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The influence of concentration and temperature on the viscoelastic properties of tomato pomace dispersions

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Abstract

The influence of concentration and temperature on the rheological properties of tomato pomace dispersions obtained by rehydration of lyophilized and grinded tomato pomace was investigated in this paper. Examined systems comprised of different lyophilized tomato pomace concentrations (18.1, 16.7, 14.3, 12.5, 11.1, 10.0, and 9.1%) heat treated at two different temperatures (60°C and 100°C) during 30 min.

According to microstructure analysis of the studied system, it could be simplified as the composite consisting of insoluble particles surrounded by the pectin network. The system behaves as viscoelastic solid (G’ > G’’ at all angular velocities), and therefore the static modulus of elasticity, the effective modulus and the damping coefficient were determined by application of modified fractional Kelvin-Voigt model. The influence of particle concentration on the rheological properties of tomato pomace system is dominant in comparison to the content and composition of pectin solubilised in the serum. Concentrated tomato pomace dispersions are much stiffer (G’ values an order of magnitude higher) than the composite systems. Heat treatment at higher temperature (100°C) decreases the stiffness of the system by breaking of non-covalent bonds between dispersed tomato particles and surrounding pectin network. Storage modulus as a function of the tomato pomace lyophilizate concentration was considered within three regimes (regime 1 – concentration <11.1%; regime 2 – concentration 11.1%–16.7%; regime 3 – concentration >16.7%) that could be used as the base for formulation of tomato pomace-based products with different desirable consistencies, such as sauce, ketchup and marmalade.

Keywords: *rheology, mathematical modeling, microstructure, tomato pomace, pectin*

1. Introduction

Tomato is one of the worldwide cultivated vegetable crops, consumed both as fresh fruit and after processing into various products such as tomato juice, tomato concentrate, ketchup, sauce, etc. During the processing of tomato, approximately 4% of total processed tomato is discarded as waste, which consists mostly of skin, seeds, and vascular tissue (Del Valle, Cámara, & Torija, 2003; Capanoglu, Beekwilder, Boyacioglu, Hall, & De Vos, 2008; Ruiz Celma, Cuadros, & López-Rodríguez, 2009; Lenucci, Durante, Anna, Dalessandro, & Piro, 2013). The attempts of resolving the problem of waste streams include their use as natural colorants (Laufenberg Kunz, & Nystroem, 2003), thickeners in ketchup production (Farahnaky, Abbasi, Jamalian, & Mesbahi, 2008), raw material for ketchup production (Torbica et al., 2016), lycopene extraction by supercritical CO_2 (Saldaña, Temelli, Guigard, Tomberli, & Gray, 2010), successive extraction of carotenoids and phenolic compounds by hexane and ethanol (Belović et al., 2016), bioethanol production (Lenucci et al., 2013), addition to meat and cereal products (Calvo, García, & Selgas, 2008; Luisa García, Calvo, & Selgas, 2009; Altan, McCarthy, & Maskana, 2008), and use as feed ingredient (Knoblich, Anderson, & Latshaw, 2005).

Tomato waste material, called tomato pomace, consists mainly of fibres that make up to 50% of its dry weight (Del Valle–et al., 2006). The insoluble-soluble fibre ratio in tomato pomace is 10:1, which makes these fibres more similar to those originating from cereals than those from fruits and vegetables (García Herrera, Sánchez-Mata, & Cámara, 2010). Types of dietary fibre that can be found in every plant material are cellulose and pectic substances, as they represent the basic components of the cell wall. According to previous research conducted by Torbica et al. (2016), tomato pomace contains 13.88% cellulose and 4.81% total pectic substances per dry weight, with the following pectin fraction composition: 1.72%

pectin, 2.47% pectic acid and 0.62% protopectin per dry weight. Del Valle et al. (2006) obtained slightly higher content of total pectic substances (7.55% d.w.).

Rheological properties are of special importance for tomato-based products because they determine process parameters and consumers' acceptability of the final product (Torbica et al., 2016). The differences between the plant tissues comprising tomato juice and tomato pomace, reflected mainly in the different dietary fibre composition, represent the cause of various structural and rheological differences between the main products (juice, concentrate) and by-product (pomace) of tomato processing industry. Structure of tomato-based products is very complex, and could be represented as a suspension of particles in the colloidal serum (Moelants et al., 2014a). Suspended particles include aggregated or disintegrated cells and cell wall material like cellulose, lignin, hemicellulose and pectic substances insoluble in water, while colloidal serum is mostly composed of pectin and other tomato components soluble in water like sugars and organic acids (Tiziani & Vodovotz, 2005; Bayod, Månsson, Innings, Bergenståhl, & Tornberg, 2007; Moelants et al., 2014a). The rheological properties of tomato products are known to be determined by both the particle properties (dispersed phase) and the properties of the serum phase (continual phase) (Anthon, Diaz, & Barrett, 2008; Moelants et al., 2013b). The particle properties that influence the rheology of the plant suspensions include the concentration, size distribution, shape, deformability and interparticle forces (Bayod et al., 2007; Lopez-Sanchez et al., 2011). Previous researches showed that the increase of particle concentration led to yield stress increase and increase of viscoelastic properties, namely G' values (Yoo & Rao 1996; Den Ouden & Van Vliet 2002; Moelants et al. 2013a). The serum properties that mainly affect the rheology of tomato products are the amount and characteristics of solubilised pectin (Anthon et al., 2008; Moelants et al., 2013b).

Tomato juice could be processed in two different ways in order to influence the pectin composition of the final products. The first is "hot-break" process, characterised by rapid heating of the tomato juice up to 95°C, which leads to the inactivation of pectolytic enzymes (primarily polygalacturonase) in order to ensure the higher viscosity of the final product. During the “cold-break” process, the tomato juice is heated only to 60°C, giving the final product lower viscosity, more natural colour and fresher flavour (Anthon, Sekine, Watanabe, & Barrett, 2002; Goodman, Fawcett, & Barringer, 2002). Generally, tomato concentrates exhibit non-Newtonian behaviour, with pronounced yield stress, shear-thinning behaviour, and shear history dependence (Bayod & Tornberg, 2011). On the other hand, fresh tomato pomace is highly inhomogeneous, possessing relatively high viscosity and yield stress in comparison with commercial tomato products (Belović et al., 2015). However, after seed removal, the amount of gelling tissue in fresh tomato pomace was too low for obtaining the desirable consistency of ketchup (Torbica et al., 2016).

Previous researches of rheological and structural properties of tomato products have extensively investigated the influence of temperature (“hot-break” and “cold-break” process) (Fito, Clemente, & Sanz, 1983; Goodman et al., 2002), particle size (Yoo & Rao, 1996; Den Ouden & Van Vliet, 1997) and concentration (Yoo & Rao, 1996; Den Ouden & Van Vliet, 2002; Bayod & Tornberg, 2011; Moelants et al., 2014a) on the rheological properties of tomato concentrate. However, the rheological properties of tomato pomace in dependence of temperature and particle concentration have not been studied before.

Besides the studies conducted with tomato products obtained directly from fresh fruits, the utilization of lyophilized tomato products also presents an interesting and promis~~s~~ing approach that enables microbiological safety and significant extension of shelf life, along with ~~and~~ preservation of heat sensitive substances and substances prone to oxidation, such as vitamins and other bioactive compounds. In addition, products obtained by lyophilisation are characterised by porous structure, which makes them suitable for rehydration. Study conducted by Barbana & El-Omri (2012) was the first whose aim was to characterize the rheological properties of tomato concentrate reconstituted from lyophilized tomato juice. However, structural and rheological properties of reconstituted lyophilized tomato pomace have not yet been investigated. Therefore, the aim of this research was to investigate the influence of concentration and temperature on the rheological properties of tomato pomace dispersions obtained by rehydration of lyophilized tomato pomace.

2. Material and Methods

2.1. Sample preparation

Tomato pomace used in this study was obtained from the production of tomato juice from commercial tomatoes in industrial plant (Zdravo Organic, Selenča, Serbia). Tomato pomace was lyophilized in industrial scale freeze-drier. The process had four stages (freezing, sublimation, primary and secondary drying) with a total duration of 36 hours. Initial and final temperature of the material was -30°C and +37°C, respectively, while the pressure in the chamber varied from 5×10^{-2} to 7×10^{-3} mbar during lyophilisation. Lyophilized tomato pomace with the moisture content of 3% was ground in a coffee grinder (Gorenje, Velenje, Slovenia) in order to obtain powder with particle mean diameter = 132 μm, as determined by rotational sieving machine equipped with seven sieves (Bühler, Uzwil, Switzerland).

The grinded tomato pomace lyophilizate was rehydrated using different pomace:water ratios (from 1:4.5 to 1:10) and the resulting concentrations were 18.1, 16.7, 14.3, 12.5, 11.1, 10.0, and 9.1% (w/w). The ratios used in the experiment were chosen on the basis of dry matter content originating from tomato in tomato-based products, such as marmalade (the highest content), ketchup, and sauce (the lowest content). Rehydrated tomato pomace samples were heated at two different temperatures (60°C and 100°C) in closed tubes during 30 min to compare their influence without water evaporation. These two temperatures were chosen as the analogy with "cold-break" and "hot-break" production processes which are the most commonly used in the industrial plants for tomato processing. Samples obtained in this way were used further for mathematical modelling. For the rheological characterization of concentrated tomato pomace particles, samples with the highest concentration of tomato pomace (18.1%) were centrifuged (Eppendorf Centrifuge 5804 R, Hamburg, Germany) for 20 min at 3000 g in order to minimize the amount of water that needs to be removed. After the supernatant was decanted, the obtained precipitate was centrifuged again for 20 min at 8000 g to remove the residual water.

2.2. Chemical analyses

Total soluble solids (TSS) content was measured instrumentally in all reconstituted tomato pomace samples using table refractometer (ATR ST Plus, Schmidt + Haensch, Germany). pH value of samples before and after heat treatment was measured by a pH meter with a temperature probe (Denver Instrument, USA).

Pectin (soluble in water), pectic acids (soluble in ammonium oxalate solution), and protopectin (soluble in alkaline solutions) content were determined spectrophotometrically (UV/Vis spectrophotometer, Cintra 303, GBC Scientific Equipment, Dandenong, Victoria, Australia) by carbazole method (Official Gazette of SFRJ, 29, ~~Regulation of methods of sampling, physical and chemical analysis for quality control of fruit and vegetable products,~~ 1983) in the samples with 16.7% of tomato pomace lyophilizate since according to our previous research (Torbica et al., 2016) this concentration was the most suitable for the chosen method due to its supposed pectin content (about 0.5%). Total pectic substances were firstly precipitated with ethanol in two steps (with 95% and 63% ethanol) using centrifugation

(3000 g). After that, the precipitate of total pectic substances was dissolved in water to separate pectin. Pectic substances insoluble in water were removed by centrifugation (3000 g), and the obtained precipitate was dissolved in ammonium oxalate solution to separate pectic acid. The centrifugation (3000 g) was repeated in order to remove the pectic substances insoluble in ammonium oxalate solution. In the final step, the precipitate obtained after the second centrifugation was dissolved in NaOH solution to separate protopectin, and remained insoluble material was separated by filtration. Extracts of three pectin fractions (1 mL) were mixed with 0.1% solution of carbazole in purified ethanol (0.5 mL) and concentrated sulphuric acid (6 mL) in test tubes. After heating of the test tubes at 85°C for 5 minutes in water bath, the absorbance was read at wavelength of 525 nm. Galacturonic acid was used to construct the standard curve, and content of pectic substances in individual fractions was expressed as % of galacturonic acid (GA) in fresh sample. Experiments were performed in triplicates.

2.3. Water retention capacity (WRC)

Water retention capacity (WRC) of tomato pomace lyophilizate after treatment at different temperatures was determined using the method described in Robertson et al. (2000) with some modifications. Two grams of tomato pomace lyophilizate were hydrated in 30 mL of distilled water at room temperature, in a closed centrifuge tube. After equilibration (18 h), the samples were heat treated at 60°C and 100°C during 30 min, and centrifuged after cooling (3,000 *g*; 20 min). The non-heated samples were used as a control. The supernatant was decanted and the sample was weighed. Determination of water retention capacity was performed in triplicate, and it was calculated using the following equation:

WRC (g/g) = (Wet residue weight – Powder weight)/ Powder weight (2)

2.4. Rheological measurements

Dynamic oscillatory measurements of reconstituted tomato pomace were performed using a Haake MARS rheometer (Thermo Scientific, Karlsruhe, Germany) at 25 °C equipped with a parallel plate geometry PP35 (35 mm diameter and 1 mm gap). Mechanical spectra (frequency sweeps) were recorded over the range 0.1-10 Hz at 1 Pa stress (which was within the linear viscoelastic region as determined by amplitude sweep). Solvent traps were used in all the tests in order to prevent sample drying. All rheological measurements were performed in triplicates.

2.5. Optical microscopy

Tomato pomace samples were observed with a Nikon SMZ18 (Tokyo, Japan) stereomicroscope, using incident light and images were acquired using Nikon DIGITAL SIGHT DS-Fi1c digital camera at x270 magnification.

2.6. Data analysis

The images were analysed using Image Pro Plus 6 software. Tomato pomace aggregate size distribution was determined by automatic counting and measurement of all objects darker than background and equal or larger than single tomato pomace particles.

Numerical data were analysed using Matlab R2011b. The model values were fitted with the experimental data by minimizing the squared magnitude of the residuals of the $\ln(G'(\omega))$

and $\ln(G''(\omega))$. The optimal model parameters obtained by this fitting procedure enabled the best comparison with the experimental data. The goodness of a fit is quantified by: (1) number of degrees of freedom of a fit, (2) standard deviation, and (3) relative error.

3. Model description

Based on our experimental observations, examined systems behave as viscoelastic solid. Rheological response of the systems points to anomalous nature of energy dissipation. For this purpose, we used the fractional derivatives (Podlubny, 1999). Modified fractional Kelvin-Voigt model equation (Djordević, Jarić, Fabry, Fredberg, & Stamenović, 2003) is applied:

$$\sigma_T(t) = G_s\, \gamma(t) + \eta\, {}_0D_t^{\alpha}(\gamma(t)) \tag{3}$$

where $\gamma(t)$ is the shear strain component, G_s is the static modulus of elasticity, and η is the effective modulus, ${}_0D_t^{\alpha}(f(t)) = \dfrac{d^{\alpha}}{dt^{\alpha}}(f(t))$ is the fractional derivative of some function $f(t)$ while α is the order of the fractional derivatives (the damping coefficient). Caputo's definition of the fractional derivative of a function $f(t)$, was used and it is given as follows (Podlubny, 1999):

$$ {}_0D_t^{\alpha}(f(t)) = \frac{1}{\Gamma(1-\alpha)} \frac{d}{dt} \int_0^t \frac{f(t')}{(t-t')^{\alpha}} dt' \tag{4}$$

where *t* is an independent variable (time) and $\Gamma(1-\alpha)$ is the gamma function. If parameter α is $\alpha = 0$, we obtain ${}_0D_t^{0}(f(t)) = f(t)$. When $\alpha = 1$, the corresponding gamma function

$\Gamma(1-\alpha)\rightarrow\infty$. For this case, the fractional derivative is not defined. However, it can be shown, that in the limit when $\alpha\rightarrow 1$, follows ${}_0D_t^{\alpha}(f(t))\rightarrow \dot{f}(t)$., where the dot denotes the first time derivative. Thus, when $0\leq\alpha\prec 1$, the equation 1 describes the dumped dissipative phenomena. Smaller value of the parameter α points to more pronounced damping effects.

The first term of the right hand side of eq. 3 represents the reversible (elastic) part and the second term represents the irreversible (viscous) part of the component of total stress. If the parameter α is $\alpha=0$, we obtain ${}_0D_t^{0}(\gamma(t))=\gamma(t)$. For such case the second term of eq. 3 additionally contributes to elastic Hookean behaviour. When $\alpha\rightarrow 1$, we obtain ${}_0D_t^{\alpha}(\gamma(t))\rightarrow\dot{\gamma}(t)$. For such case, the second term represents the purely viscous contribution to the total stress.

We transform eq. 3 from the time domain into the frequency domain using the Fourier integral transform. Transforming equation is expressed in the form $F[\sigma_T(t)]=G*F[\gamma(t)]$, where $F[\circ]$ is the Fourier operator and $G*$ is the complex dynamic modulus equal to $G*=G'+iG''$, while G' is the storage modulus and G'' is the loss modulus and $i=\sqrt{-1}$ is the imaginary unit. Fourier transform of the fractional derivative of the component of shear strain $\gamma(t)$ is expressed as $F\left[{}_0D_t^{\alpha}(\gamma(t))\right]=(i\omega)^{\alpha}F[\gamma(t)]$, where ω is the angular frequency (Djordjević et al, 2003). The storage and loss moduli are expressed as:

$$G'(\omega)=G_s+\eta\omega^{\alpha}\cos\left(\frac{\pi\alpha}{2}\right)$$

$$G''(\omega)=\eta\omega^{\alpha}\sin\left(\frac{\pi\alpha}{2}\right) \tag{5}$$

where the storage modulus $G'(\omega)$ quantify the elastic behaviour and the loss modulus $G''(\omega)$ quantify the viscous behaviour of the systems. Model parameters: G_s the static modulus of elasticity, η the effective modulus and α the damping coefficient (the order of fractional derivatives) should be determined by comparing experimental data sets $G'(\omega)$ vs. ω and $G''(\omega)$ vs. ω for various systems with the model predictions.

4. Results and Discussion

Examined systems comprised of different tomato pomace concentrations (18.1, 16.7, 14.3, 12.5, 11.1, 10.0, and 9.1%) heat treated at two different temperatures (60°C and 100°C) during 30 min. The systems could be described as the composite, consisting of coarse dispersion of plant material from tomato pomace (mostly very small cells from outer part of pericarp, as well as hard cells of seed coat, testa and insoluble cell wall components) in colloidal serum consisting of water-soluble cell wall material and other soluble solids from cell interior and intercellular spaces, such as sugars (sucrose and hexoses), acids (citrate and malate) and other minor components (amino acids, soluble pectins, ascorbic acid, phenolic compounds, tocopherols, carotenoids, and minerals) in the tomato fruit pulp.

4.1. Chemical analyses

Total soluble solids (TSS) content is important for tomato fruits, since it reflects dry matter content and it is inversely proportionate to fruit size (Beckles, 2012). In this study, TSS content was related to the tomato pomace lyophilizate concentrations to determine the amount of soluble compounds extracted from tomato pomace at different temperatures. It increased simultaneously with the increase of tomato pomace concentration, showing similar trend for both temperatures used in the study (from 6.73 to 14.02% for samples heated at 60°C and from 6.58 to 14.21% for samples heated at 100°C). This implies that tomato cells were completely disintegrated during grinding and, after the addition of water, soluble cell content (sugars, acids, salts) was dissolved, giving similar TSS values regardless of the heat treatment applied. pH value did not change~~d~~ after 30 minutes of both heat treatments, ranging from 4.32 to 4.38 in all samples.

The content of individual pectic substances was determined in the samples with tomato pomace concentration of 16.7% (Figure 1). It is clearly seen that the higher amount of pectic substances was released from the tomato pomace particles after heat treatment at 100°C. Possible explanation of observed phenomenon could be that large molecules such as polysaccharides, in contrast to small molecules which diffuse rapidly to serum even at room temperature, have to be solvated before diffusion and both processes are accelerated at higher temperatures. Higher share of pectic acid after heating at 100°C might be explained by the increase of the more water-soluble pectins, which is the consequence of thermal processing (Camara Hurtado, Greve, & Labavitch, 2002).

4.2. Water retention capacity (WRC)

Water retention capacity (WRC) values were 3.58, 3.28, and 3.10 for the non heated sample and the samples heated at 60°C and 100°C, respectively. Since these differences were not prominent, it could be concluded that heat treatment did not change the ability of dietary fibre present in the samples to bind water. Therefore any differences in the rheological behaviour between these samples could not be explained by the water bound to tomato pomace particles.

4.3. System microstructure

Microstructure of systems consisting of 9.1% and 16.7% of tomato pomace lyophilizate heat treated at 60^{o}C as seen by optical microscopy is presented in Figure 2. Generally, tomato pomace suspensions are composed of skins, seeds, and vascular tissues, representing approximately 4% of the whole fruit weight (Lenucci et al., 2013) and are mainly comprised of parenchyma cells from the pericarp, which are large (with an average diameter of approximately 250 μm), thin-walled, nearly spherical and highly deformable (Lopez-Sanchez, Chapara, Schumm, & Farr, 2012). According to that, the particles in tomato tissue suspensions are built up of mechanically destructed parenchyma tissue composed of different size cells and their parts. It is well known that thermal treatments cause an initial loss of cell firmness due to the disruption of the cell membrane through enzymatic degradation, and cell turgor is lost resulting in softer tomato particles. Optical microscopy showed that tissue-based particles in tomato pomace have different properties, such as size, type, surface, and shape. Specifically, pericarp cell fragments and clusters with rough or smooth particle surface can be visualized by micrographs (Figure 2). However, particles with the largest size arise from dominant carotenoids (orange spherical structures), seed parts, especially testa, vascular bundles or their largest parts, vessels, and outer pericarp tissue part, instead of parenchyma cell parts.

Therefore, according to micrographs, the studied system could be simplified as the composite consisting of insoluble particles surrounded by the pectin network. Different concentrations of tomato pomace lyophilizate treated at the same temperature were examined to elucidate whether concentrating affect the aggregation of smaller particles, since it could be seen that particles form clusters. The distribution of the particle cluster sizes for two tomato pomace lyophilizate concentrations was calculated (Figure 3). Particles form smaller size clusters up to 6.5 μm while 50-60% cluster population has the diameter of ~2.2 μm. The cluster size distribution is approximately the same for both tomato pomace lyophilizate concentrations. This implies that aggregation of particles does not influence the rheological properties of differently concentrated tomato pomace dispersions.

4.4. Rheological properties

The rheological behaviour of concentrated tomato pomace particles after heat treatment at 60°C and 100°C will be discussed separately in order to estimate their influence on the rheological behaviour of examined composite systems. This was encouraged by the facts that rheological properties of concentrated tomato products, as well as other plant tissue-based food suspensions, largely depend on the particle properties (Valencia et al., 2003; Bayod et al., 2007; Moelants et al., 2013b; Moelants et al., 2014a), and that tomato pomace contains higher amounts of fibre than tomato juice/concentrate (Torbica et al., 2016). The concentrated tomato pomace particles behave as viscoelastic solid ($G' > G''$). Their rheological behaviour could be described by modified fractional Kelvin-Voigt equation (eq. 2). Storage and loss moduli are compared with the values obtained by the mathematical model predictions. The model values were fitted with the experimental data by minimizing the squared magnitude of the residuals of the $\ln(G'(\omega))$ and $\ln(G''(\omega))$, respectively. The optimal model parameters obtained by this fitting procedure that enable the best comparison with the experimental data are listed in Table 1. The corresponding number of degrees of freedom of a fit for both moduli were 10. The goodness of the fit expressed as the standard deviations was: (1) 0.022 for G' and 0.031 for G'' at 60°C and (2) 0.013 for G' and 0.034 for G'' at 100°C. The model predictions correlated well with the experimental data for all examined systems, with relative error of 8±2% for storage modulus and 10±3% for loss modulus for both temperatures.

Experimental data sets of the storage and loss moduli for the systems made by concentrated tomato particles after heat treatment at 60^{o}C and 100^{o}C are shown in Figure 4.

Tomato pomace releases pectin during heat treatment and this process is pronounced at higher temperature, as could be seen from the Figure 1. The particles become softer after heat treatment at higher temperature, probably due to partial loss of pectin content and increase in share of water-soluble pectin fractions in the particles. It is quantified by the lower values of the model parameters: the static modulus of elasticity Gs and the effective modulus η. Static modulus represents the measure of the storage elastic energy while the effective modulus represents a measure of the dissipative effects during particle-particle interactions. The damping coefficient which quantified the dissipative nature of the system structural changes under strain conditions is approximately the same for both temperatures.

Finally, it is interesting to consider the rheological behaviour of the composite systems with different tomato pomace lyophilizate concentrations heat treated at 60°C or 100°C in the context of the system reinforcement trend. Storage modulus G' for the composite systems could be used as a measure of the system stiffness, so the storage modulus values for the systems heat treated at 60°C in comparison to the ones heat treated at 100°C for the same tomato pomace concentration is presented in Figure 5. The result points to the system softening during heat treatment at 100°C. The softening is presumed to be primarily caused by thermally induced breaking of the non-covalent bonds between dispersed tomato particle clusters and surrounding pectin network. Concentrated tomato pomace particles are much stiffer than the composite systems even after heat treatment at 100°C. It is in accordance with the fact that values of the storage modulus for the composite systems are the order of magnitude lower than the ones for the concentrated particle systems. Consequently, the particle softening obtained after heat treatment at 100°C could not influence the composite system softening significantly.

Storage modulus *G'* as a function of the tomato pomace lyophilizate concentration could be considered within three regimes. Regime 1 corresponds to low tomato pomace concentration up to 11.1%. Regime 2 corresponds to the tomato pomace concentration in the range from 11.1% to 16.7%. Regime 3 corresponds to tomato pomace concentration higher than 16.7%. Storage modulus is approximately constant in regime 1 for the systems heat treated at 100°C. This trend is influenced by two opposite tendencies: 1) increase of the particle concentration leads to the system stiffening and 2) breaking of the non-covalent bonds between dispersed tomato particles and surrounding pectin network leads to the system softening. Constant *G'* values at low tomato pomace concentrations were not observed for the systems heat treated at 60°C. Breaking of the non-covalent bonds between dispersed tomato particles and surrounding pectin network is not observed after the heat treatment of the system at 60°C. Tomato pomace concentration increase induces permanent increase of the storage modulus and the systems reinforcement. Generally, increase of storage modulus $G^{'}$ values with the increase of particle, pulp or TSS content was previously determined in several plant-based food suspensions (Moelants et al., 2014b).

In regime 2, storage modulus increase with the tomato pomace concentration for the systems heat treated at 60°C and 100°C. In both cases, increase of the tomato pomace concentration leads to the system reinforcement. In regime 3, storage modulus is approximately constant for the systems heat treated at 60°C. It is most likely caused by the system saturation by the particles. This trend is not observed (for the same tomato pomace concentration) for the systems heat treated at 100°C due to thermally induced particles-network bonds breaking.

These three regimes of tomato pomace concentrations could be compared by total soluble solids content with three model food materials (tomato sauce, tomato ketchup and tomato purée/marmalade). Regime 1 (tomato pomace concentration <11.1%, total soluble solids content <8.5%) would correspond to tomato sauces, because their total soluble solids content originating from tomato is in the range of 7.5-9.5%, according to our unpublished results and USDA National Nutrient Database for Standard Reference for tomato products, canned, sauce, Spanish style (https://ndb.nal.usda.gov/ndb/foods), because this tomato sauce contains 7.24% of total carbohydrates, which correspond approximately to total soluble solids content. Regime 2 (tomato pomace concentration 11.1-16.7%, total soluble solids content 8.5-13.0%) would correspond to tomato ketchups, because their total soluble solids content originating from tomato should be higher than 8%, according to Serbian Regulation of quality of fruit, vegetable, mushroom and pectin products (Official Gazette of SFRJ, 1, 1979). Regime 3 (tomato pomace concentration >16.7%, total soluble solids content >13.0%) would correspond to tomato purée (according to FAO (2009), tomato purée has a total soluble solids content of 15-20%) or single tomato concentrate (according to Official Gazette of SFRJ, 1 (1979), single tomato concentrate has a total soluble solids content of 14-16%). Analogy with the marmalades could be drawn since they are usually produced from fruit purées or concentrates.

However, these definitions vary from country to country; for example, U. S. Federal Regulation for Tomato Concentrates (http://www.ecfr.gov/cgi-bin/ECFR?page=browse) defines tomato purée or tomato pulp as a food that contains not less than 8.0% but less than 24.0% tomato soluble solids. This range encompasses both Regime 2 and Regime 3. It should be pointed out that G’ values of the tomato pomace products would vary from the values obtained for the model systems examined in this paper due to addition of water soluble substances, such as hydrocolloids, sugar, syrup, acid, salt etc. Therefore further research should include the examination of final products obtained from lyophilized tomato pomace.

The increase of storage and loss moduli with angular velocity was observed for all examined samples. This phenomenon is connected with reversible and irreversible structural changes under oscillator strain conditions. The optimal model parameters obtained by this fitting procedure that enable the best comparison with the experimental data are shown in Table 2.

The system reinforcement is quantified by the increase of the model parameters, G_s the static modulus of elasticity, and η the effective modulus, with the tomato pomace concentration. Static modulus represents the measure of the storage elastic energy while the effective modulus represents a measure of the dissipative effects during chain-chain and chain-particle non covalent bonds breaking under strain. The system reinforcement could be induced by: 1) tomato pomace concentration increase, 2) particle clusters non covalent bonding to the surrounding pectin network in the serum. For the same tomato pomace concentration, the systems heat treated at 60^{o}C are stiffer (higher values of the model parameters G_s and η) primarily due to particle clusters non covalent bonding to the surrounding pectin network.

The damping coefficient α is higher for the systems with higher tomato pomace concentrations for both temperatures. It could be connected with the particle-chain interactions. Higher particle concentrations induce the resistance effects to the pectin chain conformational changes. These resistance effects induce damping of the chains structural ordering under oscillator strain conditions.

Finally, to visually present the observed increase of storage and loss moduli with angular velocity, one representative experimental data set and model prediction, obtained for the system with tomato pomace concentration of 12.5% heat treated at 60^{o}C is shown in Figure 6. The model values were fitted with the experimental data by minimizing the squared magnitude of the residuals of the $\ln(G'(\omega))$ and $\ln(G''(\omega))$, respectively. The optimal model parameters obtained by this fitting procedure that enable the best comparison with the experimental data are listed in Table 2. . The corresponding number of degrees of freedom of a fit for both moduli were 10. The goodness of the fit expressed as the standard deviations were: 0.018 for G' and 0.023 for G''. The model predictions correlated well with the experimental data for all examined systems, with relative errors of: 6±2% for storage modulus and 8±2% for loss modulus.

5. Conclusions

Composite system examined in this study behaves as viscoelastic solid, and the influence of particle concentration on its rheological properties is dominant in comparison to the content and composition of pectin solubilised in serum. This implies that the properties of tomato pomace lyophilizate as a potential raw material could be modified by application of different milling procedures with the aim to obtain different particle sizes and milling fractions, which is also encouraged by the similarity of insoluble-soluble fibre ratio between tomato pomace and cereals. The regimes of system reinforcement by the increase of tomato pomace lyophilizate concentrations could be used as the base for formulation of tomato pomace-based products with different desirable consistencies, such as sauce, ketchup and marmalade. The previous conclusions indicate the possibility of creating the tomato pomace-based product with the increased content of natural fibres without addition of any hydrocolloids. This study also points out the importance of temperature regime used during tomato pomace processing; however, further experiments should be conducted in order to precisely determine the changes that tomato pomace pectin undergoes during processing at different temperatures.

Acknowledgements

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References

1. Altan, A., McCarthy, K. L., & Maskana, M. (2008). Evaluation of snack foods from barley–tomato pomace blends by extrusion processing. *Journal of Food Engineering, 84,* 231–242.
2. Anthon, G. E., Diaz, J. V., & Barrett, D. M. (2008). Changes in pectins and product consistency during the concentration of tomato juice to paste. *Journal of Agricultural and Food Chemistry, 56,* 7100-7105.
3. Anthon, G. E., Sekine, Y., Watanabe, N., & Barrett, D. M. (2002). Thermal inactivation of pectin methylesterase, polygalacturonase, and peroxidase in tomato juice. *Journal of Agricultural and Food Chemistry, 50,* 6153-6159.
4. Barbana, C. & El-Omri A. F. (2012). Viscometric Behavior of Reconstituted Tomato Concentrate. *Food Bioprocess Technology, 5,* 209–215.
5. Bayod, E. & Tornberg, E. (2011). Microstructure of highly concentrated tomato suspensions on homogenisation and subsequent shearing, *Food Research International, 44,* 755-764.
6. 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.
7. Beckles, D. M. (2012). Factors affecting the postharvest soluble solids and sugar content of tomato (*Solanum lycopersicum* L.) fruit. Postharvest Biology and Technology, 63(1), 129-140.

8. Belović, M. M., Gironés-Vilaplana, A., Moreno, D. A., Milovanović, I. Lj., Novaković, A. R., Karaman, M. A., & Ilić N. M. (2016). Tomato (*Solanum lycopersicum* L.) processing main product (juice) and by-product (pomace) bioactivity potential measured as antioxidant activity and angiotensin-converting enzyme inhibition. *Journal of Food Processing and Preservation, in press.* DOI: 10.1111/jfpp.12707
9. Belović, M., Torbica, A., Mastilović, J., Dapčević Hadnađev, T., Jambrec, D., Pestorić, M., & Kevrešan, Ž. (2015). Change of physicochemical properties during tomato processing into juice and high fibre ketchup made from tomato pomace. EuroFoodChem XVIII, 13-16 October 2015, Madrid, Spain, Poster Book, CHC-P-127.
10. Calvo, M. M., García, M. L., & Selgas, M. D. (2008). Dry fermented sausages enriched with lycopene from tomato peel. *Meat Science, 80,* 167–172.
11. Cámara Hurtado, M., Greve, L. C., & Labavitch, J. M. (2002). Changes in cell wall pectins accompanying tomato (*Lycopersicon esculentum* Mill.) paste manufacture. *Journal of Agricultural and Food Chemistry, 50,* 273-278.
12. Capanoglu, E., Beekwilder, J., Boyacioglu, D., Hall, R., & De Vos, R. (2008). Changes in antioxidant and metabolite profiles during production of tomato paste. *Journal of Agricultural and Food Chemistry, 56,* 964-973.
13. Celma, A. R., Cuadros, F., & López-Rodríguez, F. (2009). Characterisation of industrial tomato by-products from infrared drying process. *Food and Bioproducts Processing*, *87*, 282-291.
14. Del Valle, M., Cámara, M., & Torija, M. E. (2006). Chemical characterization of tomato pomace. *Journal of the Science of Food and Agriculture, 86,* 1232-1236.

15. Den Ouden, F.W.C. & Van Vliet, T. (1997). Particle Size Distribution in Tomato Concentrate and Effects on Rheological Properties. *Journal of Food Science, 62,* 565-567.

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

17. Djordjević, V. D., Jarić, J., Fabry, B., Fredberg, J. J., & Stamenović, D. (2003). Fractional derivatives embody essential features of cell rheological behavior. *Annals of Biomedical Engineering, 31,* 692-699.

18. FAO (2009). Agribusiness Handbook, Fruit and Vegetable Processing. Rome, Italy. http://www.fao.org/fileadmin/user_upload/tci/docs/AH6-Fruit%20and%20Veg%20Processing.pdf

19. Farahnaky, A., Abbasi, A., Jamalian, J., & Mesbahi, G. (2008). The use of tomato pulp powder as a thickening agent in the formulation of tomato ketchup. *Journal of Texture Studies, 39,* 169–182.

20. Fito, P. J., Clemente, G., Sanz F. J. (1983). Rheological Behaviour of Tomato Concentrate (Hot Break and Cold Break). Journal of Food Engineering, 2, 51-62.

21. García Herrera, P., Sánchez-Mata, M. C., & Cámara, M. (2010). Nutritional characterization of tomato fiber as a useful ingredient for food industry. *Innovative Food Science and Emerging Technologies, 11,* 707–711.

22. Goodman, C. L., Fawcett, S., & Barringer, S. A. (2002). Flavor, Viscosity, and Color Analyses of Hot and Cold Break Tomato Juices. *Journal of Food Science, 67,* 404-408.

23. Knoblich, M., Anderson, B., & Latshaw, D. (2005). Analyses of tomato peel and seed byproducts and their use as a source of carotenoids. *Journal of the Science of Food and Agriculture, 85,* 1166-1170.

24. Laufenberg, G., Kunz, B., & Nystroem, M. (2003). Transformation of vegetable waste into value added products: (A) the upgrading concept; (B) practical implementations. *Bioresource Technology, 87,* 167–198.

25. Lenucci, M. S., Durante, M., Anna, M., Dalessandro, G., & Piro, G. (2013). Possible Use of the Carbohydrates Present in Tomato Pomace and in Byproducts of the Supercritical Carbon Dioxide Lycopene Extraction Process as Biomass for Bioethanol Production. *Journal of Agricultural and Food Chemistry, 61,* 3683−3692.

26. Lopez-Sanchez, P., Chapara, V., Schumm, S., & Farr, R. (2012). Shear elastic deformation and particle packing in plant cell dispersions. *Food Biophysics, 7,* 1-14.

27. Lopez-Sanchez, P., Nijsse, J., Blonk, H. C., Bialek, L., Schumm, S., & Langton, M. (2011). 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.

28. Luisa García, M., Calvo, M., Selgas, M. D. (2009). Beef hamburgers enriched in lycopene using dry tomato peel as an ingredient. *Meat Science, 83,* 45–49.

29. Moelants, K. R. N., Cardinaels R., Jolie R. P., Verrijssen T. A. J., Buggenhout, S., Loey A. M., Moldenaers P., & Hendrickx, M. E. (2014a). Rheology of Concentrated Tomato-Derived Suspensions: Effects of Particle Characteristics. *Food and Bioprocess Technology, 7,* 248–264.

30. Moelants, K. R., Cardinaels, R., Jolie, R. P., Verrijssen, T. A., Van Buggenhout, S., Zumalacarregui, L. M., Van Loey, A. M., Moldenaers, P. & Hendrickx, M. E. (2013a). Relation between particle properties and rheological characteristics of carrot-derived suspensions. *Food and Bioprocess Technology, 6,* 1127-1143.

31. Moelants, K. R., Jolie, R. P., Palmers, S. K., Cardinaels, R., Christiaens, S., Van Buggenhout, S., Van Loey, A. M., Moldenaers, P. & Hendrickx, M. E. (2013b). The

effects of process-induced pectin changes on the viscosity of carrot and tomato sera. *Food and Bioprocess Technology, 6,* 2870-2883.

32. Moelants, K., Cardinaels, R., Buggenhout, S., Loey, A. M., Moldenaers, P., & Hendrickx, M. E. (2014b). A Review on the Relationships between Processing, Food Structure, and Rheological Properties of Plant-Tissue-Based Food Suspensions. *Comprehensive Reviews in Food Science and Food Safety, 13,* 241-260.
33. Official Gazette of SFRJ, 1 (1979). Regulation of quality of fruit, vegetable, mushroom and pectin products (in Serbian).
34. Official Gazette of SFRJ, 29 (1983). Regulation of methods of sampling, physical and chemical analysis for quality control of fruit and vegetable products~~ (1983). *Official Gazette of SFRJ,* 29~~. (in Serbian)
35. Podlubny I. (1999). Fractional Differential Equations. *Mathematics in Science and Engineering,* vol. 198, Academic Press, Inc., San Diego, CA, USA.
36. Robertson, J. A., de Monredon, F. D., Dysseler, P., Guillon, F., Amado, R., & Thibault, J. F. (2000). Hydration properties of dietary fibre and resistant starch: a European collaborative study. *LWT-Food Science and Technology, 33,* 72-79.
37. Saldaña, M.D.A., Temelli, F., Guigard, S.E., Tomberli, B., & Gray C.G. (2010). Apparent solubility of lycopene and β-carotene in supercritical CO_2, CO_2 + ethanol and CO_2 + canola oil using dynamic extraction of tomatoes. *Journal of Food Engineering, 99,* 1-8.
38. Tiziani, S. & Vodovotz, Y. (2005). Rheological effects of soy protein addition to tomato juice. *Food Hydrocolloids, 19,* 45–52.
39. Torbica, A., Belović, M., Mastilović, J., Kevrešan, Ž. Pestorić, M., Škrobot, D., & Dapčević Hadnađev, T. (2016). Nutritional, rheological, and sensory evaluation of

tomato ketchup with increased content of natural fibres made from fresh tomato pomace. *Food and Bioproducts Processing, 98,* 299-309.

40. U. S. Government Publishing Office, Electronic Code of Federal Regulations, Title 21, Chapter I, Subchapter B, Part 155 (Canned vegetables), Subpart B, §155.191 (Tomato concentrates), http://www.ecfr.gov/cgi-bin/ECFR?page=browse, accessed June 10, 2016
41. USDA National Nutrient Database for Standard Reference, Tomato products, canned, sauce, Spanish style, https://ndb.nal.usda.gov/ndb/foods, accessed June 10, 2016
42. Valencia, C., Sanchez, M. C., Ciruelos, A., Latorre, A., Madiedo, J. M., & Gallegos, C. (2003). Non-linear viscoelasticity modeling of tomato paste products. *Food Research International, 36,* 911-919.
43. 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.

Table 1. Model parameters for the concentrated tomato particles

Systems	**G_s (Pa)**	**η (Pas$^{\alpha}$)**	**α (−)**
60°C	$(1.00\pm0.01)x10^{5}$	$(0.90\pm0.01)x10^{5}$	0.21 ± 0.01
100°C	$(0.80\pm0.01)x10^{5}$	$(0.60\pm0.01)x10^{4}$	0.22 ± 0.01

Table 2. Model parameters of systems with different tomato pomace lyophilizate concentrations heat treated at two different temperatures.

Systems heated at 60ºC	**G_s (Pa)**	**η (Pas$^{\alpha}$)**	**α (−)**
18.1%	$(0.55\pm0.01)x10^4$	$(0.55\pm0.01)x10^4$	0.25 ± 0.01
16.7%	$(0.55\pm0.01)x10^4$	$(0.55\pm0.01)x10^4$	0.25 ± 0.01
14.3%	$(0.30\pm0.01)x10^4$	$(0.47\pm0.01)x10^4$	0.17 ± 0.01
12.5%	$(0.18\pm0.01)x10^4$	$(0.42\pm0.01)x10^4$	0.17 ± 0.01
11.1%	$(0.17\pm0.01)x10^4$	$(0.27\pm0.01)x10^4$	0.18 ± 0.01
10.0%	$(0.10\pm0.01)x10^4$	$(0.16\pm0.01)x10^4$	0.17 ± 0.01
9.1%	$(0.05\pm0.01)x10^4$	$(0.06\pm0.01)x10^4$	0.18 ± 0.01
Systems heated at 100ºC	**G_s (Pa)**	**η (Pas$^{\alpha}$)**	**α (−)**
18.1%	$(0.50\pm0.01)x10^4$	$(0.35\pm0.01)x10^4$	0.25 ± 0.01
16.7%	$(0.40\pm0.01)x10^4$	$(0.25\pm0.01)x10^4$	0.25 ± 0.01
14.3%	$(0.25\pm0.01)x10^4$	$(0.25\pm0.01)x10^4$	0.25 ± 0.01
12.5%	$(0.13\pm0.01)x10^4$	$(0.10\pm0.01)x10^4$	0.25 ± 0.01
11.1%	$(0.04\pm0.01)x10^4$	$(0.04\pm0.01)x10^4$	0.20 ± 0.01
10.0%	$(0.04\pm0.01)x10^4$	$(0.04\pm0.01)x10^4$	0.20 ± 0.01
9.1%	$(0.04\pm0.01)x10^4$	$(0.04\pm0.01)x10^4$	0.20 ± 0.01

Figure captions:

Figure 1: Content of individual pectic substances in samples with tomato pomace lyophilizate concentration of 16.7%.

Figure 2. The systems consisting of a) 9.1% and b) 16.7% tomato pomace lyophilizate, magnification x270.

Figure 3. Particle clusters distribution for two tomato pomace lyophilizate concentrations.

Figure 4. Experimental data and model prediction for the concentrated tomato pomace particles heat treated at 60°C and 100°C.

Figure 5. Storage modulus *G'* as the function of the tomato pomace lyophilizate concentration at a frequency of 6.813 Hz.

Figure 6. Storage and loss moduli as a function of angular velocity (experimental data and model prediction) for the system with tomato pomace concentration of 12.5% heat treated at 60°C.

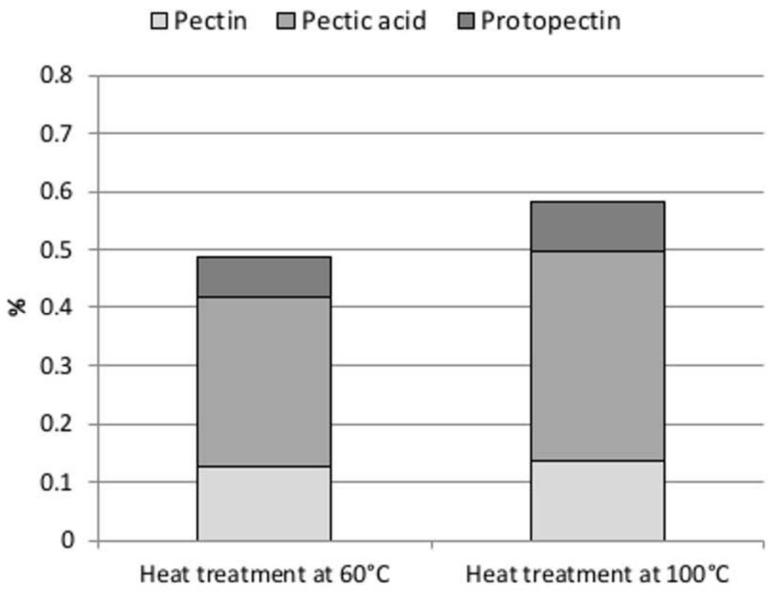
Pectin
Pectic acid
Protopectin
%
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Heat treatment at 60°C
Heat treatment at 100°C

Figure 1

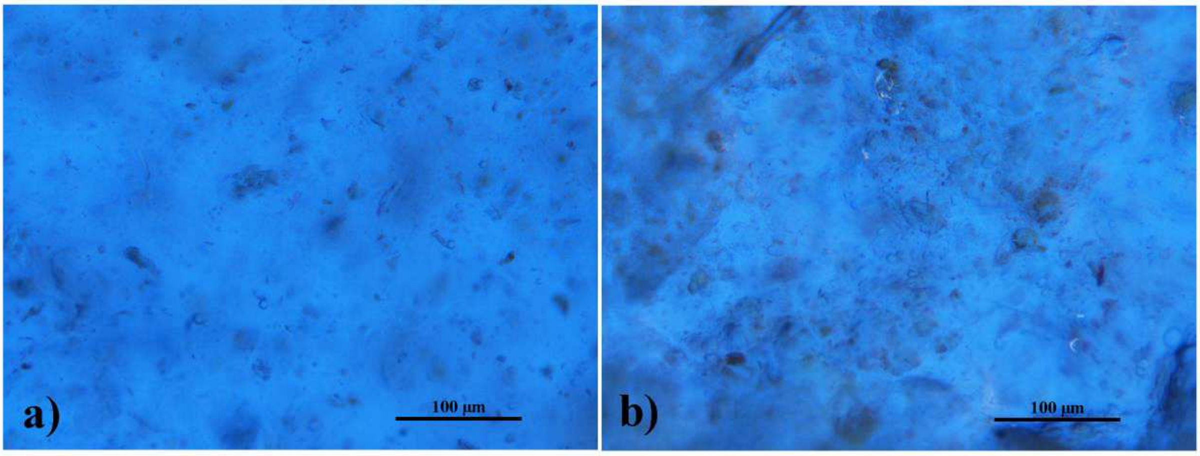

Figure 2

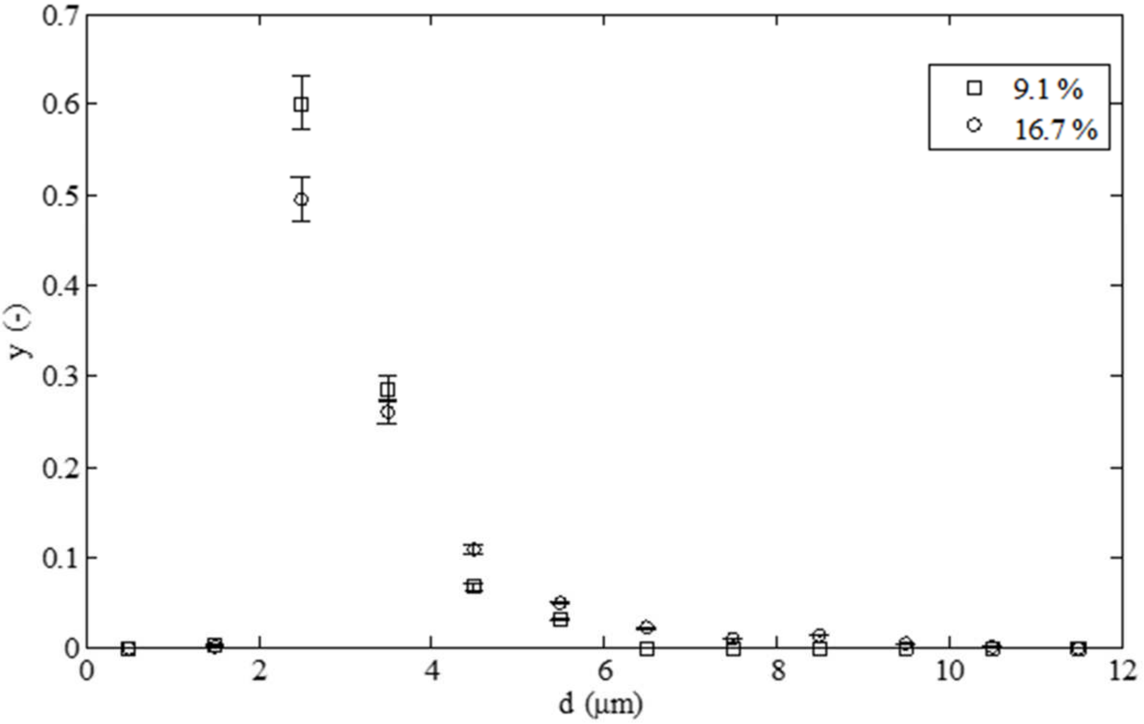

Figure 3

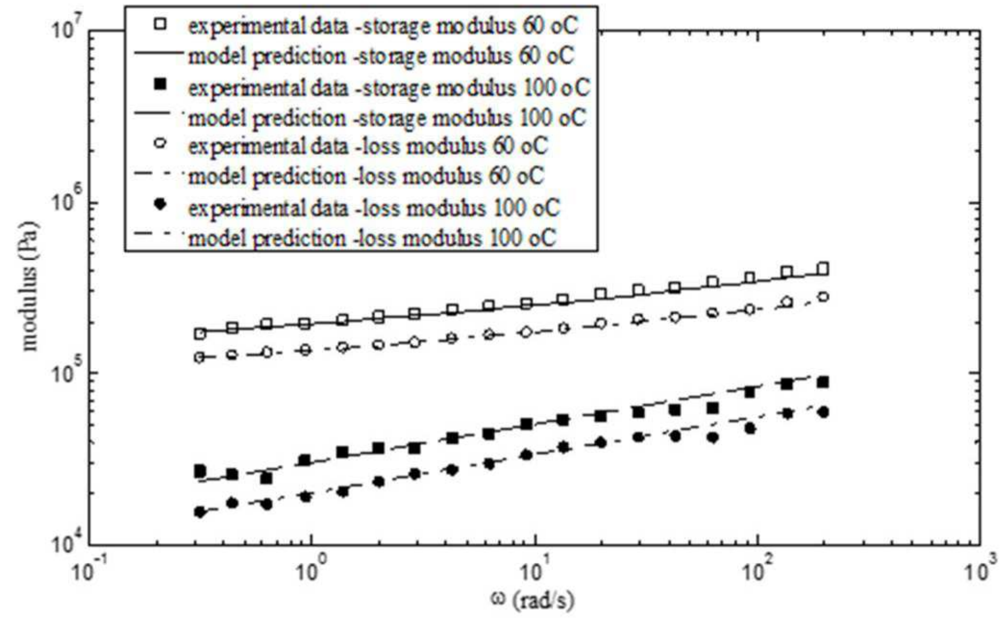
experimental data -storage modulus 60 oC
model prediction -storage modulus 60 oC
experimental data -storage modulus 100 oC
model prediction -storage modulus 100 oC
experimental data -loss modulus 60 oC
model prediction -loss modulus 60 oC
experimental data -loss modulus 100 oC
model prediction -loss modulus 100 oC
modulus (Pa)
10^7
10^6
10^5
10^4
10^-1
10^0
10^1
10^2
10^3
ω (rad/s)

Figure 4

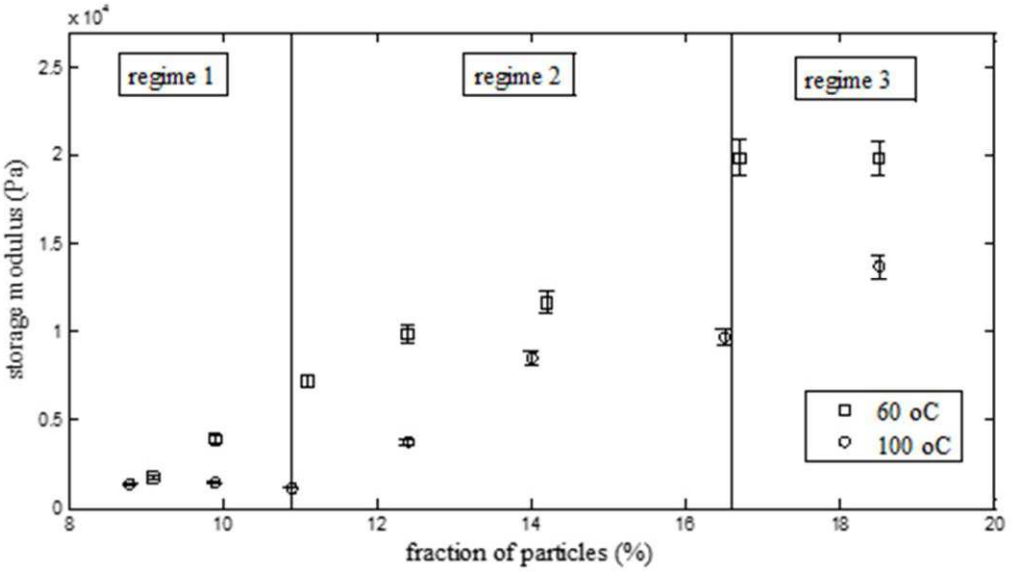
x 10^4
2.5
2
1.5
1
0.5
0
storage modulus (Pa)
8
10
12
14
16
18
20
fraction of particles (%)
regime 1
regime 2
regime 3
60 oC
100 oC

Figure 5

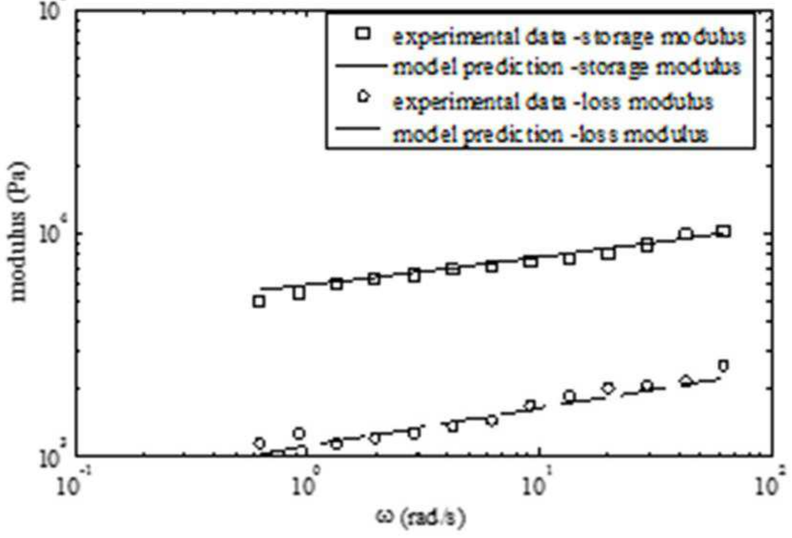
experimental data -storage modulus
model prediction -storage modulus
experimental data -loss modulus
model prediction -loss modulus
modulus (Pa)
ω (rad/s)
10^5
10^4
10^3
10^{-1}
10^0
10^1
10^2

Figure 6