (Table 4.1).

The product viscosity showed a tendency to decrease with increasing homogenization pressure (P_H; Figure 4.2). Similar results were reported for pectin solutions (Corredig and Wicker, 2001) and other biopolymers such as carboxymethylcellulose (CMC, Floury et al., 2002), flaxseed gum (Wang et al., 2011), xanthan gum (Harte and Venegas, 2010; Lagoueyte and Paquin, 1998), alginate and κ-carrageenan (Harte and Venegas, 2010).

Corredig and Wicker (2001) evaluated the effect of homogenization at 124 MPa on the viscosity of three pectins (0.3 $mg \cdot mL^{-1}$) with different DE values. While the homogenization process did not change the viscosity of two of the pectins, it did change the viscosity of the 70% DE pectin from 7 mPa·s (0 MPa) to 5 mPa·s (124 MPa). Moreover, the authors evaluated the change in molecular weight of the pectins, and showed that sample polydispersity had increased, while the average molecular weight had decreased, due to the homogenization pressure, thus explaining the results obtained.

Table 4.1. Viscosity values for fruit products.

Product	T (ºC)	η (mPa·s)	Reference
Fruit juice serum model	25	3.0	Present work
Tomato serum	20-25	1.3-6.0	Beresovsky et al. (1995), Tanglertpaibul and Rao (1987)
Carrot juice (7.6-8.4°Brix)	25	1.3-3.5	Vandresen et al. (2009)
Clarified cashew juice (12.1°Brix)	25	1.3	Cianci et al. (2005)
Red raspberry juice (10°Brix)	20	1.8	Nindo et al. (2005)
Clarified grape juice (22.9°Brix)	25	2.0	Zuritz et al. (2005)
Clarified peach juice (12.3°Brix)	20	2	Augusto et al. (2011a)
Blueberry juice (10°Brix)	20	2.9	Nindo et al. (2005)
Clarified orange juice (10-40°Brix)	25	2.4-5.8	Ibarz et al. (2009)
Clarified cherry juices (22-35°Brix)	20	2.9-5.4	Giner et al. (1996)
Clarified pomegranate juice (45.3°Brix)	20	3.5	Kaya and Sözer (2005)
Pineapple juice (4.3°Brix)	25	4	Shamsudin et al. (2009)
Clarified *M. floribunda* juice (44-45°Brix)	25	5-6	Cepeda and Villarán (1999); Cepeda et al. (1999)
Pomegranate juice (17.5°Brix)	25	7.4	Altan and Maskan (2005)

A reduction in average molecular weight of the carbohydrates due to homogenization was also observed by Floury et al. (2002) for carboxymethylcellulose (CMC) and by Lagoueyte and Paquin (1998) for xantan gum. In both cases, the homogenization process reduced the pseudoplastic behaviour (i.e. increased the flow behaviour index – n) and consistency (i.e. decreased the consistency index – k) of the products. Floury et al. (2002) suggested that the accentuated shear stress encountered by the polymer chain at the homogenization valve might produce sufficient energy to disrupt covalent bonds. Lagoueyte and Paquin (1998) suggested that the turbulence, cavitation and high shear stress produced during processing had an effect on the molecular conformation; first inducing the molecule to an ordered-disordered conformation transition, and then degrading the molecule. Similar behaviour was expected for the serum model evaluated here.

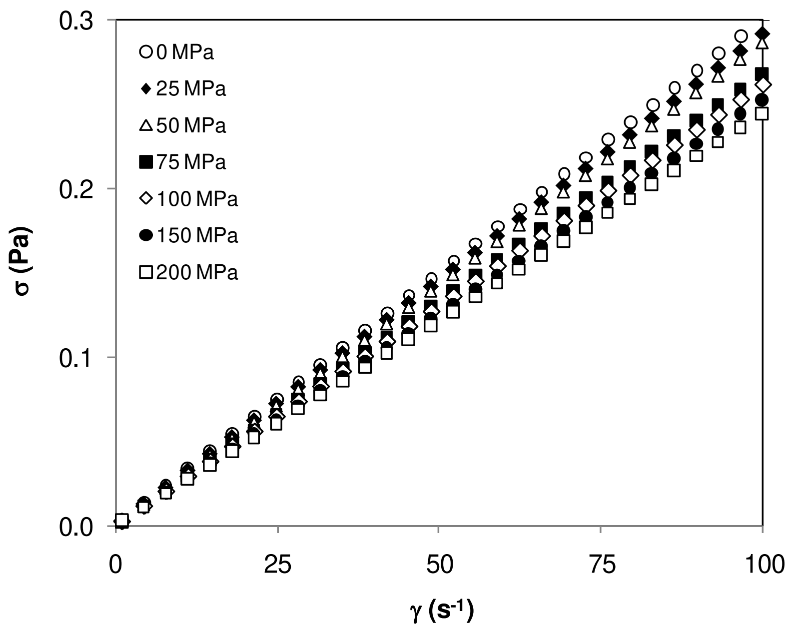

Figure 4.1. Fruit juice serum model flow curve (25°C) as a function of PH. Mean of three replicates; vertical bars represent the standard deviation for each value.

Figure 4.2 shows the viscosity of the fruit juice serum model viscosity (25°C) as a function of the homogenization pressure (P_H). The falling tendency was observed, and was modelled using two functions. Harte and Venegas (2010) proposed an exponential function (Equation 4.1) to describe the effect of homogenization pressure (P_H) on the viscosity (or apparent viscosity) of polymer suspensions. This function was used to model the present results (Equation 4.1, P_H in MPa, R^2>0.98). Moreover, due to the sigmoidal shape of the curve (Figure 4.2), a power-sigmoidal function was used (Equation 4.2, P_H in MPa, R^2>0.98) to model the effect of homogenization pressure (P_H) on the serum model viscosity. The two equations explain the reduction in viscosity due to the homogenization pressure (P_H) in the evaluated serum model well, which is of interest for the evaluation and design of HPH processing.

$$\eta(mPa \cdot s) = 3.03 \cdot \left[\frac{2.55 + \exp(-0.0059 \cdot P_H)}{2.55 + 1} \right] \quad \text{(Equation 4.1)}$$

$$\eta(mPa \cdot s) = \frac{3.02}{1 + (0.0099 \cdot P_H)^{0.856}} \quad \text{(Equation 4.2)}$$

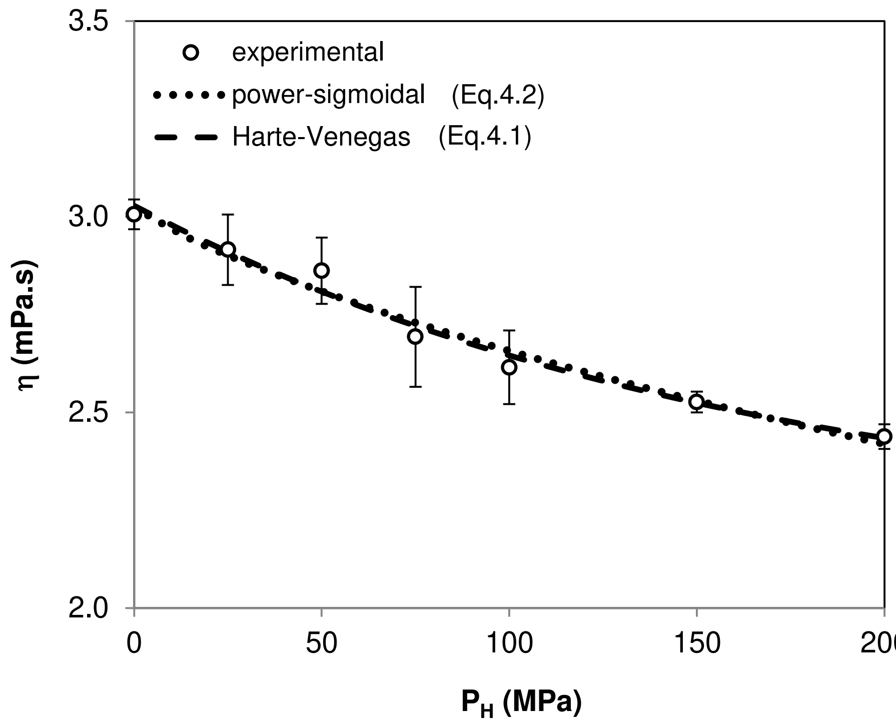

Figure 4.2. Fruit juice serum model viscosity (25°C) as a function of PH. Mean of three replicates; vertical bars represent the standard deviation for each value; curves are the evaluated models

The rheological properties of fruit juices are determined by interactions amongst the suspended particles and between these particles and the serum. The relative viscosity (η_r) of a dilute dispersion of solid particles in a liquid medium is described by the Einstein Equation (Equation 4.4, Genovese et al., 2007; Metzner, 1985), where $[\eta]$ is the intrinsic viscosity and ϕ is the particle volume fraction.

$$\eta_r = \frac{\eta_{dispersion}}{\eta_{continuous\_phase}} = 1 + [\eta] \cdot \phi \qquad \text{(Equation 4.4)}$$

According to this equation, the dispersion viscosity is affected by the continuous phase viscosity, the particle intrinsic viscosity (which depends on the particle shape) and the relative volume occupied by the particles. For fruit juices, the dispersed phase (pulp) is formed of fruit tissue cells and their fragments, cell walls and insoluble polymer clusters and chains. Although more complex and in most cases more concentrated than the fluid proposed in the Einstein Equation, a qualitative evaluation can be carried out based on this equation.

In the present work, the serum model viscosity represented a fruit juice continuous phase, and its viscosity decreased due to the HPH. Thus, the behaviour observed suggests a reduction in juice viscosity when processed by HPH. However, the final juice behaviour will also be a function of the particle volume fraction and particle intrinsic viscosity.

Bayod and Tornberg (2011) studied the microstructure of tomato suspensions homogenized at 9 MPa. The authors observed an increase in the surface area covered by particles and in its volume fraction, with a reduction on particle size due to the homogenization process. In fact, Bayod et al. (2007) observed increases in consistency and yield stress (σ_0) of the tomato concentrate when homogenized at 9 MPa. Yoo and Rao (1994) observed that the smaller the suspended particles were, the smaller the distance between them and the greater the interaction amongst them.

Silva et al. (2010) studied the effect of homogenization (up to 70 MPa) on pineapple pulp properties. Although the authors observed the same reduction in particle size, the product consistency showed the opposite behaviour of that reported for tomato products: the homogenization process reduced the pseudoplastic behaviour (i.e. increased the flow behaviour index – n) and consistency (i.e. decreased the consistency index – k) of the pulp. Similar behaviour was observed by Donsì et al. (2009) for apple juice, where the viscosity and suspended particle size were reduced by HPH processing.

Considering the reduction in viscosity due to HPH observed here and those reported for other carbohydrates (Wang et al., 2011; Harte and Venegas, 2010; Floury et al., 2002; Corredig and Wicker, 2001; Lagoueyte and Paquin, 1998), the different results obtained for tomato, apple and pineapple juices cannot be assigned to the serum phase and must be associated with differences in the dispersed phase.

In fact, Lopez-Sanchez et al. (2011) showed that the cell walls of each vegetable have different behaviours when processed by HPH. While carrot tissue requires high shear values to be disrupted, tomato cell walls were broken with moderate shear values. This suggests that the effect of HPH processing is different for each fruit product, and highlights the need for better understanding of this process.

Once again this highlights the fact that the effect of HPH on the rheological properties of fruit juices is a function of the balance between the structural changes in the pulp and serum. The present work showed the behaviour expected for the serum phase using a tomato juice serum model. The results obtained are potentially useful for understanding juice behaviour, but further work is necessary for a better understanding of the effect of high pressure homogenization on the rheological properties of tomato juice. In fact it is the subject of our next works.

4.4. Conclusions

The present work evaluated the effect of high pressure homogenization (HPH) on the rheological properties of a fruit juice serum model. The serum model was chosen and designed to be similar to tomato serum, and showed Newtonian behaviour. Product viscosity decreased with increasing homogenization pressure, and could be modelled well using two different functions (exponential and sigmoidal). Based on the results obtained, the expected behaviour of the fruit juice was discussed. The results obtained are potentially useful for future studies on product and process development.

4.5. Acknowledgments

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

4.6. Nomenclature

$\dot{\gamma}$ = shear rate [s^{-1}]

ϕ = particle volume fraction [-]

η = viscosity [Pa·s]

η_r = relative viscosity (Equation 4.4) [Pa·s]

[η] = intrinsic viscosity [Pa·s]

σ = shear stress [Pa]

σ_0 = yield stress, Herschel-Bulkley's model [Pa]

k = consistency coefficient, Herschel-Bulkley's model [$Pa{\cdot}s^n$]

n = flow behavior index, Herschel-Bulkley's model [-]

P_H = homogenization pressure [MPa]

4.7. References

Aliberti, N. C. M. (2009). *Influência da Homogeneização a Alta Pressão Sobre a Retenção de Antocianinas Presentes na Polpa de Açaí (Euterpe oleraceae Mart.).* PhD Tesis, University of São Paulo.

Altan, A. N.; Maskan, M. (2005). Rheological behavior of pomegranate (Punica granatum L.) juice and concentrate. *Journal of Texture Studies*, 36, 68–77.

Augusto, P. E. D.; Falguera, V.; Cristianini, M.; Ibarz, A. (2010). Rheological behavior of tomato juice: steady-state shear and time-dependent modeling. *Food and Bioprocess Technology, in press* (DOI: 10.1007/s11947-010-0472-8).

Augusto, P. E. D.; Falguera, V.; Cristianini, M.; Ibarz, A. (2011a). Influence of fibre addition on the rheological properties of peach juice. *International Journal of Food Science and Technology,* 46, 1086-1092.

Augusto, P. E. D.; Tribst, A. A. L.; Cristianini, M. (2011b). Thermal inactivation of Lactobacillus plantarum in a model liquid food. *Journal of Food Process Engineering*, 34, 1013-1027.

Bayod, E.; Tornberg, E. (2011). Microstructure of highly concentrated tomato suspensions on homogenisation and subsequent shearing. *Food Research International*, 44, 755-764.

Bayod, E.; Månsson, P.; Innings, F.; Bergenståhl, B.; Tornberg, E. (2007). Low shear rheology of concentrated tomato products. Effect of particle size and time. *Food Biophysics*, 2, 146-157.

Beresovsky, N.; Kopelman, I. J.; Mizrah, S. (1995). The role of pulp interparticle interaction in determining tomato juice viscosity. *Journal of Food Processing and Preservation*, 19, 2, 133-146.

Berto, M.I., Gratão, A.C.A., vitali, A.A; Silveira, J.R.V. (2003). Rheology of sucrose-CMC model solution. *Journal of Texture Studies*, 34, 391–400, 2003.

Campos, F ; Cristianini, M (2007). Inactivation of *Saccharomyces cerevisiae* and *Lactobacillus plantarum* in orange juice using ultra high-pressure homogenization. *Innovative Food Science & Emerging Technologies*, 8, 2, 226-229.

Cepeda, E.; Villarán, M. C. (1999). Density and viscosity of *Malus floribunda* juice as a function of concentration and temperature. *Journal of Food Engineering*, 41, 103-107.

Cepeda, E.; Villarán, M. C.; Ibarz, A. (1999). Rheological properties of cloudy and clarified juice of Malus floribunda as a function of concentration and temperature. *Journal of Texture Studies*, 30, 481–491.

Chou, T. D.; Kokini, J. L. (1987). Rheological properties and conformation of tomato paste pectins, citrus and apple pectins. *Journal of Food Science*, 52, 6, 1658-1664.

Cianci, F. C.; Silva, L. F. M.; Cabral, L. M. C.; Matta, V. M. (2005). Clarificação e concentração de suco de caju por processos com membranas. *Ciência e Tecnologia de Alimentos*, 25(3), 579-583.

Corbo, M. R.; Bevilacqua, A.; Campaniello, D.; Ciccarone, C.; Sinigaglia, M. (2010). Use of high pressure homogenization as a mean to control the growth of foodborne moulds in tomato juice. *Food Control*, 21, 1507-1511.

Corredig, M.; Wicker, L. (2001). Changes in the molecular weight distribution of three commercial pectins after valve homogenization. *Food Hydrocolloids,* 15, 17-23.

Dak, M.; Verma, R. C.; Jaaffrey, S. N. A. (2008). Rheological properties of tomato concentrate. *International Journal of Food Engineering*, 4, 7, article 11.

Donsì, F.; Esposito, L.; Lenza, E.; Senatore, B.; Ferrari, G. (2009). Production of self-stable Annurca apple juice with pulp by high pressure homogenization. *International Journal of Food Engineering*, 5, 4, article 12.

Floury, J.; Desrumaux, A.; Axelos, M. A.V.; Legrand, J. (2002). Degradation of methylcellulose during ultra-high pressure homogenisation. *Food Hidrocolloids*, 16, 47-53.

Genovese, D. B.; Lozano, J. E.; Rao, M. A. (2007). The rheology of colloidal and noncolloidal food dispersions. *Journal of Food Science*, 72, 2, R11-R20.

Giner, J.; Ibarz, A.; Garza, S.; Xhian-Quan, S. (1996). Rheology of clarified cherry juices. *Journal of Food* Engineering, 30, 147-154.

Harte, F.; Venegas, R. (2010). A model for viscosity reduction in polysaccharides subjected to high-pressure homogenization. *Journal of Texture Studies,* 41, 49–61.

Hsu, K. C. (2008). Evaluation of processing qualities of tomato juice induced by thermal and pressure processing. *LWT - Food Science and Technology*, 41, 450-459.

Ibarz, A.; Barbosa-Cánovas, G. V. (2003). *Unit Operations in Food Engineering*. Boca Raton: CRC Press.

Ibarz, R.; Falguera, V.; Garvín, A.; Garza, S.; Pagan, J.; Ibarz, A. (2009). Flow behavior of clarified orange juice at low temperatures. *Journal of Texture Studies,* 40, 445–456.

Kaya, A.; Sözer, N. (2005). Rheological behaviour of sour pomegranate juice concentrates (*Punica granatum* L.). *International Journal of Food Science and Technology*, 40, 223–227.

Lagoueyte, N.; Paquin, P. (1998). Effects of microfluidization on the functional properties of xanthan gum. *Food Hydrocolloids,* 12, 365-371.

Lopez-Sanchez, P.; Svelander, C.; Bialek, L.; Schummm, S.; Langton, M. (2011). Rheology and microstructure of carrot and tomato emulsions as a resulto f high-pressure homogenization conditions. *Journal of Food Science*, 76, 1, E130-E140.

Metzner, A. B. (1985). Rheology of suspensions in polymeric liquids. *Journal of Rheology*, 29, 6, 739-775.

Nindo, C. I.; Tang, J.; Powers, J. R.; Singh, P. (2005). Viscosity of blueberry and raspberry juices for processing applications. *Journal of Food Engineering*, 69, 343–350.

Nisha, P., Singhal, R. S., Pandit, A. B. (2010). Kinetic modelling of colour degradation in tomato puree (*Lycopersicon esculentum* L.). *Food and Bioprocess Technology, in press* (DOI:10.1007/s11947-009-0300-1).

Ouden, F. W. C. Den; Vliet, T. Van. (1997). Particle size distribution in tomato concentrate and effects on rheological properties. *Journal of Food Science*, 62, 3, 565-567.

Pathanibul, P.; Taylor, T. M.; Davidson, P. M.; Harte, F. (2009). Inactivation of *Escherichia coli* and *Listeria innocua* in apple and carrot juices using high pressure homogenization and nisin. *International Journal of Food Microbiology*, 129, 316-320.

Patrignani, F.; Vannini, L.; Kamdem, S. L. S.; Lanciotti, R.; Guerzoni, M. E. (2009). Effect of high pressure homogenization on *Saccharomyces cerevisiae* inactivation and physic-chemical features in apricot and carrot juices. *International Journal of Food Microbiology*, 136, 26-31.

Patrignani, F.; Vannini, L.; Kamdem, S. L. S.; Lanciotti, R.; Guerzoni, M. E. (2010). Potentialites of high pressure homogenization to inactivate *Zygosaccharomyces bailii* in fruit juices. *Journal of Food Science*, 75, 2, M116-M120.

Rao, M. A. (1999). Flow and Functional Models for Rheological Properties of Fluid Foods. In: Rao, M. A. *Rheology of Fluid and Semisolid Foods: Principles and Applications*. Gaithersburg: Aspen Publishers.

Saldo, J.; Suárez-Jacobo, Á.; Gervilla, R.; Guamis, B.; Roig-Sagués, A. X. (2009). Use of ultra-high-pressure homogenization to preserve apple juice without heat damage. *High Pressure Research*, 29, 1, 52-56.

Shamsudin, R.; Daud, W.R.W.; Takrif, M.S., Hassan, O.; Ilicali, C. (2009). Rheological properties of Josapine pineapple juice at different stages of maturity. *International Journal of Food Science and Technology*, 44, 757–762.

Silva, V.M.; Sato, A.C.K.; Barbosa, G.; Dacanal, G.; Ciro-Velásquez; H.J.; Cunha, R.L. (2010). The effect of homogenisation on the stability of pineapple pulp. *International Journal of Food Science and Technology*, 45, 2127–2133.

Tahiri, I.; Makhlouf, J.; Paquin, P.; Fliss, I. (2006). Inactivation of food spoilage bacteria and *Escherichia coli* O157:H7 in phosphate buffer and orange juice using dynamic high pressure. *Food Research International*, 39, 98-105.

Takada, N.; Nelson, P. E. (1983). Pectin-protein interaction in tomato products. *Journal of Food Science,* 48, 5, 1408-1411.

Tanglertpaibul, T.; Rao, M. A. (1987). Flow properties of tomato concentrates: effect of serum viscosity and pulp content. *Journal of Food Science*, 52, 2, 318-321.

Tribst, A. A. L.; Franchi, M. A.; Cristianini, M. Massaguer, P. R. (2009). Inactivation of *Aspergillus niger* in mango nectar by high-pressure homogenization combined with heat shock. *Journal of Food Science*, 74, 9, M509-M514.

Tribst, A. A. L.; Franchi, M. A.; Cristianini, M. Massaguer, P. R. (2011). Quality of mango nectar processed by high-pressure homogenization with optimized heat treatment. *Journal of Food Science*, 76, 2, M106-M110.

Vandresen, S., Quadri, M. G. N., Souza, J. A. R., & Hotza, D. (2009). Temperature effect on the rheological behavior of carrot juices. *Journal of Food Engineering*, 92, 269–274.

Wang, Y.; Dong, L.; Wang, L. J.; Xue, J. (2011). Effects of high pressure homogenization on rheological properties of flaxseed gum. *Carbohydrate Polymers,* 83, 489–494.

Yoo, B.; Rao, M. A. (1994). Effect of unimodal particle size and pulp content on rheological properties of tomato puree. *Journal of Texture Studies*, 25, 4, 421-436.

Zuritz, C. A.; Muñoz Puntes, E.; Mathey, H. H.; Pérez, e. h.; Gascón, A.; Rubio, L. A.; Carullo, C. A.; Chernikoff, R. E.; Cabeza, M. S. (2005). Density, viscosity and coefficient of thermal expansion of clear grape juice at different soluble solid concentrations and temperatures. *Journal of Food Engineering*, 71, 143–149.

Chapter 5: Effect of High Pressure Homogenization (HPH) on the Rheological Properties of Tomato Juice. Part I: Time-Dependent and Steady-State Shear

This chapter was developed at University of Campinas, and is currently under review as:

AUGUSTO, P. E. D.; IBARZ, A.; CRISTIANINI, M. Effect of High Pressure Homogenization (HPH) on the Rheological Properties of Tomato Juice. Part I: Time-Dependent and Steady-State Shear.

Abstract

High pressure homogenization (HPH) is a non-thermal technology that 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 works in the literature reporting the physicochemical changes caused in fruit products due to HPH, especially those regarding the rheological properties. The present work evaluated the effect of HPH (up to 150 MPa) on the time-dependent and steady-state shear rheological properties of tomato juice. HPH reduced the mean particle diameter and particle size distribution (PSD), and increased its consistency and thixotropy. The rheological results were in accordance with the PSD observed. The rheological properties of the juice were evaluated by the Herschel–Bulkley and Falguera-Ibarz models (steady-state shear) and Figoni-Shoemaker and Weltman models (time-dependent). The parameters of these equations were modelled as a function of the homogenization pressure. The models obtained described the experimental values well, and contributed to future studies on product and process development.

Keywords:

Food properties, high pressure homogenization, rheology, viscosity.

Efeito da Homogeneização a Alta Pressão (HAP) nas Propriedades Reológicas de Suco de Tomate. Parte I: Propriedades Dependentes do Tempo e Cisalhamento em Estado Estacionário

Resumo

A homogeneização a alta pressão (HAP) tem sido proposta como alternativa parcial ou total ao processo térmico de alimentos. Embora a inativação microbiana tenha sido bastante estudada, poucos trabalhos da literatura estudam alterações físico-químicas em produtos de frutas devido a HAP, especialmente em relação às características reológicas. O presente trabalho avaliou o efeito da HAP (até 150 MPa) nas características reológicas dependentes do tempo e em cisalhamento em estado estacionário de suco de tomate. A HAP reduziu o diâmetro médio das partículas e sua distribuição (PSD), aumentando a consistência e tixotropía do produto, sendo as alterações reológicas relacionadas às mudanças na PSD. As propriedades reológicas do suco foram avaliadas utilizando os modelos de Herschel–Bulkley e Falguera-Ibarz (cisalhamento em estado estacionário) e Figoni-Shoemaker e Weltman (dependentes do tempo). Os parâmetros de tais modelos foram então modelados como função da pressão de homogeneização. Os modelos obtidos descreveram bem os valores experimentais, contribuindo com futuros estudos em desenvolvimento de produtos e processos.

Palavras-chave:

Homogeneização a alta pressão, propriedades dos alimentos, reologia, viscosidade.

5.1. Introduction

High pressure homogenization (HPH) technology consists of pressurizing a fluid to flow quickly through a narrow gap valve, which greatly increases its velocity, resulting in depressurization with consequent cavitation and high shear stress. Thus particles, cells and macromolecules suspended in the fluid are subjected to high mechanical stress, becoming twisted and deformed (Pinho et al., 2011; Floury et al., 2004). Several studies have evaluated the use of HPH for microbial inactivation in fruit products. The use of HPH as a partial or total substitute for the thermal processing of foods has been studied for tomato (Corbo et al., 2010), apple (Donsì et al., 2009; Pathanibul et al., 2009; Saldo et al., 2009), mango (Tribst et al., 2011; Tribst et al., 2009), açaí (Aliberti, 2009), orange (Campos and Cristianini, 2007; Tahiri et al., 2006), carrot (Patrignani et al., 2010; Pathanibul et al., 2009; Patrignani et al., 2009), banana (Calligaris et al., 2012) and apricot (Patrignani et al., 2010; Patrignani et al., 2009) juices.

However, although microbial inactivation has been widely studied, there are only a few works in the literature regarding the physicochemical changes in fruit products due to high pressure homogenization (HPH) processing, especially regarding their rheological properties. 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). The study of the influence of processing on the rheological properties of foods is thus essential for an efficient product and process design.

Tomato is one of the most popular and widely grown vegetables in the world (Nisha et al., 2010). It is also one of the most important vegetables in the food industry, and widely included in the human diet. Homogenization is a commonly used unit operation in tomato processing, and it is well accepted that homogenization increases the apparent viscosity of tomato products (Bayod, Tornberg, 2011; Lopez-Sanchez et al., 2011a; Bayod et al., 2007; Ouden and Vliet, 2002; Ouden and Vliet, 1997; Beresovsky et al., 1995; Thakur et al., 1995; Becker et al., 1987; Foda and Mccollum, 1970; Whittenberg and Nutting, 1958). However, no papers were found in the literature studying the effect of homogenization on the rheological parameters of tomato products (i.e., the steady-state shear and time-dependent rheological parameters), especially at high pressures (HPH). The present work evaluated the effect of high pressure homogenization (HPH) on the time-dependent and steady-state shear rheological properties of tomato juice.

5.2. Materials and Methods

A 4.5ºBrix tomato juice was obtained by diluting a commercial 30ºBrix pulp in distilled water. The commercial pulp was used to guarantee standardization and repeatability. It was obtained using the hot break process, concentrated by evaporation at 65°C, thermally processed by the UHT method and aseptically packaged in bags.

The pulp was fractionated into small portions in the laboratory, packaged in high density polyethylene bottles and frozen at -18ºC until used. This procedure allowed for the use of the same product for the enire experiment. The samples were thawed at 4ºC, diluted using distilled water at 50ºC to ensure better hydration (Tehrani and Gandhi, 2007), and then allowed to rest for 24 hours at 5ºC to ensure complete hydration and release the incorporated air. The juice pH was 4.6.

5.2.1. High Pressure Homogenization (HPH) Process

The juice was homogenized at 0 MPa (control), 50 MPa, 100 MPa and 150 MPa using a high pressure homogenizer (Panda Plus, GEA Niro Soavi, Italy). Samples were introduced at room temperature into the equipment by suction and quickly cooled using an ice bath just after the homogenization valve. The maximum temperature reached was ~40°C (for the sample processed at 150 MPa just before the ice bath). The experiments were carried out with three replicates.

5.2.3. Particle Size Distribution (PSD)

Sample particle size distribution (PSD) was measured by light scattering (Malvern Mastersizer 2000 with Hydro 2000s, Malvern Instruments Ltd., UK), with three replicates, for the juices processed at 0 MPa, 50 MPa and 150 MPa. In addition to the PSD, the volume-based mean diameter was evaluated (D[4,3], Equation 5.1; where n_i is the number of particles with diameter d_i) and the area-based mean diameter (D[3,2], Equation 5.2). Both equivalent diameters were evaluated, since the D[4,3] is greatly influenced by large particles, whereas the D[3,2] is more influenced by the smaller ones (Lopez-sanchez et al., 2011a; Bengtsson and Tornberg, 2011). The particle specific surface area (A_{SF}) was also obtained, using Equation 5.3.

$$D[4,3] = \frac{\sum_i n_i d_i^{\,4}}{\sum_i n_i d_i^{\,3}} \qquad \text{(Equation 5.1)}$$

$$D[3,2] = \frac{\sum_i n_i d_i^{\,3}}{\sum_i n_i d_i^{\,2}} \qquad \text{(Equation 5.2)}$$

$$A_{SF} = \frac{6\sum_i \frac{V_i}{d_i}}{\rho \sum_i V_i} = \frac{6}{\rho \cdot D[3,2]} \qquad \text{(Equation 5.3)}$$

5.2.3. Rheological Properties

Rheological analyses were carried out using a controlled stress (σ) rheometer (AR2000ex, TA Instruments, USA) with a cross hatched plate-plate geometry (40 mm of diameter). The gap dimension (1.0 mm) was determined using a gap-independency procedure as described by Tonon et al. (2009). In this procedure, the distance between the plates was varied and the sample flow behaviour evaluated. The ideal gap dimension was observed when the sample flow behaviour was independent of variations in the gap. The temperature was maintained constant at 25ºC using a Peltier system.

The rheological evaluation was carried out with new samples, which were first placed in the rheometer and maintained at rest for 10 min before shearing. After resting, the samples were sheared at a constant shear rate (300 s^{-1}) for 10 min, while the shear stress was measured. After the time-dependent shear period, a linear decreasing stepwise protocol (300 s^{-1} to 0.1 s^{-1}) was used to guarantee steady-state shear conditions (~7 min).

The time-dependent rheological properties of the product were evaluated using the first part of the protocol. The shear stress decay was evaluated by two models widely used to describe thixotropy in foods (Ibarz and Barbosa-Cánovas 2003) and previously evaluated for tomato juice (Augusto et al., 2010). The models evaluated were the Figoni and Shoemaker (1983: Equation 5.4) and Weltman (1943; Equation 5.5) models.

$$\sigma = \sigma_e + (\sigma_0 - \sigma_e) \cdot \exp(-k_{FS} \cdot t) \qquad \text{(Equation 5.4)}$$

$$\sigma = A - B \cdot \ln t \qquad \text{(Equation 5.5)}$$

The steady-state shear rheological properties of the product were evaluated using the second part of the protocol. The product flow behaviour was modelled using the Herschel-Bulkley model (Equation 5.6), which comprises the Newton, Bingham and Ostwald-de-Waele (power law) models, and has been widely used to describe the rheological properties of food products. Moreover, the flow behaviour of the tomato juice was also evaluated using another rheological model recently proposed by Falguera and Ibarz (2010). In the Falguera–Ibarz model (Equation 5.7), the decline in apparent viscosity ($\eta_a = \sigma / \dot{\gamma}$) with the shear rate is described by a power equation, from an initial value (η_0) to an equilibrium one (η_∞).

$$\sigma = \sigma_0 + k \cdot \dot{\gamma}^n \qquad \text{(Equation 5.6)}$$

$$\eta_a = \eta_\infty + (\eta_0 - \eta_\infty) \cdot \dot{\gamma}^{(-k_{FI})} \qquad \text{(Equation 5.7)}$$

Each parameter in Equations 5.4-5.7 was then modelled as a function of the homogenization pressure (P_H) and the rheological parameter ("RP", i.e., σ for the Figoni-Shoemaker, Weltman and Herschel–Bulkley models, and η_a for the Falguera-Ibarz model) obtained by the models (RP_{model}) plotted as a function of the experimental values ($RP_{experimental}$). The regression of these data to a linear function (Equation 5.8) results in three parameters that can be used to evaluate the description of the experimental values by the models, i.e. the linear slope (α; that must be as close as possible to the unity), the intercept (β; that must be as close as possible to zero) and the coefficient of determination (R^2; that must be as close as possible to the unity).

$$RP_{model} = \alpha \cdot RP_{experimental} + \beta \qquad \text{(Equation 5.8)}$$

The parameters for 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%.

5.3. Results and Discussion

5.3.1. Particle Size Distribution (PSD)

Figure 5.1 shows the effect of HPH (0-150 MPa) on the tomato juice particle size distribution (PSD). As expected, the homogenization processing reduced the mean particle diameter, as previously observed for various tomato products (up to 9 MPa, Bayod and Tornberg, 2011; Bengtsson and Tornberg, 2011; Bayod et al., 2008; up to 60 MPa, Lopez-Sanchez et al., 2011a) and other vegetable products, such as passion fruit juice (up to 28 MPa, Okoth et al., 2000), citrus juices (up to 30 MPa, Betoret et al., 2009; Sentandreu et al., 2011; up to 170 MPa, Lacroix et al., 2005), apple juice (up to 200 MPa, Donsì et al., 2009), apple, broccoli, carrot and potato sauces (up to 9 MPa, Bengtsson and Tornberg, 2011; up to 60 MPa, Lopez-Sanchez et al., 2011a).

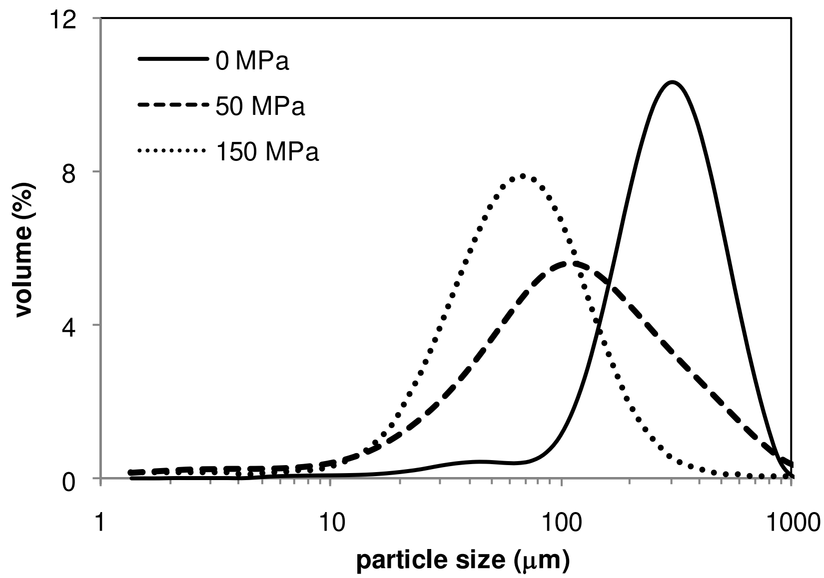

Figure 5.1. Effect of HPH (0-150 MPa) on tomato juice particles size distribution (PSD). Mean of three replicates.

Moreover, as can be seen in Figure 5.1, not only was the mean diameter affected by the HPH but also the particle size distribution (PSD). The control juice showed a monomodal distribution, with particle diameters ranging between ~100 μm and ~1000 μm. When the juice was processed at 50 MPa, a broader distribution was observed, with particles ranging between ~10 μm and ~1000 μm. Finally, when the juice processed at 150 MPa was evaluated, a further reduction in particle diameter and narrower distribution (~10 μm to ~300 μm) were seen. Moreover, the changes in particle diameter between 50 MPa and 150 MPa were less pronounced then those between 0 MPa and 50 MPa. Similar behaviour was observed by Silva et al. (2010) for pineapple pulp homogenized at pressures up to 70 MPa.

Thus the effect of homogenization pressure (P_H) on the disruption of suspended particles seems to follow an asymptotic behaviour, i.e., increases in P_H have reduced effects at higher P_H values. In fact this can be observed even in the D[4,3] and D[3,2] values (Figure 5.2) and in the following evaluation of the rheological behaviour.

Figure 5.2 shows the reduction in the volume-based mean diameter (D[4,3], Equation 5.1) and in the area-based mean diameter (D[3,2], Equation 5.2) due to the homogenization pressure. Although the equivalent diameters were both reduced during HPH, the reduction in D[3,2] between the samples treated at 0 MPa and 50 MPa (79%) was higher than in D[4,3] (45%). Since the D[4,3] is greatly influenced by large particles and the D[3,2] more influenced by smaller ones (Lopez-sanchez et al., 2011a; Bengtsson and Tornberg, 2011), this result indicated a considerable increase in the number of small particles when the juice was processed at 50 MPa. Moreover, the reduction in D[3,2] between 50 MPa and 150 MPa (20%) was smaller than in D[4,3] (53%), which indicates that the following disruptions occurred preferentially in the larger suspended particles, in accordance with the PSD values shown in Figure 5.1.

Becker et al. (1972) studied the tomato cell dimensions, and found values between 400 μm x 600 μm and 600 μm x 1000 μm. Thus it is to be expected that the control juice, with particle diameters ranging between ~100 μm and ~1000 μm, would be constituted of some whole cells and their fragments, obtained during tomato pulp processing. The homogenization process disrupts the remaining cells and breaks the fragments up into small suspended particles, and it is to be expected that the small fragments would be less susceptible breakage during processing than the larger ones or the whole cells, which explains the effect observed for P_H on the disruption behaviour of suspended particles.

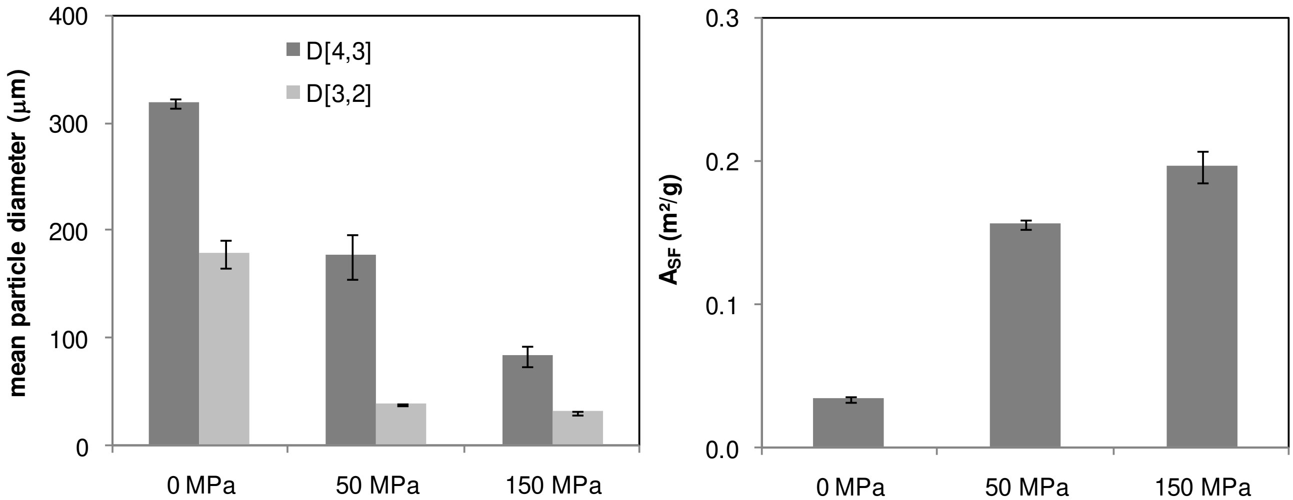

Figure 5.2. Effect of HPH (0-150 MPa) on tomato juice particles mean diameter (D[4,3] and D[3,2]; left) and specific surface area (A_{SF}, right). Mean of three replicates; vertical bars represent the standard deviation in each value.

5.3.2. Rheological Properties

Fruit juices are composed of an insoluble phase (the pulp) dispersed in a viscous solution (the serum). The dispersed phase or pulp is formed of fruit tissue cells and their fragments, cell walls and insoluble polymer clusters and chains. The serum is an aqueous solution of soluble polysaccharides, sugars, salts and acids. The fruit juice rheological properties are thus defined by the interactions inside each phase and between them.

The tomato juice serum is a Newtonian fluid, which becomes a Herschel-Bulkley fluid due to the dispersion of pulp particles (Augusto et al., 2011b; Augusto et al., 2010; Tanglertpaibul and Rao, 1987). The tomato juice particle diameters ranged between 10 μm and 1000 μm in the present work (0-150 MPa). In this range, the product is classified as a noncolloidal dispersion, where hydrodynamic forces govern its rheological properties and Brownian motion is negligible (Fischer et al., 2009; Genovese et al., 2007; Tsai and Zammouri, 1988).

The relative viscosity (η_r, Equation 5.9) of dilute solid particles dispersed in a liquid medium is described by the Einstein Equation (Equation 5.10; Genovese et al., 2007; Loveday et al., 2007; Guyot et al., 2002; Metzner, 1985). Moreover, one of the most used equations derived for concentrated dispersions is the Krieger-Dougherty equation (Equation 5.11; Fischer et al., 2009; Genovese et al., 2007; Loveday et al., 2007; Guyot et al., 2002).

$$\eta_r = \frac{\eta_{dispersion}}{\eta_{continuous\_phase}} \qquad \text{(Equation 5.9)}$$

$$\eta_r = 1 + [\eta] \cdot \phi \qquad \text{(Equation 5.10)}$$

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta] \cdot \phi_m} \qquad \text{(Equation 5.11)}$$

According to these equations, the viscosity of the dispersion is affected by the continuous phase viscosity (the juice serum), the particle intrinsic viscosity (which depends on particle shape) and the relative volume occupied by the particles (expressed by its volume fraction - ϕ - and the maximum packing fraction of solids - ϕ_m). Although more complex and in most cases more concentrated than the Einstein proposed fluid, a qualitative evaluation can be carried out based on Equations 5.10 and 5.11.

The HPH reduced the diameters of the tomato juice suspended particles, increasing its volume fraction (ϕ). Thus the observed behaviour suggests an increase in apparent viscosity of the tomato juice when processed by HPH. However, the final juice behaviour will also be a function of the serum viscosity and particle intrinsic viscosity.

Augusto et al. (2011b) studied the effect of HPH on the viscosity of a tomato juice serum model, describing a viscosity reduction due to HPH (~ 5% at 50 MPa and ~15% at 150 MPa). Thus, HPH reduces the viscosity of the tomato juice continuous phase (i.e., the serum) ($\eta_{continuous\_phase}$), which would reduce the product apparent viscosity ($\eta_{dispersion}$).

Moreover, it is to be expected that the HPH would also change the particle shapes, polydispersity, volume fraction (ϕ), maximum packing fraction of solids (ϕ_m) and intrinsic viscosity ([η]).

However, the final product rheology cannot be simply described by the hydrodynamic forces. The reduction in the diameters of the tomato juice suspended particles can improve interparticle interaction, since the particle surface area is greatly increased (Figure 5.2). The interaction of small particles can be due to van der Waals forces (Genovese et al., 2007; Tsai and Zammouri, 1988) and/or electrostatic forces due to the interaction between the negatively charged pectins and the positively charged proteins (Beresovsky et al., 1995; Takada and Nelson, 1983). Cell disruption and further fragmentation not only increase the surface area of the suspended particles, but also change the properties of the particles and serum. Cell fragmentation exposes and releases wall constituents, such as pectins and proteins, improving the particle-particle and particle-serum interactions. Thus, the non-hydrodynamic forces can be important in systems with smaller suspended particles, such as the HPH tomato juice.

Thus as observed by Guyot et al. (2002), it is still not possible to predict the rheological behaviour of a dispersed system just from its PSD. The final tomato juice behaviour in relation to the HPH will be a function of the changes in both particles and serum.

3.2. Steady-State Shear Rheological Properties

Figure 5.3 shows the flow curves (σ x $\dot{\gamma}$) of the tomato juice processed by HPH (0-150 MPa). Figure 5.4 shows the corresponding behaviour of the apparent viscosity in relation to the shear rate (η_a x $\dot{\gamma}$).

As expected (Augusto et al., 2010), the tomato juice flow behaviour was well described by the Herschel–Bulkley model (Equation 5.6; R^2>0.99), while the apparent viscosity behaviour in relation to the shear rate was well described by the Falguera-Ibarz model (Equation 5.7; R^2>0.99). Moreover, the parameters obtained for both models were in accordance with those previously described for other fruit products (Tables 5.1 and 5.2).

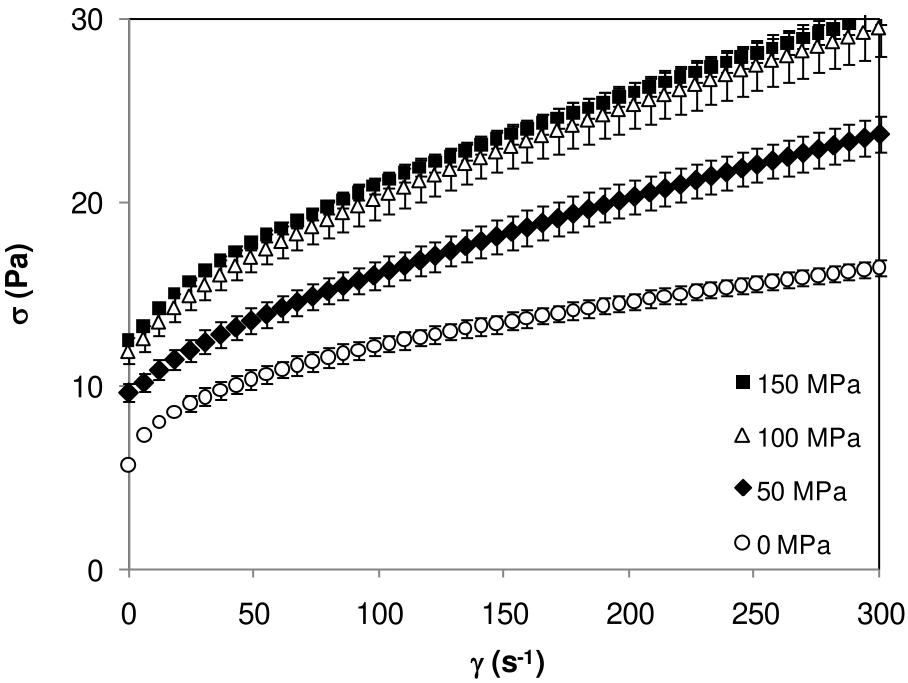

Figure 5.3. Flow curves (σ x $\dot{\gamma}$) of tomato juice processed by HPH (0-150 MPa). Mean of three replicates at 25ºC; vertical bars represent the standard deviation for each value.

Figures 5.3 and 5.4 show that HPH improves tomato juice consistency, i.e., increases the shear stress (σ) and apparent viscosity (η_a) related to each shear rate ($\dot{\gamma}$). Moreover, it can be seen that the main changes take place between 0 MPa and 50 MPa, being smaller between 50 MPa and 100 MPa and tending to an asymptotic behaviour between 100 MPa and 150 MPa. The changes are due to the reduction in the suspended particles, and are in accordance with the values observed for the PSD.

Table 5.1. Values for the parameters of Herschel-Bulkley model for fruit products.

Product	**T (ºC)**	**σ_0 (Pa)**	**k (Pa·s^n)**	**n**	**Reference**
Tomato juice (0 MPa)	25	5.38	0.92	0.44	Present work
Tomato juice	20	0.94	0.19	0.56	Augusto et al. (2010)
Concentrated tamarind juice (71ºBrix)	30	1.46	4.32	0.59	Ahmed et al. (2007)
Jabuticaba pulp	25	1.55	0.48	0.6	Sato and Cunha (2009)
Concentrated orange juice	25	2.2	3.13	0.64	Falguera and Ibarz (2010)
Peach juice (10% fiber)	20	3.26	13.1	0.46	Augusto et al. (2011a)
Açai pulp	25	4.35	0.17	0.78	Tonon et al. (2009)
Butia pulp	20	32.54	0.15	0.86	Haminiuk et al. (2006)
Peach puree (12-21ºBrix)	25	1.11-25.3	2.46-11.3	0.32-0.34	Massa et al. (2010)
Umbu pulp (10-25ºBrix)	20	3.18-8.06	14.00-37.74	0.29-0.31	Pereira et al. (2007 and 2008)
Apple, apricot and banana based babyfood	20	3.38-7.41	4.76-13.7	0.18-0.38	Ahmed and Ramaswamy (2007)
Mango pulp	20	3.81-6.24	8.82-11.33	0.31-0.34	Ahmed et al. (2005)
S.purpurea L. pulp	20	13.26	15.22	0.3	Augusto et al. (2012)

Table 5.2. Values for the parameters of Falguera-Ibarz model for fruit products.

Product	**T (ºC)**	**η_∞ (Pa·s)**	**η_0 (Pa·s)**	**k_{FI}**	**Reference**
Tomato juice (0 MPa)	25	0.016	5.68	0.866	Present work
Tomato juice	20	0.008	1.11	0.807	Augusto et al. (2010)
Concentrated orange juice	25	0.214	6.08	0.584	Falguera and Ibarz (2010)

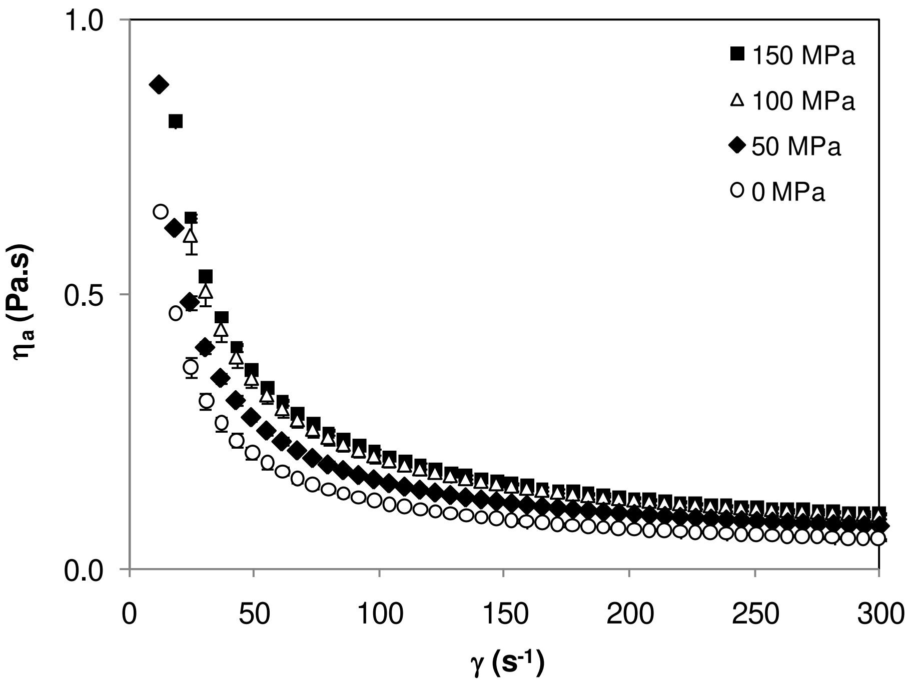

Figure 5.4. Apparent viscosity (η_a x $\dot{\gamma}$) of tomato juice processed by HPH (0-150 MPa). Mean of three replicates at 25ºC; vertical bars represent the standard deviation for each value.

Figures 5.5 and 5.6 show the Herschel–Bulkley (Equation 5.6) and Falguera-Ibarz (Equation 5.7) model parameters as a function of the homogenization pressure (P_H). The increase in homogenization pressure (P_H) decreased the consistency index in the Herschel–Bulkley model (k), and increased the other Herschel–Bulkley (σ_0, n) and Falguera-Ibarz model parameters (η_0, η_∞,k_{FI}), as discussed below. Moreover, the Herschel–Bulkley yield stress (σ_0) and the Falguera-Ibarz initial viscosity (η_0) increased systematically due to the P_H.

Bengtsson and Tornberg (2011), Lopez-Sanchez et al. (2011a), Bayod et al. (2008) and Ouden and Vliet (1997) observed that the yield stress (σ_0) of tomato products increased due to homogenization (P_H < 60 MPa). However, the authors did not model it as a function of the homogenization pressure (P_H), or study the other steady-state shear rheological parameters (i.e., the consistency index - k, and the flow behaviour index – n) or the time-dependent rheological properties.

Shijvens et al. (1998) observed that a reduction in the suspended particle diameter increased the yield stress (σ_0) and apparent viscosity (η_a) of apple sauce. Moreover, Tsai and Zammouri (1988) showed that a decrease in particle size resulted in increases in both the flow behaviour index (n) and apparent viscosity (η_a) in shear thinning fluids. Thus the rheological and PSD results described here are in accordance with those reported by Shijvens et al. (1998) and Tsai and Zammouri (1988).

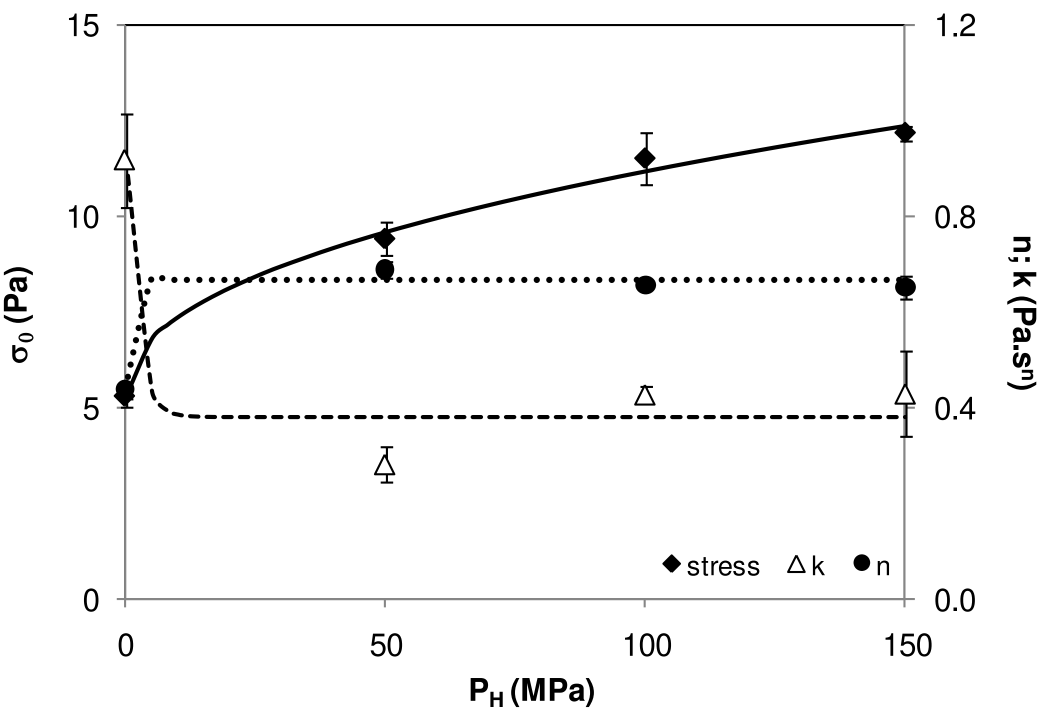

Figure 5.5. Parameters of Herschel–Bulkley model as a function of homogenization pressure (P_H). Vertical bars are the standard deviation for each mark, and curves are the empirical regressions of Table 5.3.

Servais et al. (2002) described the effect of PSD on the Herschel–Bulkley model parameters. According to these authors, the yield stress (σ_0) mostly depends on the amount of small particles (i.e., the specific surface area) and on the interactions between them (due to mechanical friction or chemical interactions). Moreover, the flow behaviour index (n) depends on the distribution of small and large particles and the rheology of the suspending fluid; while the consistency index (k) depends on the maximum packing fraction (ϕ_m) and the distribution of small and large particles.

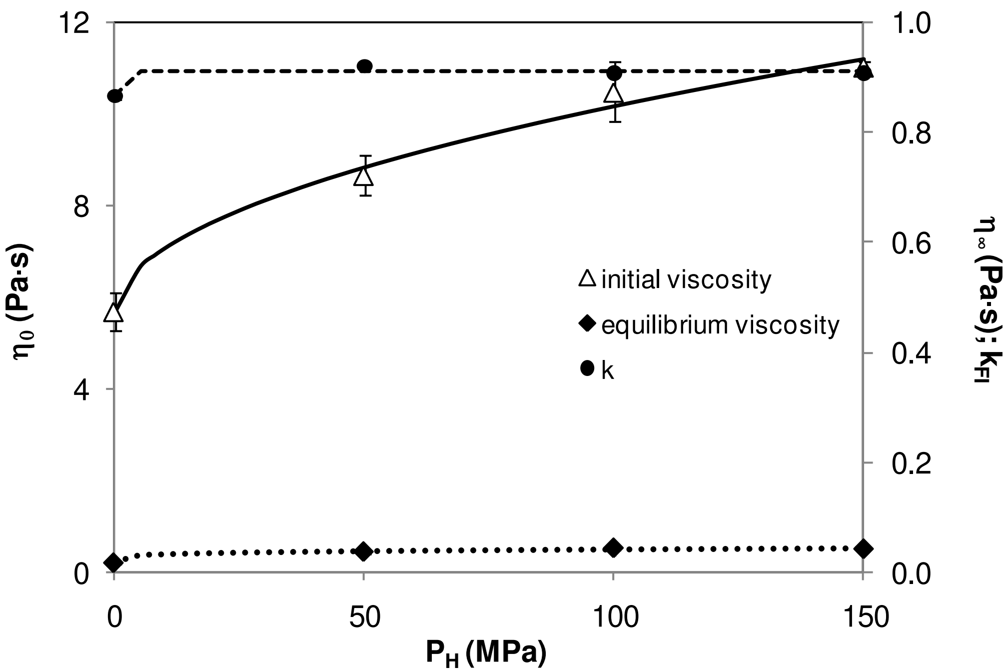

Figure 5.6. Parameters of Falguera-Ibarz model as a function of homogenization pressure (P_H). Vertical bars are the standard deviation for each mark, and the curves are the empirical regressions of Table 5.3.

Silva et al. (2010) studied the HPH of pineapple pulp up to 70 MPa. The product consistency index (k) and the flow behaviour index (n) showed the same behaviour as those reported here. Similar behaviour was shown by Floury et al. (2002) studying the HPH of methylcellulose up to 350 MPa. However, Silva et al. (2010) observed that the apparent viscosity of pineapple pulp decreased with increase in homogenization pressure, as observed by Lopez-Sanchez et al. (2011a) for carrot and broccoli homogenized at 60 MPa.

In fact, Lopez-Sanchez et al. (2011b) showed that each vegetable cell wall had a different behaviour when processed by HPH. While carrot tissue requires higher shears to be disrupted, the cell walls of tomato cells were broken even at moderate shear values. The increases and decreases in the viscosities of homogenized tomato, carrot and broccoli were directly related to their volume fraction (ϕ), highlighting the importance of hydrodynamic forces in product rheology.

This suggests that the effect of HPH processing is different for each fruit product, and highlight the need for better understanding of this process.

The Herschel–Bulkley (Equation 5.6) and Falguera-Ibarz (Equation 5.7) model parameters were then modelled as a function of the homogenization pressure (P_H; Figures 5.5 and 5.6, Table 5.3). Due to the behaviour observed (Figures 5.5 and 5.6), a power-type function with an initial value (related to original properties of the tomato juice, i.e., those processed at 0 MPa) was used to model the parameters, with the exception of the consistency index in the Herschel–Bulkley model (k), due to its reduction with increase in P_H.

The shear stress and apparent viscosity obtained using the models (Table 5.3) were compared with the experimental values. Using Equation 5.8, it is observed that the models obtained described the experimental values well (Table 5.4).

The Peclet Number is related to the particle transport due to shearing (non-Brownian systems) and diffusion (Brownian systems) (Fischer et al., 2009; Rao, 1999). Therefore, as the particle size is reduced, the Pe decreases and the system approximates to the Brownian domain.

At small Pe values Brownian motion dominates, while at higher Pe values, structure distortions due to shear flow are more pronounced, and Brownian motion cannot restore the structure of the suspension to its equilibrium state; therefore shear thinning and shear thickening will occur (Fischer et al., 2009).

Yoo and Rao (1994) and Tsai and Zammouri (1988) described a decreasing linear relationship between the logarithm of the relative viscosity ($\ln(\eta_r)$) and the logarithm of the Peclet number ($\ln(Pe)$) for shear thinning fluids. The Peclet number (Pe) is the product of the Reynolds number (Re) and the Schmidt number (Sc), being described by Equation 5.12 (Fischer et al., 2009; Yoo and Rao, 1994; Tsai and Zammouri, 1988).

$$Pe = \frac{\eta_{continuous\_phase} \cdot \bar{r}_{particle}^{3} \cdot \dot{\gamma}}{k_B \cdot T} \qquad \text{(Equation 5.12)}$$

If the reduction in tomato juice serum model viscosity described by Augusto et al. (2011b) is considered (~15% at 150 MPa), as well as the observed reduction in D[4,3] (~85% at 150 MPa), it can be seen that HPH reduces the Peclet number of the product (Pe, considering the $\bar{r}_{particle}$ based on the D[4,3] values), as presented in Figure 5.7. As described by Yoo and Rao (1994) and Tsai and Zammouri (1988), a reduction in Pe increases the relative viscosity (η_r) of the product, and consequently its apparent viscosity (η_a). The linear correlation between the Pe and the relative viscosity (η_r) can also be used as an approach to estimate the η_r as a function of Pe and P_H.

Once again, the results obtained for PSD described the effect of HPH on the rheological properties of the tomato juice well.

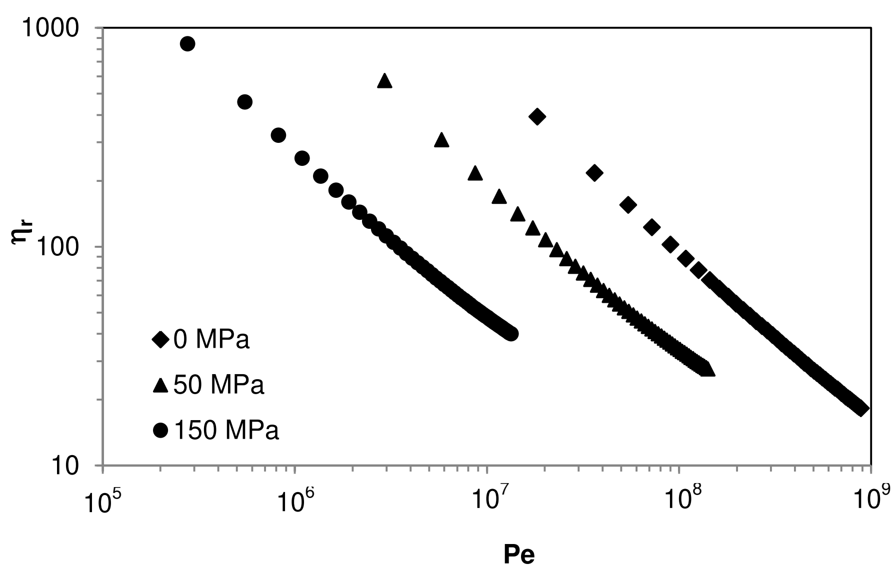

Figure 5.7. Effect of HPH (0-150 MPa) on tomato juice Peclet number (Pe) and relative viscosity (η_r). Mean of three replicates at 25ºC.

5.3.2. Time-Dependent Rheological Properties

The time-dependent rheological behaviour is related to the structural change due to shear (Ramos and Ibarz 1998), i.e., destruction of the internal structure during flow (Cepeda et al. 1999). Consequently, the time-dependent rheological characterization is important to understand the product changes during processing (Augusto et al., 2010). In the original product, the internal structure formed by the insoluble pulp dispersed in the serum showed greater resistance to deformation, resulting in higher shear stress. When shearing is carried out, this structure is broken, which can be noticed by the decline in stress.

Figure 5.8 shows the decline in shear stress of the samples when sheared at 300 s^{-1} for 10 min. As expected (Augusto et al., 2010), the tomato juice showed thixotropic behaviour, and even the Figoni-Shoemaker (Equation 5.4) and Weltman (Equation 5.5) models could describe its time-dependent rheological behaviour well ($R^2>0.92$). Moreover, the parameters obtained for both models are in agreement with those previously described by Augusto et al. (2010) for a refined commercial tomato juice (Table 5.5) and for other fruit products.

In concentrated orange juice the k_{FS} value of the Figoni-Shoemaker model varied from 0.073 to 0.600 s^{-1} ($7.2 \leq \gamma$ (s^{-1}) ≤ 57.6; Ramos and Ibarz, 1998), while in gilaboru juice at 43ºBrix, it varied from 0.0027 to 0.0031 s^{-1} ($50 \leq \gamma$ (s^{-1}) ≤ 150; Altan et al., 2005). Under the same conditions, the value of B (Weltman model) varied from 0.89 to 1.17 $Pa \cdot s^{-1}$. Abu-Jdayil et al. (2004) used the Weltman model to model the time dependent rheological behaviour of tomato paste (5.7% solids). The value of B varied from 10^{-14} to 0.0187 $Pa \cdot s^{-1}$ in the shear rate range of 2.2–79 s^{-1}.

Figure 5.8 shows that HPH improves tomato juice thixotropy, since the difference between the initial and equilibrium stress in relation to the homogenization pressure (P_H) was bigger, as well as the time taken to stabilize (~200-300 s for 0 MPa and ~500-600 s for 100-150 MPa). Moreover, as observed in the results for the steady-state shear properties and PSD, the main changes take place between 0 MPa and 50 MPa, being smaller between 50 MPa and 100 MPa and tending to stabilize between 100 MPa and 150 MPa.

Table 5.3. Parameters of Figoni- Shoemaker, Weltman, Herschel–Bulkley and Falguera-Ibarz models as function of homogenization pressure (P_H in MPa). Tomato juice, 25ºC, 0 MPa ≤ P_H ≤ 150 MPa.

Model		Equation	R^2
Figoni-Shoemaker ($\dot{\gamma}$ = 300 s^{-1})	σ_0 (Pa)	$\sigma_0 = 19.58 + 2.298 \cdot P_H^{0.6230}$	0.98
	σ_e (Pa)	$\sigma_e = 16.31 + 1.101 \cdot P_H^{0.5460}$	0.99
	k_{FS} (s^{-1})	$k_{FS} = 0.0048 + 0.0027 \cdot P_H^{0.2495}$	0.99
Weltman ($\dot{\gamma}$ = 300 s^{-1})	A (Pa)	$A = 22.52 + 4.305 \cdot P_H^{0.5839}$	0.99
	B (Pa·s^{-1})	$B = 0.9381 + 0.5405 \cdot P_H^{0.5962}$	0.99
Herschel–Bulkley	σ_0 (Pa)	$\sigma_0 = 5.320 + 0.7254 \cdot P_H^{0.4538}$	0.99
	k (Pa·s^n)	$k = 0.380 + \left(0.920 - 0.380\right) \cdot e^{-0.4636 P_H}$	0.94
	n	$n = 0.4402 + 0.2263 \cdot P_H^{4.83 \cdot 10^{-9}}$	0.98
Falguera-Ibarz	η_0 (Pa·s)	$\eta_0 = 5.668 + 0.4347 \cdot P_H^{0.5078}$	0.99
	η_∞ (Pa·s)	$\eta_\infty = 0.0160 + 0.0093 \cdot P_H^{0.2063}$	0.99
	k_{FI}	$k_{FI} = 0.8664 + 0.0465 \cdot P_H^{1.12 \cdot 10^{-8}}$	0.94

Bayod and Tornberg (2011) studied the effect of homogenization (9 MPa) on the properties of the suspended particles in a tomato suspension containing salt, sugar and acetic acid. Using micrographs, the authors observed that the structure of the suspension formed a network due to processing by homogenization, which could be disrupted by shearing.

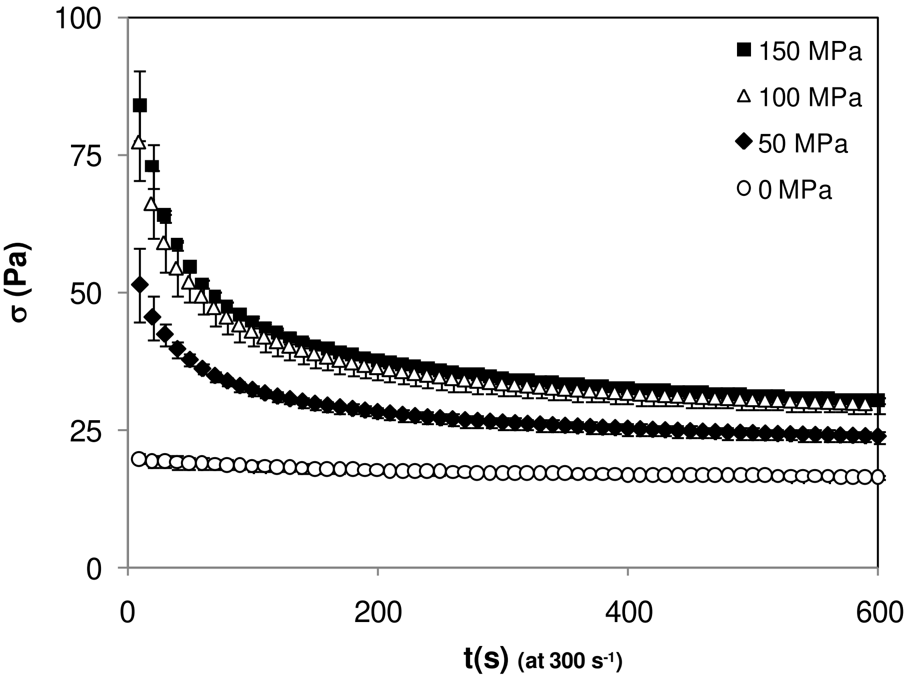

Figure 5.8. HPH (0-150 MPa) tomato juice stress decline during shearing at 300 s^{-1} for 10 min. Mean of three replicates at 25ºC; vertical bars represent the standard deviation for each value.

The PSD analysis showed that HPH reduced the diameter of the suspended particles in the tomato juice, increasing the particle surface area (Figure 5.2) and the interaction forces between them. Thus, it is to be expected that HPH processing would result in small particles aggregating to form a network, as described by Bayod and Tornberg (2011), resulting in a more thixotropic fluid.

However, as described by Genovese et al. (2007) and Tsai and Zammouri (1988), the van der Waals and electrostatic forces only dictate interparticle interactions between small particles at low shear rates ($\dot{\gamma}$). At higher shear rates ($\dot{\gamma}$), the hydrodynamic forces dictate the rheological properties of the fluid.

This explains the results obtained for yield stress (σ_0) and consistency index (k) in the Herschel–Bulkley model and the thixotropic behaviour. When the tomato juice is at rest or submitted to low shear rates ($\dot{\gamma}$), the inter-particle interactions result in a network structure. It characterizes the increasing in the yield stress values (σ_0) and thixotropy of the product due to HPH. Since the particle structure is broken by shear, interparticle interaction is low and hence the consistency index (k) is also low.

The Figoni-Shoemaker (Equation 5.4) and Weltman (Equation 5.5) parameters were then modelled as a function of the homogenization pressure (P_H; Figures 5.9 and 5.10, Table 5.3). Due to the behaviour observed, a power-type function with an initial value (related to the original properties of the tomato juice, i.e., those processed at 0 MPa) was used. The values obtained for shear stress using the models were compared with the experimental values. Using Equation 5.8, it is observed that the models obtained described the experimental values well (Table 5.4).

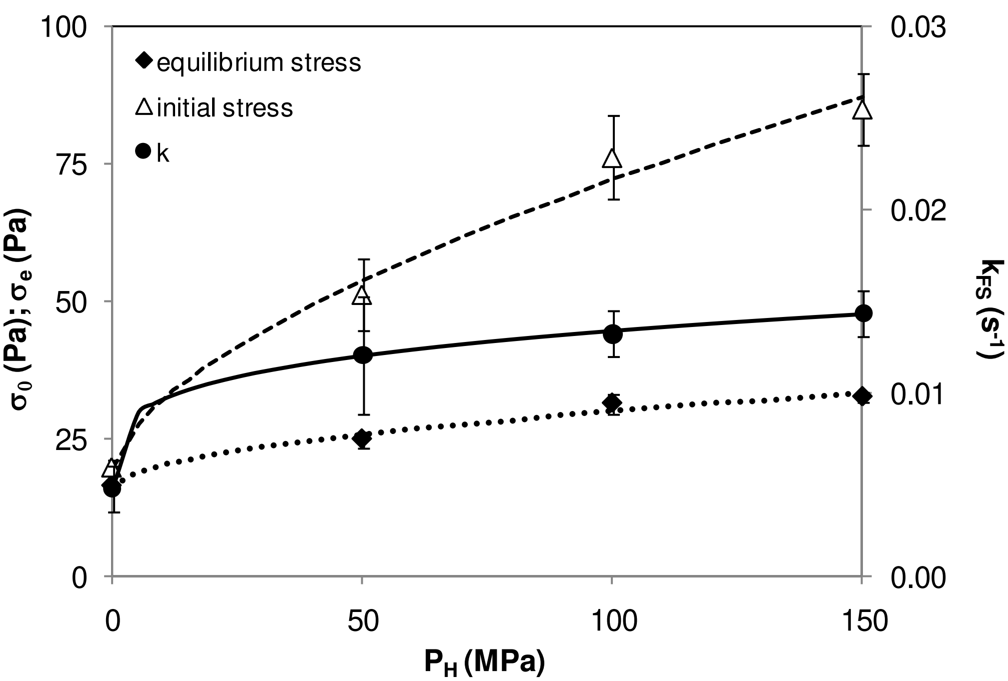

Figure 5.9. Parameters of Figoni and Shoemaker model as a function of homogenization pressure (P_H). Vertical bars are the standard deviation for each mark, and curves are empirical regressions of Table 5.3.

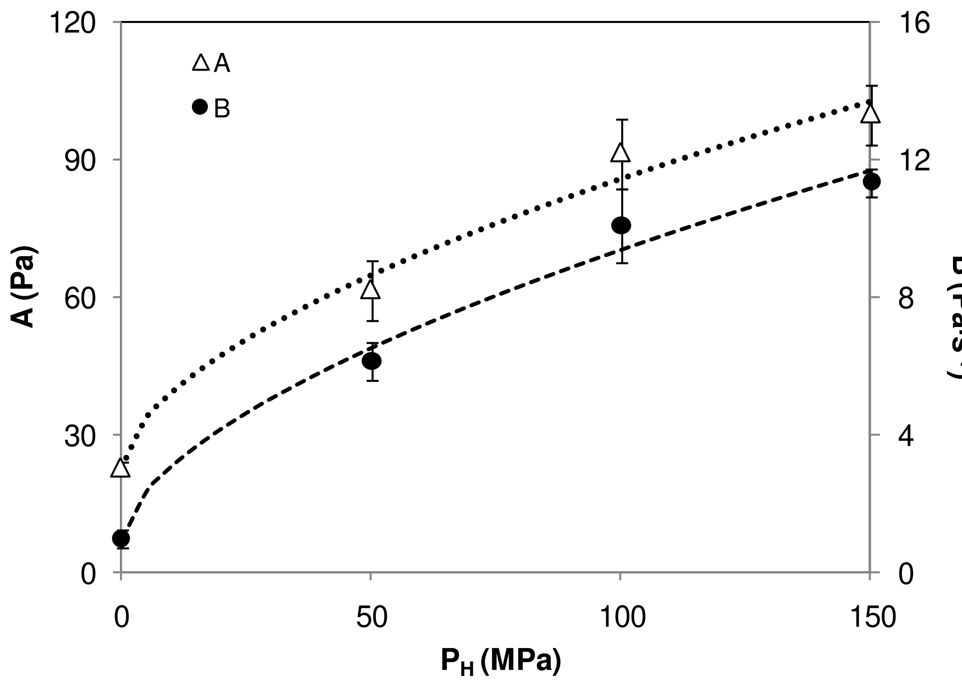

Figure 5.10. Parameters of Weltman model as a function of homogenization pressure (P_H). Vertical bars are the standard deviation for each mark, and the curves are the empirical regressions of Table 5.3.

Table 5.4. Figoni-Shoemaker, Weltman, Herschel–Bulkley and Falguera-Ibarz models parameters as function of homogenization pressure (P_H, Table 5.3): accuracy evaluation by using Equation 5.8.

Models	α	β	R^2
Figoni- Shoemaker	0.98	0.65	0.98
Weltman	0.97	1.05	0.97
Herschel–Bulkley	0.94	1.25	0.96
Falguera-Ibarz	0.99	0.00	0.99

Table 5.5. Values for the parameters of Figoni-Shoemaker and Weltman models for fruit products ($\dot{\gamma}$ = 300 s^{-1}).

Model		Tomato juice (0 MPa) (25ºC, present work)	Commercial tomato juice (20ºC, Augusto et al., 2010)
Figoni-Shoemaker	**σ_0 (Pa)**	19.82	5.68
	σ_e (Pa)	16.37	6.49
	k_{FS} (s^{-1})	0.0048	0.0056
Weltman	**A (Pa)**	22.81	6.98
	B ($Pa \cdot s^{-1}$)	0.976	0.193

5.3.3. General Discussion and Importance

High pressure homogenization (HPH) is a non-thermal technique widely studied to obtain safe, stable products such as fruit juices. Its importance is growing due to increasing scientific research associated with food processing and even industrial applications. However, there are still only a few papers in the literature regarding the physicochemical changes in fruit products due to this technique, especially regarding their rheological properties.

In the present work, the effect of HPH (up to 150 MPa) on the time-dependent and steady-state shear rheological properties of tomato juice was studied. HPH reduced the suspended particle diameters and the particle size distribution (PSD), increasing product consistency and thixotropy.

Moreover, the results obtained indicated that HPH could be used to increase tomato juice consistency, improving its sensory acceptance, reducing the need for the addition of hydrocolloids, and reducing particle sedimentation and serum separation.

Thus, the effect of homogenization pressure (P_H) on the tomato juice rheological parameters was modelled. Using the models obtained (Table 5.3), the tomato juice flow properties could be predicted well as a function of homogenization pressure (P_H), shear rate ($\dot{\gamma}$) and time of shearing (t). This could be useful in the design of equipment and processes for food products.

The main effect was observed at low homogenization pressures (P_H ~ 50 MPa), followed by asymptotic behaviour. This indicates that simpler and less expensive equipment could be used to obtain the desirable effects of HPH in tomato juice.

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

5.4. Conclusions

The present work evaluated the effect of high pressure homogenization (HPH) on the time-dependent and steady-state shear rheological properties of tomato juice. The tomato juice particle size distribution (PSD) and rheological properties were evaluated at homogenization pressures (P_H) of up to 150 MPa. HPH reduced the mean particle diameter and the particle size distribution (PSD), increasing the tomato juice consistency. Moreover, HPH increased tomato juice thixotropy, in agreement with the observed PSD. The steady-state shear rheological properties of the juice were evaluated by the Herschel–Bulkley and Falguera-Ibarz models, whose parameters were modelled as a function of the homogenization pressure (P_H). The tomato juice time-dependent rheological properties were evaluated by the Figoni-Shoemaker and Weltman models, whose parameters were then modelled as a function of the P_H. The models obtained described the experimental values well.

5.5. Acknowledgments

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5.6. Nomenclature

α = slope index of the linear model for the evaluation of the experimental values versus those obtained by models (Equation 5.8) [-]

β = intercept index of the linear model for the evaluation of the experimental values versus those obtained by models (Equation 5.8) [-]

$\dot{\gamma}$ = shear rate [s^{-1}]

ϕ = particle volume fraction [-]

ϕ_m = maximum packing fraction of solids [-]

η = viscosity [Pa·s]

η_a = apparent viscosity (= σ / γ) [Pa·s]

η_r = relative viscosity (Equation 5.9) [Pa·s]

η_0 = initial viscosity in the Falguera-Ibarz model (Equation 5.7) [Pa·s]

η_∞ = equilibrium viscosity in the Falguera-Ibarz model (Equation 5.7) [Pa·s]

[η] = intrinsic viscosity [Pa·s]

ρ = particle density [$kg \cdot m^{-3}$]

σ = shear stress [Pa]

σ_0 = yield stress, Herschel-Bulkley model (Equation 5.6) [Pa]

σ_0 = initial stress in the Figoni-Shoemaker model (Equation 5.4) [Pa]

σ_e= equilibrium stress in the Figoni-Shoemaker model (Equation 5.4) [Pa]

A = structural parameter in the Weltman model (Equation 5.5) [Pa]

A_{SF} = particle specific surface area (Equation 5.3) [$m^3 \cdot g^{-1}$]

B = kinetic parameter in the Weltman model (Equation 5.5) [$Pa \cdot s^{-1}$]

d = particle diameter [m]

D[4,3] = particle volume-based diameter (Equation 5.1) [m]

D[3,2] = particle area-based diameter (Equation 5.2) [m]

k = consistency coefficient, Herschel-Bulkley model (Equation 5.6) [$Pa \cdot s^n$]

k_B = Boltzman constant [= $1.38 \cdot 10^{-23}$ $N \cdot m \cdot K^{-1}$]

k_{FS} = kinetic parameter in the Figoni-Shoemaker model (Equation 5.4) [s^{-1}]

k_{FI} = viscosity decline parameter in the Falguera-Ibarz model (Equation 5.7) [-]

n = flow behavior index, Herschel-Bulkley model (Equation 5.5) [-]

Pe = Peclet number (Equation 5.12) [-]

P_H = homogenization pressure [MPa]

$\bar{r}_{particle}$ = mean suspended particle radius [m]

V = particle volume [m^3]

t = time [s]

T = absolute temperature [K]

5.7. References

Abu-Jdayil, B.; Banat, F.; Jumah, R.; Al-Asheh, S.; Hammad, S. A. (2004). Comparative study of rheological characteristics of tomato paste and tomato powder solutions. *International Journal of Food Properties*, 7(3), 483–497.

Ahmed, J.; Ramaswamy, H. S. (2007). Dynamic and steady shear rheology of fruit puree based baby foods. *Journal of Food Science and Technology*, 44(6), 579-585.

Ahmed, J.; Ramaswamy, H. S.; Hiremath, N. (2005). The effect of high pressure treatment on rheological characteristics and colour of mango pulp. *International Journal of Food Science & Technology*, 40(8), 885-895.

Ahmed, J.; Ramaswamy, H. S.; Sashidhar, K. C. (2007). Rheological characteristics of tamarind (*Tamarindus indica* L.) juice concentrates. *LWT - Food Science and Technology*, 40, 225-231.

Aliberti, N. C. M. (2009). *Influência da Homogeneização a Alta Pressão Sobre a Retenção de Antocianinas Presentes na Polpa de Açaí (Euterpe oleraceae Mart.).* PhD Tesis, University of São Paulo.

Altan, A.,; Kus, S.; Kaya, A. (2005). Rheological behaviour and time dependent characterization of gilaboru juice (*Viburnum opulus* L.). *Food Science and Technology International*, 11(2), 129–137.

Augusto, P. E. D.; Falguera, V.; Cristianini, M.; Ibarz, A. (2010). Rheological behavior of tomato juice: steady-state shear and time-dependent modeling. *Food and Bioprocess Technology, in press* (DOI: 10.1007/s11947-010-0472-8).

Augusto, P. E. D.; Falguera, V.; Cristianini, M.; Ibarz, A. (2011a). Influence of fibre addition on the rheological properties of peach juice. *International Journal of Food Science and Technology*, 46, 1086-1092.

Augusto, P. E. D.; Ibarz, A.; Cristianini, M. (2011b). Effect of high pressure homogenization (HPH) on the rheological properties a fruit juice serum model. *Journal of Food Engineering, under review.* (Chapter 4)

Augusto, P. E. D.; Cristianini, M.; Ibarz, A. (2012). Effect of temperature on dynamic and steady-state shear rheological properties of siriguela (*Spondias purpurea* L.) pulp. *Journal of Food Engineering*, 108, 183-289.

Bayod, E.; Månsson, P.; Innings, F.; Bergenståhl, B.; Tornberg, E. (2007). Low shear rheology of concentrated tomato products. Effect of particle size and time. *Food Biophysics*, 2, 146-157.

Bayod, E.; Tornberg, E. (2011). Microstructure of highly concentrated tomato suspensions on homogenization and subsequent shearing. *Food Research International*, 44, 755-764.

Bayod, E.; Willers, E. P.; Tornberg, E. (2008). Rheological and structural characterization of tomato paste and its influence on the quality of ketchup. *LWT - Food Science and Technology*, 41, 1289-1300.

Becker, R.; Miers, J. C.; Nutting, M. D.; Dietrich, W. C.; Wagner, J. R. (1972). Consistency of tomato products: 7, effect of acidification on cell walls and cell breakage. *Journal of Food Science*, 37, 1, 118-125.

Bengtsson, H.; Tornberg, E. (2011). Physicochemical characterization of fruit and vegetable fiber suspensions. I: Effect of homogenization. *Journal of Texture Studies,*
42, 4, 268–280.

Beresovsky, N.; Kopelman, I. J.; Mizrahi, S. (1995). The role of pulp interparticle interaction in determining tomato juice viscosity. *Journal of Food Processing and Preservation*, 19, 133-146.

Betoret, E.; Betoret, N.; Carbonell, J. V.; Fito, P. (2009). Effect of pressure homogenization on particle size and the functional properties of citrus juices. *Journal of Food Engineering*, 92, 18-23.

Campos, F.; Cristianini, M. (2007). Inactivation of *Saccharomyces cerevisiae* and *Lactobacillus plantarum* in orange juice using ultra high-pressure homogenization. *Innovative Food Science & Emerging Technologies*, 8, 2, 226-229.

Corbo, M. R.; Bevilacqua, A.; Campaniello, D.; Ciccarone, C.; Sinigaglia, M. (2010). Use of high pressure homogenization as a mean to control the growth of foodborne moulds in tomato juice. *Food Control*, 21, 1507-1511.

Donsì, F.; Esposito, L.; Lenza, E.; Senatore, B.; Ferrari, G. (2009). Production of self-stable Annurca apple juice with pulp by high pressure homogenization. *International Journal of Food Engineering*, 5, 4, article 12.

Falguera,V.; Ibarz,A. (2010). A new model to describe flow behaviour of concentrated orange juice. *Food Biophysics*, 5, 114–119.

Figoni, P. I.; Shoemaker, C. F. (1983). Characterization of time dependent flow properties of mayonnaise under steady shear. *Journal of Texture Studies*, 14, 431–442.

Fischer, P.; Pollard, M.; Erni, P.; Marti, I.; Padar, S. (2009). Rheological approaches to food systems. *Comptes Rendus Physique*, 10, 740-750.

Floury, J.; Bellettre, J. ; Legrand, J.; Desrumaux, A. (2004). Analysis of a new type of high pressure homogeniser. A study of the flow pattern. *Chemical Engineering Science*, 59, 843-853.

Floury, J.; Desrumaux, A.; Axelos, M. A.V.; Legrand, J. (2002). Degradation of methylcellulose during ultra-high pressure homogenisation. *Food Hidrocolloids*, 16, 47-53.

Foda, Y. M.; Mccollum, J. P. (1970). Viscosity as affected by various constituents of tomato juice. *Journal of Food Science*, 35, 333-338.

Genovese, D. B.; Lozano, J. E.; Rao, M. A. (2007). The rheology of colloidal and noncolloidal food dispersions. *Journal of Food Science*, 72, 2, R11-R20.

Guyot, A.; Chu, F.; Schneider, M.; Graillat, C.; McKenna, T. F. (2002). High solid content latexes. *Progress in Polymer Science*, 27, 1573–1615.

Haminiuk, C. W. I.; Sierakowski, M. R.; Maciel, G. M.; Vidal, R. M. B.; Branco, I. G.; Masson, M. L. (2006). Rheological properties of butia pulp. *International Journal of Food Engineering*, 2(1), Article 4.

Ibarz, A.; Barbosa-Cánovas, G. V. (2003). *Unit Operations in Food Engineering*. Boca Raton: CRC Press.

Lacroix, N.; Fliss, I.; Makhloue, J. (2005). Inactivation of pectin methylesterase and stabilization of opalescence in orange juice by dynamic high pressure. *Food Research International*, 38, 569-576.

Lopez-Sanchez, P.; Nijsse, J.; Blonk, H. C. G.; Bialek, L.; Schumm, S.; Langton, M. (2011a). Effect of mechanical and thermal treatments on the microstructure and rheological properties of carrot, broccoli and tomato dispersions. *Journal of the Science of Food and Agriculture*, 91, 207-217.

Lopez-Sanchez, P.; Svelander, C.; Bialek, L.; Schummm, S.; Langton, M. (2011b). Rheology and microstructure of carrot and tomato emulsions as a result of high-pressure homogenization conditions. *Journal of Food Science*, 76, 1, E130-E140.

Loveday, S. M.; Creamer, L. K.; Singh, H.; Rao, M. A. (2007). Phase and rheological behavior of high-concentration colloidal hard-sphere and protein dispersions. *Journal of Food Science*, 72, 7.

Massa, A.; González, C.; Maestro, A.; Labanda, J.; Ibarz, A. (2010). Rheological characterization of peach purees. *Journal of Texture Studies*, 41, 532–548.

Metzner, A. B. (1985). Rheology of suspensions in polymeric liquids. *Journal of Rheology*, 29, 6, 739-775.

Nisha, P., Singhal, R. S., Pandit, A. B. (2010). Kinetic modelling of colour degradation in tomato puree (*Lycopersicon esculentum* L.). *Food and Bioprocess Technology, in press* (DOI:10.1007/s11947-009-0300-1).

Okoth, M. W.; Kaahwa, A. R.; Imungi, J. K. (2000). The effect of homogenisation, stabiliser and amylase on cloudiness of passion fruit juice. *Food Control*, 11, 305-311.

Ouden, F. W. C. Den; Vliet, T. Van. (1997). Particle size distribution in tomato concentrate and effects on rheological properties. *Journal of Food Science*, 62, 3, 565-567.

Ouden, F. W. C. Den; Vliet, T. Van. (2002). Effect of concentration on the rheology and serum separation of tomato suspensions. *Journal of Texture Studies*, 33, 91-104.

Pathanibul, P.; Taylor, T. M.; Davidson, P. M.; Harte, F. (2009). Inactivation of *Escherichia coli* and *Listeria innocua* in apple and carrot juices using high pressure homogenization and nisin. *International Journal of Food Microbiology*, 129, 316-320.

Patrignani, F.; Vannini, L.; Kamdem, S. L. S.; Lanciotti, R.; Guerzoni, M. E. (2009) Effect of high pressure homogenization on *Saccharomyces cerevisiae* inactivation and physic-chemical features in apricot and carrot juices. *International Journal of Food Microbiology*, 136, 26-31.

Patrignani, F.; Vannini, L.; Kamdem, S. L. S.; Lanciotti, R.; Guerzoni, M. E. (2010). Potentialites of high pressure homogenization to inactivate *Zygosaccharomyces bailii* in fruit juices. *Journal of Food Science*, 75, 2, M116-M120.

Pereira, E. A.; Brandão, E. M.; Borges, S. V.; Maia, M. C. A. (2007). Effect of xanthan gum addition on the rheological properties of umbu fruit pulp. *Boletim do CEPPA*, 25(2), 285-294.

Pereira, E. A.; Brandão, E. M.; Borges, S. V.; Maia, M. C. A. (2008). Influence of concentration on the steady and oscillatory shear behavior of umbu pulp. *Revista Brasileira de Engenharia Agrícola e Ambienta,*12(1), 87–90.

Pinho, C. R. G.; Franchi, M. A.; Augusto, P. E. D.; Cristianini, M. (2011). Milk flow evaluation during high pressure homogenization (HPH) using computational fluid dynamics (CFD). *Brazilian Journal of Food Technology*, 14, 3, 232-240, (*in Portuguese*).

Ramos, A. M.; Ibarz, A. (1998). Thixotropy of orange concentrate and quince puree. *Journal of Texture Studies,* 29, 313-324.

Rao, M. A. (1999). Flow and Functional Models for Rheological Properties of Fluid Foods. In: Rao, M. A. *Rheology of Fluid and Semisolid Foods: Principles and Applications*. Gaithersburg: Aspen Publishers.

Saldo, J.; Suárez-Jacobo, Á.; Gervilla, R.; Guamis, B.; Roig-Sagués, A. X. (2009). Use of ultra-high-pressure homogenization to preserve apple juice without heat damage. *High Pressure Research*, 29, 1, 52-56.

Sato, A. C. K.; Cunha, R. L. (2009). Effect of particle size on rheological properties of jaboticaba pulp. *Journal of Food Engineering*, 91, 566-570.

Sentandreu, E.; Gurrea, M. C.; Betoret, N.; Navarro, J. L. (2011). Changes in orange juice characteristics due to homogenization and centrifugation. *Journal of Food Engineering*, 105, 241-245.

Servais, C.; Jones, R.; Roberts, I. (2002). The influence of particle size distribution on the processing of foods. *Journal of Food Engineering*, 51, 201-208.

Shijvens, E.P.H.M.; Van Vliet, T.; Van Dijk, C. (1998). Effect of processing conditions on the composition and rheological properties of applesauce. *Journal of Texture Studies*, 29, 123–143.

Silva, V.M.; Sato, A.C.K.; Barbosa, G.; Dacanal, G.; Ciro-Velásquez; H.J.; Cunha, R.L. (2010). The effect of homogenisation on the stability of pineapple pulp. *International Journal of Food Science and Technology*, 45, 2127–2133.

Sinchaipanit, P.; Kerr, W. L. (2007). Effect of reducing pulp-particles on the physical properties of carrot juice. *ASEAN Food Journal*, 14, 3, 205-214.

Takada, N.; Nelson, P. E. (1983). Pectin-protein interaction in tomato products. *Journal of Food Science*, 48, 5, 1408-1411.

Tanglertpaibul, T.; Rao, M. A. (1987). Flow properties of tomato concentrates: effect of serum viscosity and pulp content. *Journal of Food Science*, 52, 2, 318-321.

Tehrani, M. M.; Ghandi, A. (2007). Modification of Bostwick method to determine tomato concentrate consistency. *Journal of Food Engineering*, 79, 1483-1486.

Thakur, B. R.; Singh, R. K.; Handa, A. K. (1995). Effect of homogenization pressure on consistency of tomato juice. *Journal of Food Quality*, 18, 389-396.

Tonon, R. V.; Alexandre, D.; Hubinger, M. D.; Cunha, R. L. (2009). Steady and dynamic shear rheological properties of açai pulp (*Euterpe oleraceae* Mart.). *Journal of Food Engineering*, 92, 425–431.

Tribst, A. A. L.; Franchi, M. A.; Cristianini, M. Massaguer, P. R. (2009). Inactivation of *Aspergillus niger* in mango nectar by high-pressure homogenization combined with heat shock. *Journal of Food Science*, 74, 9, M509-M514.

Tribst, A. A. L.; Franchi, M. A.; Cristianini, M. Massaguer, P. R. (2011). Quality of mango nectar processed by high-pressure homogenization with optimized heat treatment. *Journal of Food Science*, 76, 2, M106-M110.

Tsai, S. C.; Zammouri, K. (1988). Role of interparticular Van der Waals force in rheology of concentrated suspensions. *Journal of Rheology*, 32, 7, 737-750.

Weltman, R. N. (1943). Breakdown of thixotropic structure as function of time. *Journal of Applied Physics*, 14, 343–350.

Whittenberg, R. T.; Nutting, G. C. (1958). High viscosity of cell wall suspensions prepared from tomato juice. *Food Technology*, 12, 420-422.

Yoo, B.; Rao, M. A. (1994). Effect of unimodal particle size and pulp content on rheological properties of tomato puree. *Journal of Texture Studies*, 25, 4, 421-436.

Chapter 6: Effect of High Pressure Homogenization (HPH) on the Rheological Properties of Tomato Juice. Part II: Viscoelastic Properties and the Cox-Merz Rule

This chapter was developed at University of Campinas, and is currently under review as:

AUGUSTO, P. E. D.; IBARZ, A.; CRISTIANINI, M. Effect of High Pressure Homogenization (HPH) on the Rheological Properties of Tomato Juice. Part II: Viscoelastic Properties and the Cox-Merz Rule.

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') and loss (G'') moduli. The parameters G' and G'' were modelled as a power function of the oscillatory frequency (ω), 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.

Keywords:

Food properties, high pressure homogenization, rheology, viscoelasticity, viscosity.

Efeito da Homogeneização a Alta Pressão (HAP) nas Propriedades Reológicas de Suco de Tomate. Parte II: Propriedades Viscoelásticas e Regra de Cox-Merz

Resumo

A homogeneização a alta pressão (HAP) tem sido proposta como alternativa parcial ou total ao processo térmico de alimentos. Embora a inativação microbiana tenha sido bastante estudada, poucos trabalhos da literatura estudam alterações físico-químicas em produtos de frutas devido a HAP, especialmente em relação às características reológicas. O presente trabalho avaliou o efeito da HAP (até 150 MPa) nas propriedades viscoelásticas de suco de tomate. A HAP aumentou os módulos de armazenamento (G') e dissipação (G'') do suco. Tais módulos foram modelados como função potência da frequência de oscilação (ω), sendo os parâmetros obtidos avaliados como função da pressão de homogeneização. A HAP aumentou a consistência do suco de tomate, sendo esse efeito mais expressivo do que a alteração em seu comportamento. As alterações reológicas puderam ser relacionadas ao rompimento das partículas em suspensão devido ao processo. Ainda, duas modificações da Regra de Cox-Merz foram utilizadas para correlacionar as propriedades reológicas em cisalhamento em estado estacionário e viscoelasticidade. Os resultados obtidos indicam a possibilidade de uso da HAP para promoção de alterações físicas em alimentos, tais como o aumento das características elásticas e viscosas.

Palavras-chave:

Homogeneização a alta pressão, propriedades dos alimentos, reologia, viscoelasticidade, viscosidade.

6.1. 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 (Nisha et al., 2010). It is also one of the most important vegetables in the food industry, and widely included in the human diet. However, Valencia et al. (2004) and Sánchez et al. (2002) observed that there were 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 (Pinho et al., 2011; Floury et al., 2004). 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.

6.2. Materials and Methods

As described by Augusto et al. (2011c), a 4.5ºBrix tomato juice was obtained by diluting a commercial 30ºBrix pulp in distilled water. A commercial pulp was used for guarantee of standardization and repeatability. It was obtained using the hot break process, concentrated by evaporation at 65°C, thermally processed by the UHT method and aseptically packaged in bags.

The pulp was fractionated into small portions in the laboratory, packaged in high density polyethylene bottles and frozen at -18ºC until used. This procedure allowed for the use of the same product throughout the entire work. The samples were thawed at 4ºC, diluted using distilled water at 50ºC to ensure better hydration (Tehrani and Gandhi, 2007), and allowed to rest for 24 hours at 5ºC to ensure complete hydration and release of the incorporated air. The juice pH value was 4.6.

6.2.1. High Pressure Homogenization (HPH) Process

The juice was homogenized at 0 MPa (control), 25 MPa, 50 MPa, 100 MPa and 150 MPa using a high pressure homogenizer (Panda Plus, GEA Niro Soavi, Italy). The samples were introduced into the equipment at room temperature, and quickly cooled using an ice bath just after the homogenization valve. The maximum temperature reached by a sample was ~40°C (for the sample homogenized at 150 MPa, just before the ice bath). The experiments were carried out with three replicates.

6.2.2. Rheological Properties

Rheological analyses were carried out using a controlled stress (σ) rheometer (AR2000ex, TA Instruments, USA) with a cross hatched plate-plate geometry (40 mm in diameter). The dimension of the gap (1.0 mm) was determined by using a gap-independency procedure, as described by Tonon et al. (2009). In this procedure, the distance between the plates was varied and the sample flow behaviour evaluated. The ideal gap dimension was observed when the sample flow behaviour was independent of variation in the gap. The temperature was maintained constant at 25ºC using a Peltier system.

Oscillatory stress sweeps between 0.01 and 10 Pa were carried out at a frequency of 1 Hz to determine the linear viscoelastic range. Samples were placed in the rheometer and maintained at rest for 10 min before the frequency sweep measurements. A fixed shear stress value within the linear viscoelastic range of 0.01 to 100 Hz was used. The storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) were thus obtained as a function of the oscillatory frequency (ω).

The storage (G') and loss (G'') moduli were modelled as a power function of the oscillatory frequency (ω) (Equations 6.1 and 6.2), as commonly used to describe the viscoelastic behaviour of food and dispersions (Rao, 1999).

$$G' = k' \cdot \omega^{n'} \qquad \text{(Equation 6.1)}$$

$$G'' = k'' \cdot \omega^{n''} \qquad \text{(Equation 6.2)}$$

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 Kokini, 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 ($\eta_a = \sigma / \dot{\gamma}$) at a specific shear rate ($\dot{\gamma}$) is equal to the complex viscosity (η^*) at a specific oscillatory frequency (ω), when $\dot{\gamma} = \omega$ (Equation 6.3; Rao, 2005). 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.

$$\eta^*(\omega) = \eta_a(\dot{\gamma})\Big|_{\dot{\gamma}=\omega} \qquad \text{(Equation 6.3)}$$

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., 2010c). Thus, a linear decreasing stepwise protocol (100 s^{-1} 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 Equations 6.1 and 6.2 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.

6.3. Results and Discussion

6.3.1. 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.

Figure 6.1 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 Hz to 100 Hz, the linear viscoelastic region was limited by the frequency of ~25 Hz for all the samples. Thus Figure 6.1 only shows the results obtained in the linear range, in accordance with that reported for tomato juice (Augusto et al., 2011b), tomato concentrates (Ouden and 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 Equations 6.1 and 6.2 were only evaluated in this frequency range.

The storage modulus (G’) was always higher than the loss modulus (G’’) in the oscillatory frequency (ω) 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 products (Augusto et al., 2011b; Bayod and Tornberg, 2011; Bengtsson and Tornberg, 2011; Bayod et al. 2008; Valencia et al. 2002; Yoo and Rao, 1996; Rao and Cooley, 1992) and other fruit products such as peach puree (Massa et al. 2010), açai pulp (Tonon et al. 2009), jabuticaba pulp (Sato and Cunha, 2009), umbu pulp (Pereira et al. 2008), vegetable-based baby foods (Ahmed and Ramaswamy, 2006; Ramamoorthi et al. 2009), potato puree (Alvarez et al. 2004), siriguela pulp (Augusto et al., 2012) and peach juice with fibres (Augusto et al. 2011a).

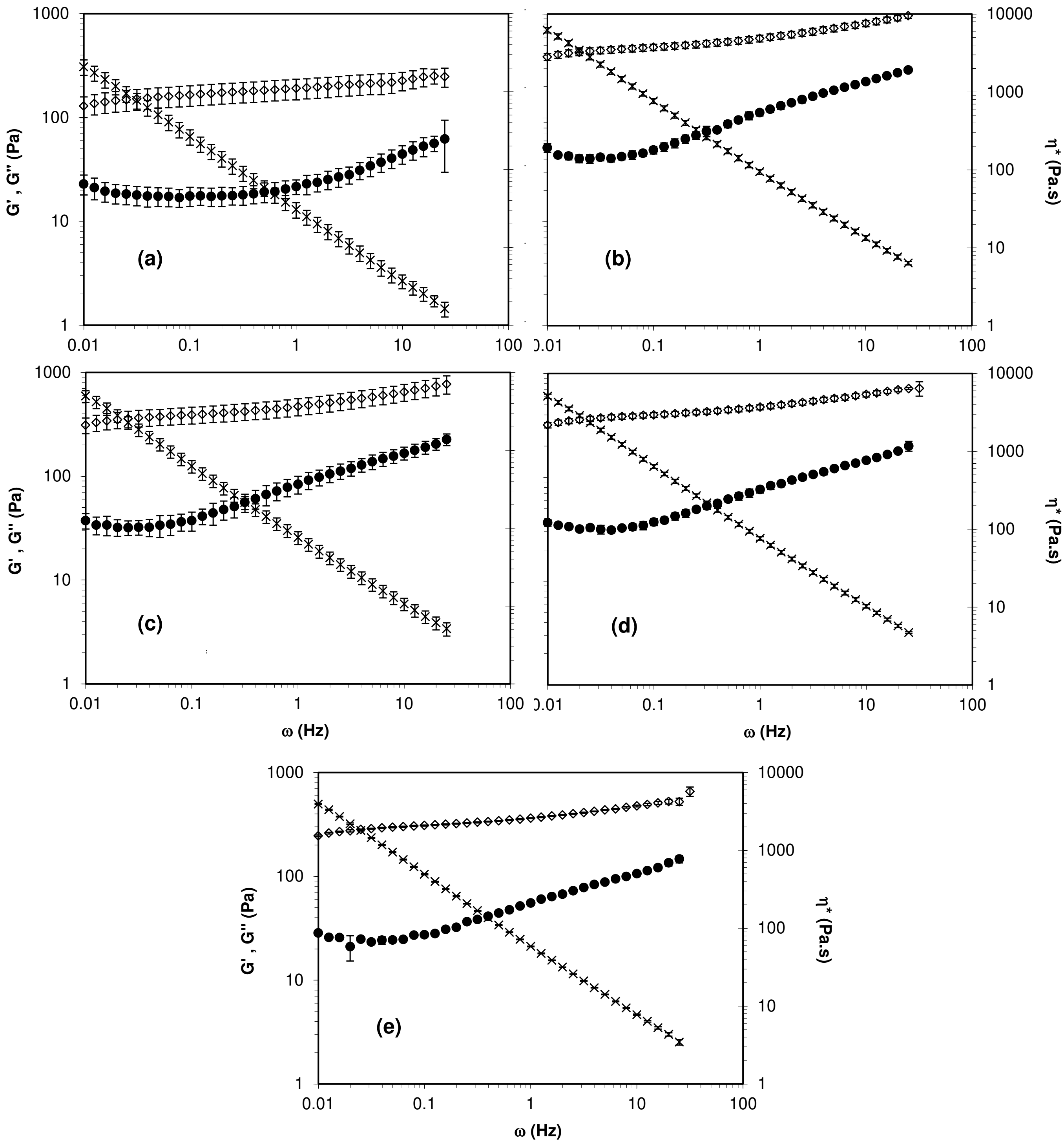

Figure 6.1. Tomato juice mechanical spectra: effect of HPH (0-150 MPa) on storage modulus (G', ◇), loss modulus (G'', ●) and complex viscosity (η*, ×). Vertical bars represent the standard deviation for each value. (a) 0 MPa, (b) 25 MPa, (c) 50 MPa, (d) 100 MPa and (e) 150 MPa.

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 (η*). 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 (Equations 6.1 and 6.2). 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. Figure 6.2 shows the effect of high pressure homogenization on the parameters of Equations 6.1 and 6.2. The values obtained were in accordance with those described for other tomato and vegetable products (Table 6.1).

The values for n'' were always higher than those for n' (Figure 6.2), 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).

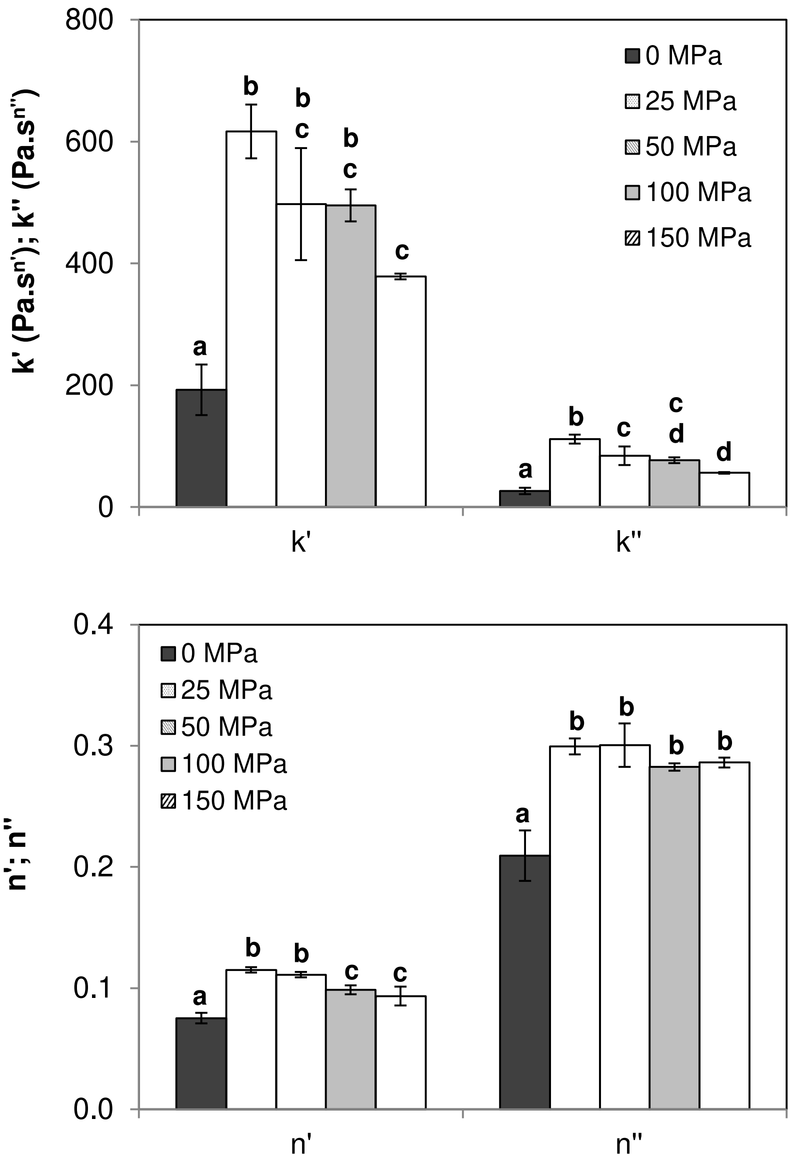

Figure 6.2. Effect of HPH (0-150 MPa) on tomato juice viscoelastic properties (k’, k’’, n’ and n’’ from Equations 6.1 and 6.2). Vertical bars represent the standard deviation for each value. For each parameter, different letters represent significantly different values ($P < 0.05$).

Table 6.1. Values for parameters of the power law model for storage (G') and loss (G'') modules as a function of oscillatory frequency (ω; Equations 6.1 and 6.2) for vegetable products.

Product	n'	n''	Reference
Tomato juice (HPH 0-150 MPa)	0.08-0.12	0.21-0.30	Present work
Tomato concentrates (21-34ºBrix)	0.08-0.24	0.11-0.25	Bayod et al. (2008), Yoo, Rao (1996), Rao, Cooley (1992)
Ketchups	0.10-0.18	0.24-0.42	Yilmaz et al. (2011), Bayod et al. (2008), Sharoba et al. (2005)
Potato puree	0.06-0.10	0.10-0.19	Alvarez et al. (2004)
Peach juice with fibres	0.22-0.24	0.33-0.40	Augusto et al. (2011a)
Vegetable-based baby foods	0.06-0.14	0.16-0.22	Ahmed, Ramaswamy (2006)
Siriguela pulp	0.14	0.27	Augusto et al. (2012)

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. (2011c).

The parameters k', n' (Equation 6.1), k'' and n'' (Equation 6.2) first increased, and then decreased, with increasing homogenization pressure (P_H) (Figure 6.2). 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. (2011c). 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. (2011c) 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 μm and ~1000 μm. When the juice was processed at 50 MPa, a broader distribution was observed, with particles ranging between ~10 μm and ~1000 μm. Finally, when the juice processed at 150 MPa was evaluated, a further reduction in the particle diameter and a narrow distribution (~10 μm to ~300 μm) was observed. Moreover, the changes in particle diameter were less pronounced between 50 MPa and 150 MPa than between 0 MPa 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., 2011d), 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 25-50 MPa range results in a broader PSD (Augusto et al., 2011c) with a greater particle volume fraction (ϕ), 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.

Ouden and Vliet (2002) studied the effect of homogenizing tomato concentrates at 17 MPa on their storage modulus (G'). After homogenization, the G' at 1 Hz had changed from ~50 Pa to ~80-90 Pa for the 5°Brix product. In the present work, the tomato juice G' 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.

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 understand of the unit operations in food processing. While homogenization increased the yield stress (σ_0), apparent viscosity (η_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.

6.3.2. Applicability of the Cox-Merz Rule

As observed in Figure 6.1, the Cox-Merz rule could not be used directly (Augusto et al., 2011b). As commonly observed in food products, the complex viscosity (η^*) magnitudes were always higher than the apparent viscosity (η_a) magnitudes (Figure 6.3). 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 modifications to the Cox-Merz rule (Rao, 2005; Gunasekaran and Ak, 2000). Augusto et al. (2011b) showed the four possible linear modifications to the Cox-Merz rule, and discussed the fact that the studies reported in the literature did not follow a specific one. Thus, a linear (Equation 6.4) and a power (Equation 6.5) modified Cox-Merz rule were used for the evaluation of the rheological properties.

$$\eta^*(\omega) = \lambda \eta_a(\dot{\gamma})\Big|_{\dot{\gamma}=\omega} \qquad \text{(Equation 6.4)}$$

$$\eta^*(\omega) = \alpha\left[\eta_a(\dot{\gamma})\right]^{\beta}\Big|_{\dot{\gamma}=\omega} \qquad \text{(Equation 6.5)}$$

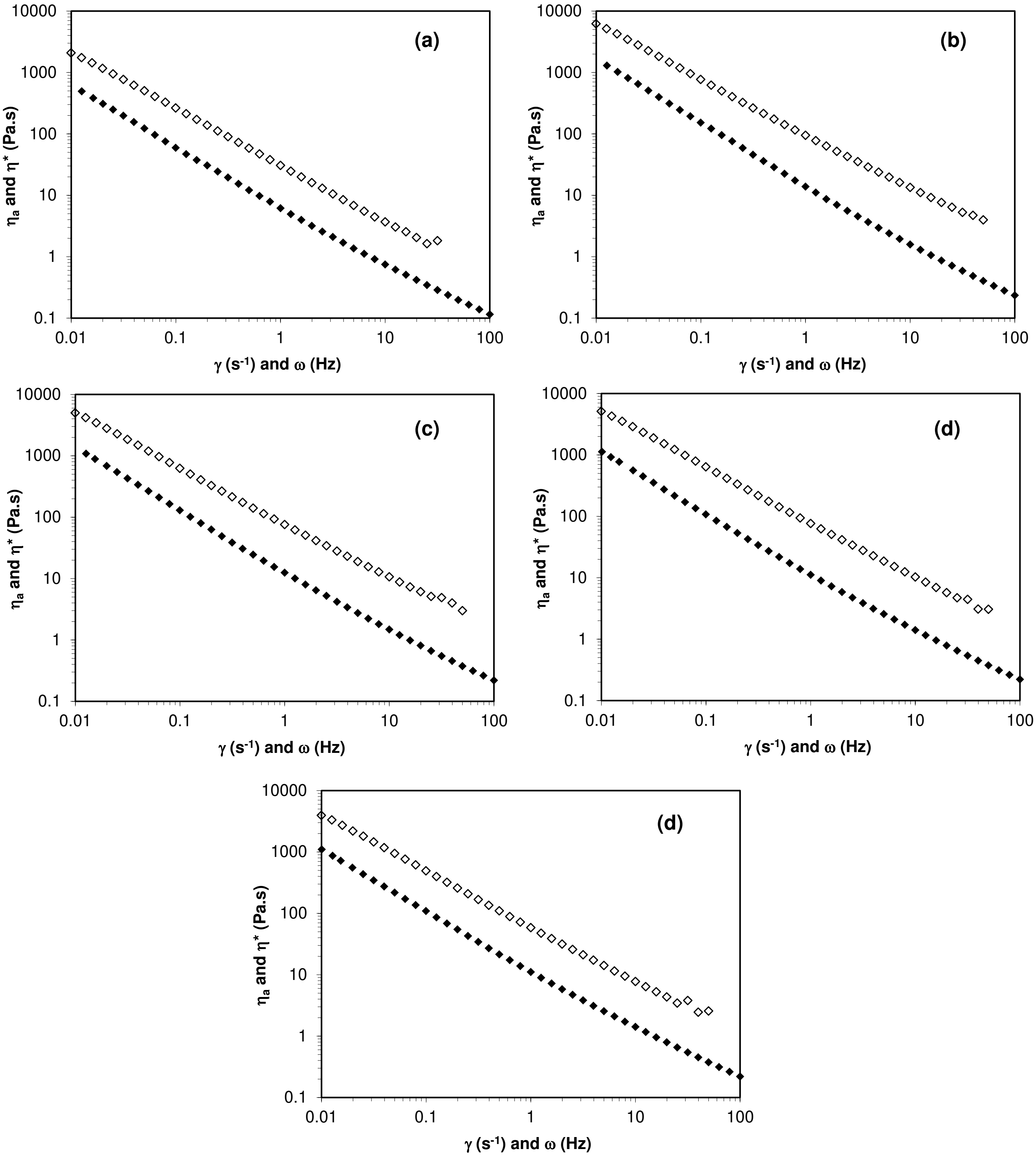

Figure 6.3. Tomato juice complex (η^*, ◇) and apparent (η_a, ◆) viscosities. Effect of HPH . (a) 0 MPa, (b) 25 MPa, (c) 50 MPa, (d) 100 MPa and (e) 150 MPa.

The values of the parameters λ (Equation 6.4) and α and β (Equation 6.5) are shown in Table 6.2, with R^2 always higher than 0.99. Moreover, the complex viscosity values obtained by the models (η^*_{model}) were plotted as a function of the experimental values ($\eta^*_{experimental}$). The regression of these data to a linear function (Equation 6.6) 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 Equation 6.6, it can be seen that the models obtained describe the experimental values well (Table 6.3). Moreover, it was observed that the power model (Equation 6.5) fitted the experimental values better than the linear model (Equation 6.4).

$$\eta^*_{model} = A \cdot \eta^*_{experimental} + B \qquad \text{(Equation 6.6)}$$

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 6.4 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 λ (Equation 6.6.4) and α and β (Equation 5) showed similar behaviour in relation to the homogenization pressure (P_H), to the behaviour observed for the parameters k', n' (Equation 6.1), k'' and n'' (Equation 6.2). The parameters λ and α first increased and then decreased with increase in P_H, while parameter β 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 λ, α and β in relation to the homogenization pressure (P_H) were relatively small. The value for α is related to the magnitude of the difference between the apparent (η_a) and complex (η^*) viscosities, and was the parameter that changed more (up to

40%). The value for β is related to the differences in behaviour between η_a and η^* in relation to the shear rate ($\dot{\gamma}$) and oscillatory frequency (ω), and only changed 2%.The linear model only had one parameter, λ, 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.

Table 6.2. Modified Cox-Merz Rule (Equations 6.4 and 6.5) parameters as function of homogenization pressure (P_H).

P_H (MPa)	**Equation 6.4**		**Equation 6.5**		
	λ	**R^2**	**α**	**β**	**R^2**
0	3.731	0.99	7.951	0.8745	0.99
25	3.961	0.99	10.41	0.8622	0.99
50	4.078	0.99	10.46	0.8616	0.99
100	4.758	0.99	11.25	0.8704	0.99
150	3.813	0.99	7.974	0.8882	0.99

Table 6.3. Modified Cox-Merz Rule (Equations 6.4 and 6.5) parameters as function of homogenization pressure (P_H): accuracy evaluation by using Equation 6.6.

P_H	**Equation 6.4**			**Equation 6.5**		
(MPa)	**A**	**B**	**R^2**	**A**	**B**	**R^2**
0	1.06	-20.1	0.99	1.04	4.01	0.99
25	1.00	-64.5	0.99	0.99	8.59	0.99
50	1.07	-54.5	0.99	1.05	9.09	0.99
100	1.01	-49.7	0.99	0.99	8.28	0.99
150	0.98	-23.9	0.99	0.99	8.21	0.99

Table 6.4. Values for the parameters of the linear (Equation 6.4) and power (Equation 6.5) modified Cox-Merz Rule for vegetable products.

Product	T (ºC)	Eq.6.4	Eq.6.5		Reference
		λ	α	β	
Tomato juice (HPH 0-150 MPa)	25	3.73-4.76	7.95-11.3	0.86-0.88	Present work
Tomato juice	25	5.56	-	-	Augusto et al. (2011b)
Sweet potato baby food	20	7.14	-	-	Ahmed, Ramaswamy (2006)
Potato puree	25-65	-	0.90-1.35	2.15-39.83	Alvarez et al. (2004)
Apple baby food	5-80	-	1.15-1.20	4.64-6.99	Ahmed, Ramaswamy (2007)
Apricot baby food	5-80	-	1.16-1.44	0.41-1.26	Ahmed, Ramaswamy (2007)
Banana baby food	5-80	-	1.15-1.33	1.91-11.80	Ahmed, Ramaswamy (2007)
Ketchup	25	-	0.94	13.97	Bistany, Kokini (1983)
Tamarind juice	10-90	-	0.67-1.06	0.86-30.82	Ahmed et al. (2007)

6.4. 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 (ω), 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.

6.5. Acknowledgments

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6.6. Nomenclature

α = magnitude index in power modified Cox-Merz Rule (Equation 6.5) [-]

β = behavior index in power modified Cox-Merz Rule (Equation 6.5) [-]

λ = magnitude index in linear modified Cox-Merz Rule (Equation 6.4) [-]

$\dot{\gamma}$ = shear rate [s^{-1}]

η_a = apparent viscosity (= σ / γ) [Pa·s]

η^* = complex viscosity [Pa·s]

σ = shear stress [Pa]

σ_0 = yield stress, Herschel-Bulkley model [Pa]

ω = oscillatory frequency [Hz]

A = slope index in the linear model for evaluation of experimental values versus those obtained by models (Equation 6.6) [-]

B = intercept index in the linear model for evaluation of experimental values versus those obtained by models (Equation 6.6) [-]

G' = storage modulus [Pa]

G'' = loss modulus [Pa]

k', k'' = consistency coefficients in the power law model of the viscoelastic properties (Equations 6.1 and 6.2) [$Pa \cdot s^{n'}$, $Pa \cdot s^{n''}$]

n', n'' = behaviour index in the power law model of the viscoelastic properties (Equations 6.1 and 6.2) [-]

P_H = homogenization pressure [MPa]

6.7. References

Ahmed, J.; Ramaswamy, H. S. (2007). Dynamic and steady shear rheology of fruit puree based baby foods. *Journal of Food Science and Technology*, 44(6), 579-585.

Ahmed, J., & Ramaswamy, H. S. (2006). Viscoelastic and thermal characteristics of vegetable puree-based baby foods. *Journal of Food Process Engineering*, 29, 219–233.

Ahmed, J.; Ramaswamy, H. S.; Sashidhar, K. C. (2007). Rheological characteristics of tamarind (*Tamarindus indica* L.) juice concentrates. *LWT - Food Science and Technology*, 40, 225-231.

Alvarez, M. D., Fernández, C., & Canet, W. (2004). Rheological behaviour of fresh and frozen potato puree in steady and dynamic shear at different temperatures. *European Food Research Technology*, 218, 544-553.

Augusto, P. E. D.; Falguera, V.; Cristianini, M.; Ibarz, A. (2010). Rheological behavior of tomato juice: steady-state shear and time-dependent modeling. *Food and Bioprocess Technology, in press* (DOI: 10.1007/s11947-010-0472-8).

Augusto, P. E. D.; Falguera, V.; Cristianini, M.; Ibarz, A. (2011a). Influence of fibre addition on the rheological properties of peach juice. *International Journal of Food Science and Technology*, 46, 1086-1092.

Augusto, P. E. D.; Falguera, V.; Cristianini, M.; Ibarz, A. (2011b). Viscoelastic properties of tomato juice: applicability of the Cox-Merz Rule. *Food and Bioprocess Technology, in press* (DOI: 10.1007/s11947-011-0655-y).

Augusto, P. E. D.; Ibarz, A.; Cristianini, M. (2011c). Effect of high pressure homogenization (HPH) on the rheological properties of tomato juice. Part I: time-dependent and steady-state shear. *Journal of Food Engineering*, *under review.* (Chapter 5).

Augusto, P. E. D.; Cristianini, M.; Ibarz, A. (2012). Effect of temperature on dynamic and steady-state shear rheological properties of siriguela (*Spondias purpurea* L.) pulp. *Journal of Food Engineering*, 108, 283-289.

Bayod, E.; Tornberg, E. (2011). Microstructure of highly concentrated tomato suspensions on homogenization and subsequent shearing. *Food Research International*, 44, 755-764.

Bayod, E.; Willers, E. P.; Tornberg, E. (2008). Rheological and structural characterization of tomato paste and its influence on the quality of ketchup. *LWT - Food Science and Technology*, 41, 1289-1300.

Bengtsson, H.; Tornberg, E. (2011). Physicochemical characterization of fruit and vegetable fiber suspensions. I: Effect of homogenization. *Journal of Texture Studies,* 42, 268-280.

Bistany, K. L.; Kokini, J. L. (1983). Dynamic viscoelastic properties of foods in texture control, *Journal of Rheology,* 27, 605–620.

Da Silva, J. A. L., & Rao, M. A. (1992). Viscoelastic Properties of Food Hydrocolloid Dispersions. In: Rao, M. A., Steffe, J. F. *Viscoelastic Properties of Foods*. London: Elsevier Science Publishers Ltd.

Dogan, H.; Kokini, J. L. (2007). Rheological Properties of Foods. In: Heldman, D. R.; Lund, D. B. (Ed.). *Handbook of Food Engineering*, 2nd ed. Boca Raton: Taylor & Francis Group.

Floury, J.; Bellettre, J. ; Legrand, J.; Desrumaux, A. (2004). Analysis of a new type of high pressure homogeniser. A study of the flow pattern. *Chemical Engineering Science*, 59, 843-853.

Gunasekaran, S., & Ak, M. M. (2000). Dynamic oscillatory shear testing of foods – selected applications. *Trends in Food Science and Technology*, 11, 115-127.

Ibarz, A.; Barbosa-Cánovas, G. V. (2003). *Unit Operations in Food Engineering*. Boca Raton: CRC Press.

Lopez-Sanchez, P.; Nijsse, J.; Blonk, H. C. G.; Bialek, L.; Schumm, S.; Langton, M. (2011a). Effect of mechanical and thermal treatments on the microstructure and rheological properties of carrot, broccoli and tomato dispersions. *Journal of the Science of Food and Agriculture*, 91, 207-217.

Lopez-Sanchez, P.; Svelander, C.; Bialek, L.; Schummm, S.; Langton, M. (2011b). Rheology and microstructure of carrot and tomato emulsions as a result of high-pressure homogenization conditions. *Journal of Food Science*, 76, 1, E130-E140.

Massa, A.; González, C.; Maestro, A.; Labanda, J.; Ibarz, A. (2010). Rheological characterization of peach purees. *Journal of Texture Studies*, 41, 532–548.

Nisha, P., Singhal, R. S., Pandit, A. B. (2010). Kinetic modelling of colour degradation in tomato puree (*Lycopersicon esculentum* L.). *Food and Bioprocess Technology, in press* (DOI:10.1007/s11947-009-0300-1).

Ouden, F. W. C. Den; Vliet, T. Van. (2002). Effect of concentration on the rheology and serum separation of tomato suspensions. *Journal of Texture Studies*, 33, 91-104.

Pereira, E. A.; Brandão, E. M.; Borges, S. V.; Maia, M. C. A. (2008). Influence of concentration on the steady and oscillatory shear behavior of umbu pulp. *Revista Brasileira de Engenharia Agrícola e Ambienta,*12(1), 87–90.

Pinho, C. R. G.; Franchi, M. A.; Augusto, P. E. D.; Cristianini, M. (2011). Milk flow evaluation during high pressure homogenization (HPH) using computational fluid dynamics (CFD). *Brazilian Journal of Food Technology*, 14, 3, 232-240, (*in Portuguese*).

Ramamoorthi, L., Lee, Y., & Brewer, S. (2009). Effect of food matrix and heat treatment on the rheological properties of salmon-based baby food. *Journal of Food Engineering*, 95, 432–437.

Rao, M. A. (1999). *Rheology of Fluid and Semisolid Foods: Principles and Applications*. Gaithersburg: Aspen Publishers.

Rao, M. A. (2005). Rheological Properties of Fluid Foods. In: Rao, M. A., Rizvi, S. S. H., & Datta, A. K. *Engineering Properties of Foods*. Boca Raton: CRC Press, 3rd ed..

Rao, M. A., & Cooley, H. J. (1992). Rheological behavior of tomato pastes in steady and dynamic shear. *Journal of Texture Studies*, v.23, p.415-425.

Sánchez, M. C., Valencia, C., Gallegos, C., Ciruelos, A., & Latorre, A. (2002). Influence of processing on the rheological properties of tomato paste. *Journal of the Science of Food and Agriculture*, v.82, p.990-997.

Sato, A. C. K.; Cunha, R. L. (2009). Effect of particle size on rheological properties of jaboticaba pulp. *Journal of Food Engineering*, 91, 566-570.

Sharoba, A. M.; Senge, B.; El-Mansy, H. A.; Bahlol, H. ElM.; Blochwitz, R. (2005). Chemical, sensory and rheological properties of some commercial German and Egyptian tomato ketchups. *European Food Research Technology*, 220, 142–151.

Silva, V.M.; Sato, A.C.K.; Barbosa, G.; Dacanal, G.; Ciro-Velásquez; H.J.; Cunha, R.L. (2010). The effect of homogenisation on the stability of pineapple pulp. *International Journal of Food Science and Technology*, 45, 2127–2133.

Steffe, J.F. (1996). *Rheological Methods in Food Process Engineering*, 2nd ed. East Lansing: Freeman Press

Tehrani, M. M.; Ghandi, A. (2007). Modification of Bostwick method to determine tomato concentrate consistency. *Journal of Food Engineering*, 79, 1483-1486.

Tonon, R. V.; Alexandre, D.; Hubinger, M. D.; Cunha, R. L. (2009). Steady and dynamic shear rheological properties of açai pulp (*Euterpe oleraceae* Mart.). *Journal of Food Engineering*, 92, 425–431.

Valencia, C., Sánchez, M. C., Ciruelos, A., Latorre, A., Franco, J. M., & Gallegos, C. (2002). Linear viscoelasticity of tomato sauce products: influence of previous tomato paste processing. *European Food Research Technology*, 214, 394–399.

Valencia, C., Sánchez, M. C., Ciruelos, A., & Gallegos, C. (2004). Influence of tomato paste processing on the linear viscoelasticity of tomato ketchup. *Food Science and Technology International*, v.10, n.2, p.95-100.

Yoo, B.; Rao, M. A. (1994). Effect of unimodal particle size and pulp content on rheological properties of tomato puree. *Journal of Texture Studies*, 25, 4, 421-436.

Yoo, B., & Rao, M. A. (1996). Creep and dynamic rheological behavior of tomato concentrates: effect of concentration and finisher screen size. *Journal of Texture Studies*, 27, 451-459 .

Yılmaz, M. T.; Karaman, S.; Cankurt, H.; Kayacier, A.; Sagdic, O. (2011). Steady and dynamic oscillatory shear rheological properties of ketchup–processed cheese mixtures: Effect of temperature and concentration. *Journal of Food Engineering*, 103, 197–210.

Chapter 7: Effect of High Pressure Homogenization (HPH) on the Rheological Properties of Tomato Juice. Part III: Creep and Recovery Behaviour

This chapter was developed at University of Campinas, and is currently under review as:

AUGUSTO, P. E. D.; IBARZ, A.; CRISTIANINI, M. Effect of High Pressure Homogenization (HPH) on the Rheological Properties of Tomato Juice. Part III: Creep and Recovery Behaviour.

Abstract

High pressure homogenization (HPH) is a non-thermal technology that has been proposed as a partial or total substitute of food thermal processing. Although its effect on microbial inactivation is widely studied, the rheological changes in fruit products, as well as the effects on juice constituents, need better describing. The present work evaluated the effect of HPH (up to 150 MPa) on the creep and recovery properties of tomato juice. The mechanical Burger model well explained the juice creep compliance, and its parameters (Newtonian dashpots and Hookean springs) were evaluated as function of the homogenization pressure (P_H). The HPH processing improved tomato juice elastic and viscous behaviour, whose changes could be attributed to the suspended particles disruption during processing. Moreover, each Burger model constituent could be related to the product internal structure. The obtained results highlighted the possible applications of the high pressure homogenization (HPH) process as a valuable tool to promote physical properties changes in food products.

Keywords:

Creep, compliance, food properties, high pressure homogenization, recovery, rheology.

Efeito da Homogeneização a Alta Pressão (HAP) nas Propriedades Reológicas de Suco de Tomate. Parte III: Comportamento de Fluência e Recuperação

Resumo

A homogeneização a alta pressão (HAP) tem sido proposta como alternativa parcial ou total ao processo térmico de alimentos. Embora a inativação microbiana tenha sido bastante estudada, poucos trabalhos da literatura estudam alterações físico-químicas em produtos de frutas devido a HAP, especialmente em relação às características reológicas. O presente trabalho avaliou o efeito da HAP (até 150 MPa) nas propriedades de fluência e recuperação (*creep and recovery*) de suco de tomate. O modelo mecânico de Burger explicou adequadamente o comportamento de fluência (*creep compliance*) do suco, sendo seus parâmetros (amortecedores Newtonianos e molas Hookeanas) avaliados como função da pressão de homogeneização (P_H). O processo de HAP aumentou os comportamentos elásticos e viscosos do suco de tomate, sendo as alterações atribuídas ao rompimento das partículas em suspensão durante processamento. Cada constituinte do modelo de Burger pôde então ser relacionado às estruturas internas do produto. Os resultados obtidos destacam a possibilidade de uso da HAP como uma valiosa ferramenta na promoção de alterações físicas em alimentos.

Palavras-chave:

Fluência, homogeneização a alta pressão, propriedades dos alimentos, reologia.

7.1. Introduction

The food rheological characterization is important for unit operations design, process optimization and high quality products assurance (Ibarz and Barbosa-Cánovas, 2003; Rao, 1999). The viscoelastic properties are very useful in the design and prediction of products stability (Ibarz and Barbosa-Cánovas, 2003), being important to describe many processing and storage phenomena (Steffe, 1996). Thus, the study and description of liquid foods viscoelastic properties are important for better understand its behaviour during processing, storage and consumption.

The high pressure homogenization (HPH) technology consists in pressurizing a fluid for quickly flow through a narrow gap valve, which greatly increases its velocity, resulting in depressurization with consequent cavitation and high shear stress. Thus, particles, cells and macromolecules suspended in the fluid are subjected to high mechanical stresses, being twisted and deformed (Pinho et al., 2011; Floury et al., 2004). This technology has been studied by many authors as a non-thermal food preservation technique, especially for fruit products.

Tomato is one of the most important vegetables for the food industry, being widely included in human diet. Although the homogenization is a unit operation generally used in tomato processing, there are just a few works related to the effect of high pressure homogenization (HPH) on tomato products rheology, in special to the viscoelastic properties. Ibarz and Barbosa-Cánovas (2003) observed that by conducting creep and recovery experiment, it is possible to describe the product rheological behaviour using mechanical models and constitutive equations, combining the viscosity equation of Newton and the elasticity equation of Hooke.

In the first part of this work (Augusto et al., 2011d) it was evaluated the effect of HPH (up to 150 MPa) on the time-dependent and steady-state shear rheological properties of tomato juice. In the second part Augusto et al. (2011e) studied the effect of HPH on the tomato juice viscoelastic properties, focusing on the parameters storage modulus (G'), loss modulus (G'') and complex viscosity

(η*). Moreover, the Cox-Merz rule applicability was evaluated. The present work evaluated the effect of high pressure homogenization (HPH) on the viscoelastic properties of tomato juice related to its behaviour on the creep and recovery test.

7.2. Materials and Methods

As described by Augusto et al. (2011d), a 4.5ºBrix tomato juice was obtained by diluting a commercial 30ºBrix pulp in distilled water. The commercial pulp was used for guaranty of standardization and repeatability. It was obtained through the hot break process, being concentrated by evaporation at 65°C, thermally processed by the UHT method and aseptically packaged.

The pulp was fractionated in small portions in the laboratory, packaged in high density polyethylene bottles and frozen at -18ºC. This procedure has allowed the use of the same product during the whole work. The samples were then thawed at 4ºC and diluted using distilled water at 50ºC to ensure better hydration (Tehrani and Gandhi, 2007). The juice was then allowed to rest for 24 hours at 5ºC to ensure complete hydration and release of incorporated air. The juice pH was 4.6.

7.2.1. High Pressure Homogenization (HPH) Process

The juice was homogenized at 0 MPa (control), 25 MPa, 50 MPa, 100 MPa and 150 MPa using a high pressure homogenizer (Panda Plus, GEA Niro Soavi, Italy). Samples were introduced at room temperature in the equipment, and quickly cooled using an ice bath just after the homogenization valve. The maximum temperature reached was ~40°C (for the sample of 150 MPa just before the ice bath). The experiments were carried out in three replicates.

7.2.2. Rheological Procedures

Rheological analyses were carried out using a controlled stress (σ) rheometer (AR2000ex, TA Instruments, USA) and a four-bladed vanned geometry (bob diameter = 28 mm; cup diameter = 30 mm; bob length = 42 mm; bottom vertical gap = 4.0 mm). Temperature was maintained constant at 25ºC by a Peltier system.

Previously, oscillatory stress sweeps between 0.01 and 10 Pa were performed at a frequency of 1 Hz to determine the samples linear viscoelastic region (LVR). The native tomato juice LVR limit was set at 0.1 Pa (Augusto et al., 2011b; Augusto et al., 2011e), while the other sample limits were close to 1.0 Pa (Augusto et al., 2011e). Thus, the shear stress of 0.1 Pa was selected for the creep procedure, as it can be used for all the samples.

Then, samples were placed in the rheometer and kept at rest for 10 min before the experiment. The creep procedure was conducted at 0.1 Pa during 5 min, being the sample strain (γ) recorded. The stress was then instantly removed ($\sigma_{applied}$ = 0.0 Pa), and sample strain (γ) was recorded during 5 min in the recovery procedure.

7.2.3. Rheological Properties Evaluation

The results were expressed by the compliance function against time (J(t); Equation 7.1). The creep and recovery portions were then evaluated.

$$J(t) = \frac{\gamma(t)}{\sigma_{applied}} \quad \text{(Equation 7.1)}$$

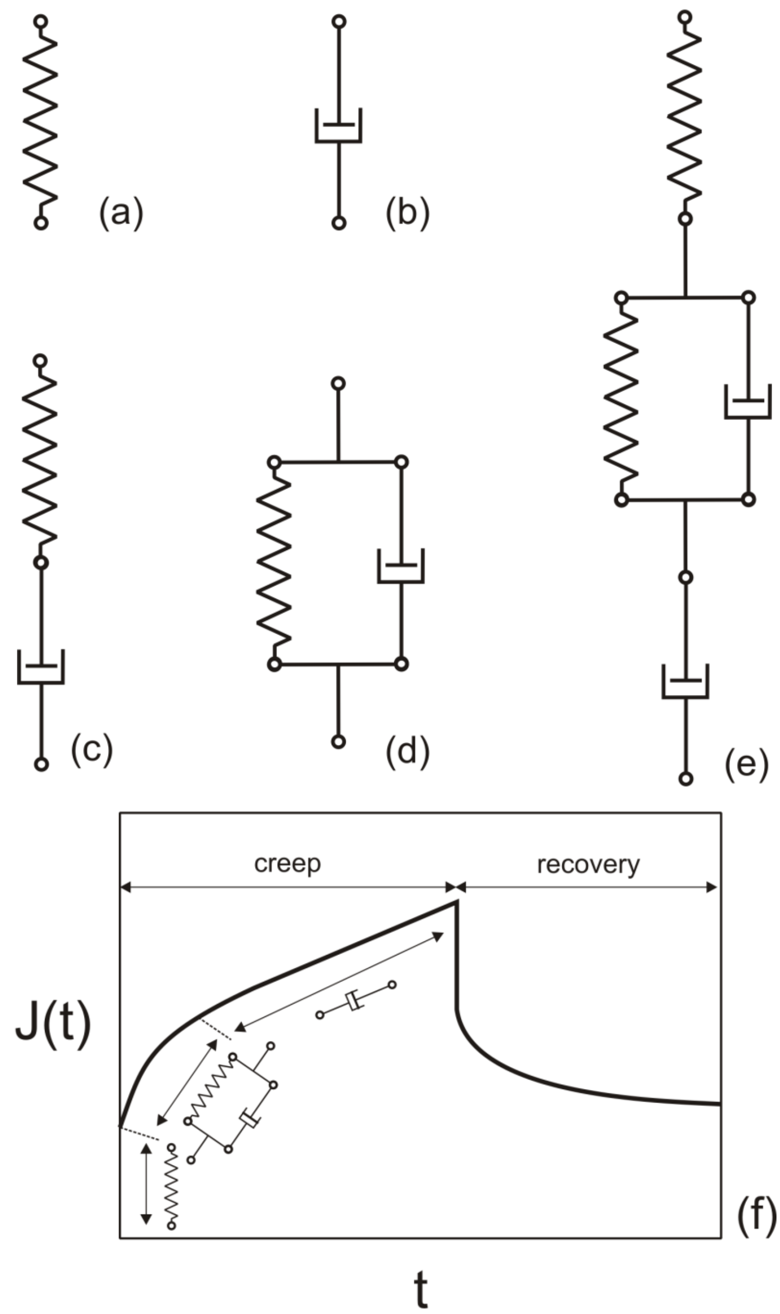

Figure 7.1. Mechanical models used to describe the viscoelastic properties of foods: (a) the Hookean spring, (b) the Newtonian dashpot, (c) the Maxwell model, (d) the Kelvin-Voigt model, (e) the Burger model, (f) a typical creep and recovery plot described by the Burger model. Adapted from Ibarz and Barbosa-Cánovas (2003) and Steffe (1996).

The tomato juice creep behaviour was described by the Burger model (Equation 7.2). The Burger model comprises a Kelvin-Voigt (a Hookean spring and a Newtonian dashpot placed in parallel) and a Maxwell (a Hookean spring and a Newtonian dashpot placed in series) models placed in series. It is illustrated in Figure 7.1. It is widely used to describe the creep behaviour of different biological materials, as lentil starch (Ahmed and Auras, 2011), wheat dough (Bockstaele et al., 2011), organogels (Toro-Vazquez et al., 2010), emulsions (Yilmaz et al., 2012; Dolz et al., 2008) and frozen and melted ice cream (Sherman, 1966).

The compliance during the recovery procedure was described by an exponential decay function (Equation 7.3), similar to the evaluated by Yilmaz et al. (2012), Toro-Vazquez et al. (2010), Bayarri et al. (2009) and Dolz et al. (2008).

$$J(t) = \frac{1}{G_0} + \frac{1}{G_1}\left(1 - \exp\left(\frac{-G_1 t}{\eta_1}\right)\right) + \frac{t}{\eta_0} \qquad \text{(Equation 7.2)}$$

$$J(t) = J_\infty + J_{KV} \cdot \exp(-B \cdot t^C) \qquad \text{(Equation 7.3)}$$

The parameters of each model were obtained by non-linear regression using the software CurveExpert Professional v.1.2.3 using a significant probability level of 95%. Moreover, the effect of homogenization pressure (P_H) on the parameters of Equations 7.2 and 7.3 was evaluated by using the analysis of variance (ANOVA) and the Tukey test at a 95% confidence level. The software STATISTICA 5.5 (StatSoft, Inc., USA) was used for this purpose.

7.3. Results and Discussion

Figure 7.2 shows the tomato juice creep and recovery behaviour as function of the homogenization pressure (P_H). As expected, the increase in P_H reduced the juice compliance, which is due to the development of a stronger internal structure. This behaviour is in accordance to our previous results of steady-state shear and viscoelasticity (Augusto et al., 2011d; Augusto et al., 2011e).

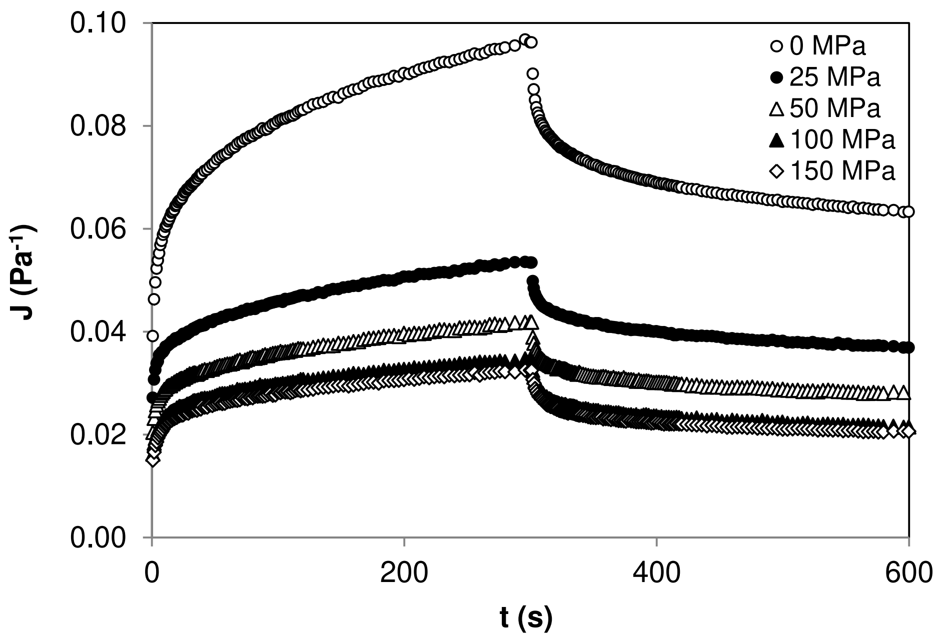

Figure 7.2. Tomato juice creep and recovery behaviour: effect of HPH.

Augusto et al. (2011d) studied the effect of HPH (up to 150 MPa) on the time-dependent and steady-state shear rheological properties of tomato juice. The HPH processing reduced both the tomato juice mean particle diameter and particle size distribution (PSD), increasing the particle surfaces area and the interaction forces among then. Consequently, the HPH increased the juice consistency and thixotropy. In fact, Bengtsson and Tornberg (2011), Lopez-Sanchez et al. (2011a), Bayod et al. (2008) and Ouden and Vliet (1997) observed the tomato products yield stress (σ_0) increasing due to homogenization (P_H < 60 MPa).

Augusto et al. (2011e) studied the effect of HPH (up to 150 MPa) on the viscoelastic properties of tomato juice. The HPH increased tomato juice storage (G') and loss (G'') modules, increasing both product elastic and viscous behaviour. Moreover, the HPH processing improved tomato juice consistency more than modified its nature/behaviour. The observed changes on the viscoelastic properties were then attributed to the suspended particles disruption during processing.

Similar results were observed by Ouden and Vliet (2002), Bengtsson and Tornberg (2011) and Bayod and Tornberg (2011). Ouden and Vliet (2002) studied the effect of tomato concentrates homogenization at 17 MPa on its storage modulus (G'), observing an increasing after processing. 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 the G' increasing in tomato, potato and carrot suspensions; for apple fibre suspensions, however, the G' remained constant. The G' increasing due to homogenization (up to three passes at 9 MPa) was also observed by Bayod and Tornberg (2011) for tomato suspensions.

Figure 7.2 shows that the effect of HPH describes an asymptotic behaviour in relation to the P_H, i.e., the product changes are higher at "low" P_H and progressively lower at "high" P_H. This is also in accordance to the previously observed for PSD, steady-state shear and viscoelastic behaviour (Augusto et al., 2011d; Augusto et al., 2011e).

Augusto et al. (2011d) observed that the increasing in the P_H progressively reduced the bigger suspended particles diameter, while the small particles diameter remained quasi-constant after a reduction close to 50 MPa.

The homogenization process disrupts the remained suspended cells and breaks its fragments in small suspended particles. It is expected that the small fragments are less susceptible to be broken during processing when compared to the bigger ones or even to the entire cells. Consequently, as the P_H is increased, the bigger particles are still broken, while the smaller ones remained intact, explaining the observed PSD behaviour. Therefore, the rheological properties asymptotic behaviour in relation to the P_H was attributed to the suspended particle disruption due to HPH (Augusto et al., 2011d).

Figure 7.3 shows the effect of HPH on the mechanical Burger model parameters. The tomato juice creep compliance behaviour could be well described by the Burger model (Equation 7.2), with high coefficient of determination (R^2>0.98). In Burger's model, the G_0 is the instantaneous elastic modulus, associated to the Maxwell spring and the G_1 is the retarded elastic modulus, associated to the Kelvin-Voigt spring. Moreover, the η_0 is the Newtonian flow viscosity, associated to the Maxwell dashpot, and the η_1 is the retarded viscosity, associated to the Kelvin-Voigt dashpot.

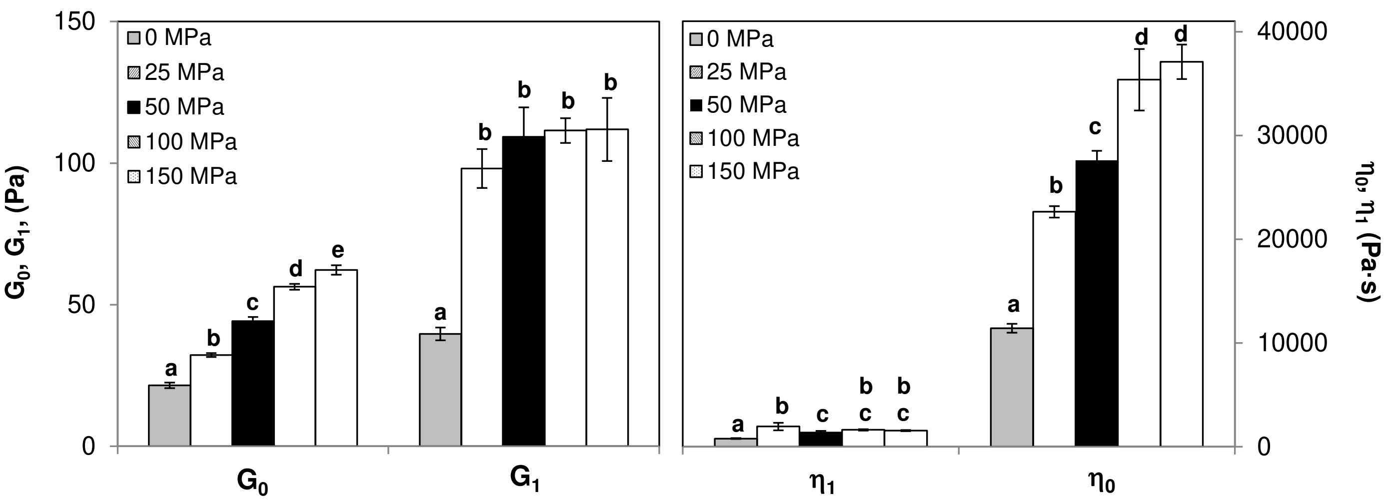

Figure 7.3. Tomato juice creep compliance behaviour: effect of HPH on the mechanical Burger model parameters. Mean of four replicates at 25ºC; vertical bars represent the standard deviation in each value. For each parameter, different letters represent significantly different values ($P < 0.05$).

The creep compliance behaviour can be described by models combining higher numbers of Newtonian (η_n) and Hookean (G_n) elements, as the six-elements model used by Yoo and Rao (1996) for describing the tomato concentrates (21-32ºBrix) behaviour. However, especially from an engineering standpoint, a model should be better as less parameters are associated to then. Thus, the four-elements Burger model was considered adequate for describing the tomato juice creep compliance behaviour.

When the P_H was increased, it was observed a gradual G_0 and η_0 increasing. The values of G_1 and η_1, however, showed the same asymptotic behaviour previously observed for G', G'' (Augusto et al., 2011e), k, n and σ_0 (Augusto et al., 2011e), with higher changes at $P_H < 25$ MPa and constant values at higher P_H.

Furthermore, as the increase in P_H progressively reduced the bigger suspended particles diameter, while the small particles diameter remained quasi-constant (Augusto et al., 2011d), the G_0 and η_0 values can be associated to the bigger particles behaviour, while the G_1 and η_1 values can be associated to the smaller ones.

Fruit juices are composed by an insoluble phase (the pulp) dispersed in a viscous solution (the serum). The dispersed phase or pulp is formed by fruit tissue cells and its fragments, cell walls and insoluble polymer clusters and chains. The serum is a water solution of soluble polysaccharides, sugars, salts and acids. The fruit juices rheological properties are thus defined by the interactions inside each phase and between them (Augusto et al., 2011c). The tomato juice serum is a Newtonian fluid, which become a Herschel-Bulkley fluid due to the pulp particles dispersion (Augusto et al., 2011c; Augusto et al., 2010; Tanglertpaibul and Rao, 1987).

The cell disruption and further fragmentation during HPH not only increase the suspended particles surface area, but also change particles and serum properties. The cell fragmentation exposes and releases wall constituents, as pectins and proteins, improving the particle-particle and particle-serum interactions (Augusto et al., 2011d). When the tomato serum is evaluated separately, a small viscosity reduction is observed due to the HPH (~15% at 150 MPa; Augusto et al., 2011c). However, when the cell fragmentation is considered, the improvement in serum constituents can increase its viscosity. It is important to highlight that concentration exponentially increases the viscosity and consistency (Ibarz and

Barbosa-Cánovas, 2003; Rao, 1999; Steffe, 1996), as can be seen by varying the concentration of cell wall constituents (Augusto et al., 2001a).

Moreover, the Hookean (G) elements describe the material elastic behaviour, while the Newtonian (η) elements describe its viscous behaviour. Thus, the Hookean (G) elements can be associated to the interactions among the suspended particles, while the Newtonian (η) elements can be associated to the serum and to the interaction among particles and serum (i.e., the fluid resistance to flow). Thus, it explains why the Newtonian behaviour, related to the Burger dashpots (η_0, η_1,), can be associated to the suspended particles.

The results here obtained, associated to the previous ones (Augusto et al., 2011c, 2011d and 2011e) permit the following interpretation to the HPH processing effect on tomato juice structure and rheological behaviour.

As the P_H is increased, the larger suspended particles diameter are progressively reduced, while the smaller particles diameter are highly reduced at "low" P_H (< 50 MPa) and then remained quasi-constant. As particles are disrupted, its components are passed to the serum, improving its viscosity. Moreover, the higher particle surfaces area is improved and its volume fraction (ϕ) is increased, resulting in higher inter-particle and particles-serum interaction. The reduction in particle diameter increases product elastic behaviour (G_0, G_1) due to the larger surface area and volume fraction (ϕ), resulting in bigger interactions among particles. Moreover, the particle soluble materials release and large particle volume fraction (ϕ) increase the product viscous behaviour (η_0, η_1) As the major particle changes are associated to P_H up to 50 MPa, the main rheological changes take place at this processing level.

The non-hydrodynamic forces can be important in systems with smaller suspended particles, as the HPH tomato juice (Augusto et al., 2011d). Small particles interaction can be due to van der Waals forces (Genovese et al., 2007; Tsai and Zammouri, 1988) and/or electrostatic forces due to the interaction between the negatively charged pectins and the positively charged proteins (Beresovsky et al., 1995; Takada and Nelson, 1983). Thus, it is expected that the HPH processing results in small particles aggregation with a network formation, as described by Bayod and Tornberg (2011), resulting in a more thixotropic fluid (Augusto et al., 2011d). Moreover, as the P_H is increased, a big number of aggregates are expected.

Therefore, the elements of Burger model can be associated to each tomato juice component.

The first Hookean element (G_0), associated to the Maxwell spring, describes the product elastic behaviour and could be related to the large particles behaviour in the HPH. Therefore, it can be associated to the suspended particles, i.e., to the inter-particle interactions.

The first Newtonian element (η_0), associated to the Maxwell dashpot, describes the product viscous behaviour and also could be related to the large particles behaviour in the HPH. Therefore, it can be associated to the product resistance to flow, related to the serum viscosity and to the particle drag contribution during flow (i.e., particle-serum interaction).

The Kelvin-Voigt element could be related to the small particles behaviour in the HPH, while the small particles were related to the particle aggregates formation. Therefore, the Kelvin-Voigt element can be associated to the tomato juice particle aggregates. Moreover, the Kelvin-Voigt Hookean element (G_1) can be associated to the inter-particle interactions inside the aggregates, while the Kelvin-Voigt Newtonian element (η_1) can be associated to the aggregates drag during flow (i.e., aggregates-serum interaction).

Therefore, by using the creep compliance analysis, it was possible to better understand the tomato juice rheological behaviour, as well as the influence of HPH. The proposed tomato juice description, using the Burger model, is illustrated in Figure 7.4.

After the creep period, the applied stress was instantly removed ($\sigma_{applied}$ = 0.0 Pa), and sample compliance (J) was recorded during in the recovery procedure. The tomato juice recovery compliance behaviour could be well described by the exponential decay model (Equation 7.3), with high coefficient of determination (R^2>0.97). Figure 5 shows the effect of HPH on the tomato juice recovery compliance behaviour, considering the described exponential decay model (Equation 7.3). The B and C parameters are the proportional and power kinetic parameters in the recovery model, respectively. Thus, the parameter B is related to the magnitude of time involved in the compliance decay, while C describes the curvature shape. The compliance J_∞ is the residual compliance corresponding to the permanent deformation of the Maxwell dashpot, while the J_{KV} is the recovery compliance due to the Kelvin-Voigt element.

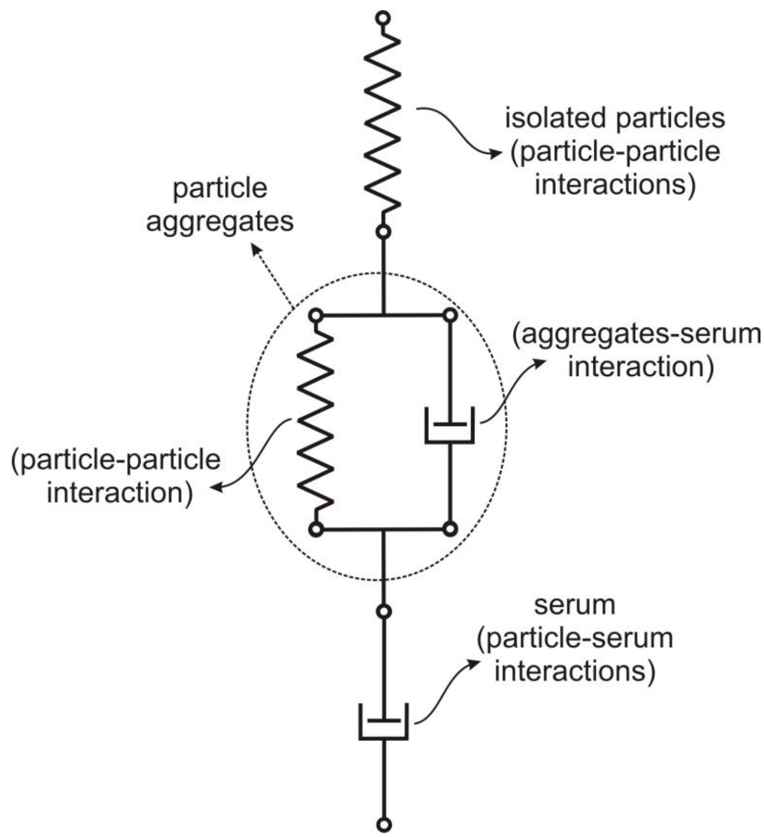

Figure 7.4. Proposed model to describe the tomato juice creep compliance behaviour.

Both compliance parameters (J_∞, J_{KV}) showed an asymptotic-decreasing behaviour in relation to the P_H (i.e., increasing the resistance of deformation), indicating once more the tomato juice stronger internal structure due to HPH. The compliance J_∞ is related to the Maxwell dashpot and to the sample permanent deformation (i.e., the energy dissipated to flow). As expected (as $J_\infty = t/\eta_0$;

Equation 7.2), its behaviour was similar to those obtained by the first Newtonian element (η_0, Figure 7.3). Furthermore, the compliance J_{KV} is the recovery compliance due to the Kelvin-Voigt element, being function of G_1 and η_1 (Equation 7.2). Once more, its behaviour was similar to those obtained by the Kelvin-Voigt spring and dashpot (Figure 7.3). The proportional kinetic parameter (B) showed no dependency to the P_H, being close to 0.25 s^{-C} for all the samples. The power kinetic parameter (C) showed values close to 0.35 at $P_H \leq 50$ MPa, and then a slight increase at $P_H \geq 100$ MPa (~0.4).

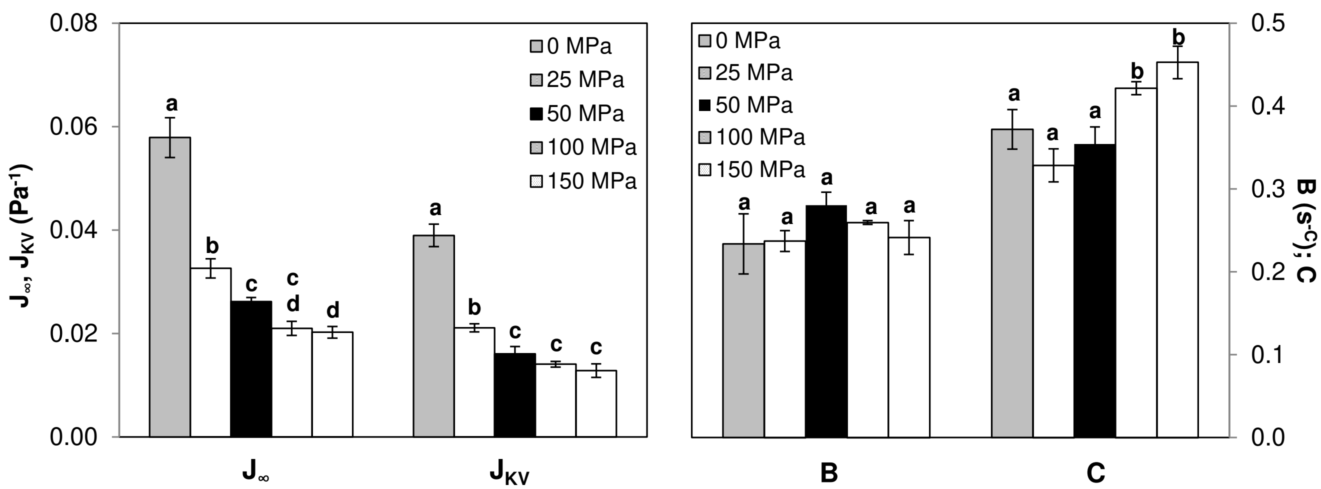

Figure 7.5. Tomato juice recovery compliance behaviour: effect of HPH on the exponential decay model parameters. Mean of four replicates at 25ºC; vertical bars represent the standard deviation in each value. For each parameter, different letters represent significantly different values ($P < 0.05$).

By using creep and recovery experiments, it was thus possible to better understand the effect of high pressure homogenization (HPH) on the tomato juice rheological properties. The obtained results described the HPH effect on the tomato juice internal structure. It indicates the possible applications for this process as a valuable tool to promote physical properties changes in food products, as improve both product elastic and viscous behaviour. Thus, HPH can be used in order to increase tomato juice consistency, improving it sensory acceptance, reducing the need for hydrocolloids and reducing particle sedimentation or serum separation.

7.4. Conclusions

The present work evaluated the effect of high pressure homogenization (HPH) on the creep and recovery properties of tomato juice. The mechanical Burger model well explained the juice creep compliance, and its parameters were evaluated as function of the homogenization pressure (P_H). The HPH processing improved tomato juice elastic and viscous behaviour, whose changes could be related to the product internal structure. The obtained results highlighted the possible applications of the high pressure homogenization (HPH) process as a valuable tool to promote physical properties changes in food products.

7.5. Acknowledgments

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7.6. Nomenclature

γ = strain [-]

ϕ = particle volume fraction [-]

η = viscosity, associated to the Newtonian dashpot [Pa·s]

η_0 = Newtonian flow viscosity, associated to the Maxwell dashpot [Pa·s]

η_1 = retarded viscosity, associated to the Kelvin-Voigt dashpot [Pa·s]

η^* = complex viscosity [Pa·s]

σ = shear stress [Pa]

σ_0 = yield stress, Herschel-Bulkley's model [Pa]

B = proportional kinetic parameter in recovery model (Equation 7.3) [s^{-C}]

C = power kinetic parameter in recovery model (Equation 7.3) [-]

G = elastic modulus, associated to the Hookean spring [Pa]

G_0 = instantaneous elastic modulus, associated to the Maxwell spring [Pa]

G_1 = retarded elastic modulus, associated to the Kelvin-Voigt spring [Pa]

G' = storage modulus [Pa]

G'' = loss modulus [Pa]

J = compliance (Equation 1) [Pa^{-1}]

J_∞ = residual compliance corresponding to the permanent deformation of the Maxwell dashpot [Pa^{-1}]

J_{KV} = recovery compliance due to the Kelvin-Voigt element [Pa^{-1}]

k = consistency coefficient, Herschel-Bulkley's model [$Pa \cdot s^n$]

n = flow behavior index, Herschel-Bulkley's model [-]

P_H = homogenization pressure [MPa]

t = time [s]

7.7. References

Ahmed, J.; Auras, R. (2011). Effect of acid hydrolysis on rheological and thermal characteristics of lentil starch slurry. LWT - Food Science and Technology, 44, 976-983.

Augusto, P. E. D.; Falguera, V.; Cristianini, M.; Ibarz, A. (2010). Rheological behavior of tomato juice: steady-state shear and time-dependent modeling. *Food and Bioprocess Technology, in press* (DOI: 10.1007/s11947-010-0472-8).

Augusto, P. E. D.; Falguera, V.; Cristianini, M.; Ibarz, A. (2011a). Influence of fibre addition on the rheological properties of peach juice. *International Journal of Food Science and Technology*, 46, 1086-1092.

Augusto, P. E. D.; Falguera, V.; Cristianini, M.; Ibarz, A. (2011b). Viscoelastic properties of tomato juice: applicability of the Cox-Merz Rule. *Food and Bioprocess Technology, in press* (DOI: 10.1007/s11947-011-0655-y).

Augusto, P. E. D.; Ibarz, A.; Cristianini, M. (2011c). Effect of high pressure homogenization (HPH) on the rheological properties a fruit juice serum model. *Journal of Food Engineering, under review.* (Chapter 4)

Augusto, P. E. D.; Ibarz, A.; Cristianini, M. (2011d). Effect of high pressure homogenization (HPH) on the rheological properties of tomato juice. Part I: time-dependent and steady-state shear. *Journal of Food Engineering*, *under review.* (Chapter 5)

Augusto, P. E. D.; Ibarz, A.; Cristianini, M. (2011e). Effect of high pressure homogenization (HPH) on the rheological properties of tomato juice. Part II: Viscoelastic Properties and the Cox-Merz Rule. *Journal of Food Engineering*, *under review.* (Chapter 6)

Bayarri, S.; Dolz, M.; Hernández, M. J. (2009). Effect of carboxymethyl cellulose concentration on rheological behavior of milk and aqueous systems. A creep and recovery study. *Journal of Applied Polymer Science*, 114, 1626-1632.

Bayod, E.; Tornberg, E. (2011). Microstructure of highly concentrated tomato suspensions on homogenization and subsequent shearing. *Food Research International*, 44, 755-764.

Bayod, E.; Willers, E. P.; Tornberg, E. (2008). Rheological and structural characterization of tomato paste and its influence on the quality of ketchup. *LWT - Food Science and Technology*, 41, 1289-1300.

Bengtsson, H.; Tornberg, E. (2011). Physicochemical characterization of fruit and vegetable fiber suspensions. I: Effect of homogenization. *Journal of Texture Studies,* 42, 268-280.

Beresovsky, N.; Kopelman, I. J.; Mizrahi, S. (1995). The role of pulp interparticle interaction in determining tomato juice viscosity. *Journal of Food Processing and Preservation*, 19, 133-146.

Bockstaele, F. V.; Leyn, I. D.; Eeckhout, M.; Dewettinck, K. (2011). Non-linear creep-recovery measurements as a tool for evaluating the viscoelastic properties of wheat flour dough. *Journal of Food Engineering*, 107, 50-59.

Dolz, M.; Hernández, M. J.; Delegido, J. (2008). Creep and recovery experimental investigation of low oil content food emulsions. *Food Hydrocolloids*, 22, 421-427.

Floury, J.; Bellettre, J. ; Legrand, J.; Desrumaux, A. (2004). Analysis of a new type of high pressure homogeniser. A study of the flow pattern. *Chemical Engineering Science*, 59, 843-853.

Genovese, D. B.; Lozano, J. E.; Rao, M. A. (2007). The rheology of colloidal and noncolloidal food dispersions. *Journal of Food Science*, 72, 2, R11-R20.

Ibarz, A.; Barbosa-Cánovas, G. V. (2003). *Unit Operations in Food Engineering*. Boca Raton: CRC Press.

Lopez-Sanchez, P.; Nijsse, J.; Blonk, H. C. G.; Bialek, L.; Schumm, S.; Langton, M. (2011a). Effect of mechanical and thermal treatments on the microstructure and rheological properties of carrot, broccoli and tomato dispersions. *Journal of the Science of Food and Agriculture*, 91, 207-217.

Ouden, F. W. C. Den; Vliet, T. Van. (1997). Particle size distribution in tomato concentrate and effects on rheological properties. *Journal of Food Science*, 62(3), 565-567.

Ouden, F. W. C. Den; Vliet, T. Van. (2002). Effect of concentration on the rheology and serum separation of tomato suspensions. *Journal of Texture Studies*, 33, 91-104.

Pinho, C. R. G.; Franchi, M. A.; Augusto, P. E. D.; Cristianini, M. (2011). Milk flow evaluation during high pressure homogenization (HPH) using computational fluid dynamics (CFD). *Brazilian Journal of Food Technology*, 14, 3, 232-240, (*in Portuguese*).

Rao, M. A. (1999). *Rheology of Fluid and Semisolid Foods: Principles and Applications*. Gaithersburg: Aspen Publishers.

Steffe, J.F. (1996). *Rheological Methods in Food Process Engineering*, 2nd ed. East Lansing: Freeman Press

Sherman, P. (1966). The texture of ice cream. 3: rheological properties of mix and melted ice cream. *Journal of Food Science*, 31, 707-716.

Takada, N.; Nelson, P. E. (1983). Pectin-protein interaction in tomato products. *Journal of Food Science*, 48, 5, 1408-1411.

Tanglertpaibul, T.; Rao, M. A. (1987). Flow properties of tomato concentrates: effect of serum viscosity and pulp content. *Journal of Food Science*, 52, 2, 318-321.

Tehrani, M. M.; Ghandi, A. (2007). Modification of Bostwick method to determine tomato concentrate consistency. *Journal of Food Engineering*, 79, 1483-1486.

Toro-Vazquez, J. F.; Morales-Rueda, J.; Malia, V. A.; Weiss, R. G. (2010). Relationship between molecular structure and termo-mechanical properties of candelilla waz and amides derived from (r)-12-hydroxystearic acid as gelators of safflower oil. *Food Biophysics*, 5, 193-202.

Tsai, S. C.; Zammouri, K. (1988). Role of interparticular Van der Waals force in rheology of concentrated suspensions. *Journal of Rheology*, 32, 7, 737-750.

Yoo, B., & Rao, M. A. (1996). Creep and dynamic rheological behavior of tomato concentrates: effect of concentration and finisher screen size. *Journal of Texture Studies*, 27, 451-459 .

Yilmaz, M. T.; Karaman, S.; Dogan, M.; Yetim, H.; Kayacier, A. (2012). Characterization of O/W model system meat emulsions using shear creep and creep recovery tests based on mechanical simulation models and their correlation with texture profile analysis (TPA) parameters. *Journal of Food Engineering*, 108, 2, 327-336.

Conclusões Gerais

Conclusões Gerais

A homogeneização a alta pressão (HAP) tem sido estudada por diversos autores como metodologia não térmica para a conservação de produtos de frutas. Trabalhos realizados com esses produtos e testes industriais indicam aumento de consistência devido a HAP. No entanto, poucos trabalhos da literatura estudam alterações físico-químicas em produtos de frutas devido à HAP, especialmente em relação às características reológicas. A avaliação de tais alterações é essencial não só para o entendimento e dimensionamento do processo, mas também permite a utilização do método para provocar alterações intencionais e desejáveis em alimentos, como aumento de consistência. O presente trabalho estudou o efeito da homogeneização a alta pressão (HAP) nas características reológicas de suco de tomate.

Na primeira parte do trabalho, avaliou-se as propriedades reológicas dependentes do tempo, em estado estacionário e de viscoelasticidade linear de sucos não processados. Essa abordagem permitiu, além do treinamento de técnicas e aprofundamento no assunto, determinar os modelos matemáticos mais adequados para utilização nas demais etapas do projeto.

As propriedades reológicas dependentes do tempo e em cisalhamento em estado estacionário de suco de tomate foram avaliadas no Capítulo 2. Como esperado, o suco de tomate se mostrou um fluido tixotrópico, com tensão de cisalhamento inicial (σ_0) e comportamento pseudoplástico ($n < 1$) durante o escoamento. Os modelos de Figoni–Shoemaker, Weltman, e Hahn–Ree–Eyring foram utilizados para descrever as propriedades dependentes do tempo, sendo seus parâmetros modelados como função da taxa de deformação. Os modelos de Herschel–Bulkley e Falguera–Ibarz foram utilizados para as propriedades em estado estacionário, sendo seus parâmetros modelados como função da temperatura. Todos os modelos avaliados descreveram bem os dados experimentais, se mostrando apropriados para utilização. Entretanto, destacou-se que o modelo de Hahn–Ree–Eyring é matematicamente semelhante ao de Figoni–

Shoemaker, optando-se então pela utilização apenas do último nas demais etapas do projeto.

As propriedades reológicas de viscoelasticidade linear de suco de tomate foram avaliadas no Capítulo 3, assim como a utilização da Regra de Cox-Merz. O suco de tomate apresentou comportamento de gel fraco, com módulo de armazenamento (G') sempre superior ao de dissipação (G''). Conforme esperado, a Regra de Cox-Merz não se ajustou aos dados experimentais. Entretanto, duas modificações lineares puderam ser utilizadas para correlacionar as propriedades reológicas em cisalhamento em estado estacionário e de viscoelasticidade linear do suco.

Procedeu-se então com a avaliação do efeito da homogeneização a alta pressão (HAP) nas características reológicas de suco de tomate.

Primeiramente, avaliou-se o efeito da HAP nas propriedades reológicas de um modelo de soro de suco de tomate (Capítulo 4). Sabendo-se que os sucos de frutas são formados por partículas suspensas (polpa) em um meio viscoso (soro), avaliou-se o efeito da HAP no meio dispersante com o objetivo de melhor entender o produto final. O modelo de soro foi formado por água, glicose e pectina, cujo grau de esterificação foi semelhante ao obtido em tomates processados pelo método de trituração a quente. O pH da solução modelo foi ajustado para representar o soro do suco de tomate. Conforme esperado, a solução modelo apresentou comportamento Newtoniano, semelhante a de soro de tomate e outros sucos de frutas. A HAP reduziu a viscosidade do modelo de soro, cujo efeito foi mais pronunciado quão maior foi a pressão de homogeneização (P_H) aplicada. A redução de viscosidade pôde ser modelada como função da P_H através de duas funções (exponencial e sigmoidal). Com base nos resultados obtidos, discutiu-se o comportamento esperado do suco de tomate.

Avaliou-se então o efeito da HAP nas propriedades reológicas dependentes do tempo e em cisalhamento em estado estacionário do suco de tomate, modelando os parâmetros que descrevem tais propriedades como função da P_H (Capítulo 5). A HAP reduziu o tamanho das partículas em suspensão e sua distribuição, promovendo maior interação entre partículas e entre partículas e o soro. Como consequência, resultou em aumento da consistência e tixotropía dos produtos. O efeito da P_H se mostrou assintótico, sendo discutidas as razões para tal. Os modelos de Figoni–Shoemaker e Weltman foram utilizados para descrever as propriedades dependentes do tempo, enquanto os modelos de Herschel–Bulkley e Falguera–Ibarz foram utilizados para as propriedades em estado estacionário. Os parâmetros obtidos foram então modelados como função da P_H, sendo que avaliação dos modelos finais apresentou grande descrição dos dados experimentais.

O efeito da HAP nas propriedades viscoelásticas do suco de tomate, assim como na aplicação da Regra de Cox-Merz, foram avaliados no Capítulo 6. A HAP aumentou os valores dos módulos de armazenamento (G') e dissipação (G''), promovendo aumento tanto do comportamento elástico quanto do viscoso do material. Modelou-se G' e G'' como função potência da frequência de oscilação (ω), cujos parâmetros foram avaliados em função da P_H. Mais uma vez o efeito da P_H se mostrou assintótico, sendo as modificações observadas atribuídas a ruptura das partículas em suspensão.

Por fim, avaliou-se o efeito da HAP nas propriedades de fluência e relaxação (*creep compliance*) do suco de tomate (Capítulo 7). O modelo mecânico de Burger, composto por molas Hookeanas e amortecedores Newtonianos, foi utilizado para descrever as propriedades reológicas do suco de tomate, sendo seus parâmetros avaliados em relação a P_H. Mais uma vez se observou aumento do comportamento elástico e viscoso do produto homogeneizados, sendo tais mudanças associadas à estrutura interna do material. Utilizando o modelo de Burger, identificou-se os componentes estruturais do suco de tomate associados aos comportamentos reológicos.

Dessa forma, o presente trabalho avaliou o efeito da HAP nas características reológicas do suco de tomate, descrevendo as mudanças estruturais associadas ao processo que afetam a reologia do produto. Conclui-se que a HAP é uma poderosa ferramenta para promoção de alterações físicas em produtos de frutas.

Sugestões para Trabalhos Futuros

Primeiramente sugere-se continuação do presente trabalho através da avaliação do efeito da homogeneização a alta pressão (HAP) na estabilidade física do suco de tomate (em especial separação de fases) e morfologia das partículas em suspensão.

Tendo em vista as possíveis diferenças de comportamento de produtos ou até mesmo tecidos diferentes, destaca-se a necessidade de expansão do presente trabalho para demais sucos e polpas de frutas.

Por fim, sugere-se maior análise e exploração em relação ao efeito de parâmetros do processo de HAP nas características de sucos e polpas de frutas, tais como o efeito da concentração de sólidos do produto, ciclos de homogeneização e diferentes geometrias de válvula para otimização dos resultados esperados.