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Physicochemical, functional, oxidative stability and rheological properties of red pepper (*Capsicum annuum* L.) powder and paste

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ABSTRACT

Red pepper (*Capsicum annuum* L.) is one of the major spices consumed globally, recognized for its aroma and nutrient properties, and it has a major economic value for high producing countries. However, characterization of its techno-functional properties and in-depth understanding of oxidative stability is needed to produce food of high quality and stability. Thus, this work focused on the chemical, functional, thermal, oxidative stability and rheological properties of red pepper powder and paste. Experiment was designed in a Completely Randomized Design (CRD) fashion. The red pepper powder contained 14.50 g/100 g, 44.00 g/100 g and 7.57 g/100 g of crude fat, crude fiber and ash, respectively. The concentration of total phenols, carotenoids and antioxidants activity of the powder were 1.04 g GAE/100 g, 374 mg βc/100 g and 38.61 µmol TE/g, respectively. Functional properties showed lower bulk density (395.1 kg/m^3) and higher tapped density (583.4 kg/m^3) indicating the higher compressibility of the powder. In contrast, Hausner ratio (1.48), Carr's index (32%) and angle of repose (45°) indicated poor flowability of the powder. Particle size distribution also indicated that the volume weighted mean values $D_{[4,3]}$ of the powder and paste were 262.20 and 201.46, respectively. Emulsifying capacity of the powder was 47.5%. Oil and water absorption capacities varied from 1.41 to 1.73 and 0.86 to 2.29 g/g of initial weight, respectively. Higher glass transition temperature was observed for the powder (62.54°C) than the paste (45.64°C). The induction period indicated that red pepper was more stable against oxidation in powder (5.2 h) than in the paste form (3.2 h). Rheological analysis revealed that the paste exhibited shear-thinning behavior. Overall, understanding of the properties of red pepper could contribute to enhance quality.

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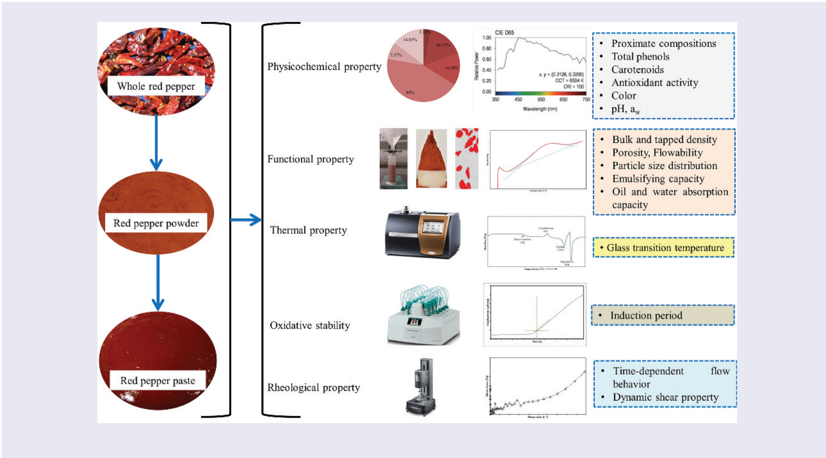

Introduction

Red pepper (*Capsicum annuum* L.), genus *Capsicum*, family *Solanaceae*, is one of the major spices consumed globally[1] and a key ingredient valued for its unique aroma, pungency, color, [2] and nutritional benefits.[3] It is also a good source of fiber, protein, lipid, minerals, vitamins, phenols[4,5] and phytochemicals like ascorbic acid, tocopherols, capsaicinoids, carotenoids and flavonoids.[6] These phytochemicals have functional health benefits in preventing oxidation of biomolecules, and it is claimed that they can contribute in preventing diabetes, cancer, heart disease and lower serum cholesterol level .[7,8]

Red pepper has also huge economic value, [6] especially for high producing countries in Africa and Asia. According to FAOSTAT, [9] India, China, Thailand, Ethiopia, Pakistan, Bangladesh, Myanmar, Viet Nam, Ghana and Côte d'Ivoire are the top 10 major dry pepper producing countries.[9] The dry pepper production in Ethiopia was estimated at 300,000 tons in a total area of 150,000 ha in 2018 with *C. annuum* L. as the most extensively grown and consumed variety.[10]

Low moisture content of foods allows improved microbial stability and reduces quality degradation rate during storage. Also, the use of granular materials such as powders is beneficial for multiple reasons in industrial applications.[11] However, techno-functional properties of powders including shape, size, aspect ratio, sphericity, porosity, true density, bulk density, angle of repose, and flowability should be characterized, [12,13] and an in-depth understanding of the oxidative stability is required to produce high-quality stable food products with desired shelf life. Studying thermodynamic properties of food powders such as heat capacity (Cp), enthalpy (H) and glass transition temperature (T_g) may provide information relevant for product development and quality improvement.[14] Similarly, knowledge on rheological properties of food products is essential during processing, storage and for obtaining desired texture.[15,16] In fact, the design and optimization of different food processing equipment such as pumps, mixers, heat exchangers, etc., require accurate and reliable data on rheological properties of foods to be processed.[15,17–19]

Several studies investigated microbiological and mycotoxin contamination of agricultural produces including red pepper, paprika, and dried chili[20–24] as well as different microbial and mycotoxin decontamination methods.[25–28] Some of the studies reported proximate composition, [29] content of minerals, [30,31] carotenoids, capsaicinoids and ascorbic acid, [32] carotenoid and vitamin C, [33] antioxidants, [34] polyphenol content and antioxidant capacity, [35] pigment composition and color value.[36] Yet, comprehensive studies related to the functional, thermal, oxidative stability and rheological properties of red pepper powder and paste are limited. Therefore, the present study aimed to give a broad range of information on physicochemical, functional, oxidative stability, thermal, and rheological properties of red pepper powder and paste produced from Ethiopian variety.

Materials and methods

Sample collection and preparation

Whole red pepper sample (10 kg) was procured from local market in Addis Ababa, Ethiopia in August 2019. Sample was prepared according to the methods described by Woldemariam, Kiessling .[28] Foreign matters and stalks were manually removed after sun drying for 3 days. The sample was coarsely crushed with cutter mixer (Hobart, USA) and milled with laboratory scale hammer mill (Perten Instruments, Finland). Then, the powder was sieved using 0.5-mm screen and packed in a polyethylene bag. The packed sample was stored at room temperature for one week and transported to Germany until further analysis. Red pepper paste sample was prepared by mixing red pepper powder with distilled water for 2 minutes in the ratio of 1:3 (powder: water), just before the analysis.

Moisture content

Moisture content was determined according to the standard method of the Federal Office for Consumer Protection and Food Safety of Germany (L18.00–23). Briefly, an evaporating dish was covered with 30 g of sea sand (Busch Quarz GmbH, Germany) and pre-dried with a glass rod. About 5 g of sample was weighed into the dish using Mettler Toledo XS204 balance (Sartorius Lab instruments GmbH, Switzerland). The sample and the sea sand were then rubbed evenly in the dish placed on a white sheet. It was dried for 4 h at 103 ± 2°C in a drying oven (Memmert UL 50, Schwabach, Germany). Afterward, it was cooled down and weighed. Commercial pasta product was used as a control.

Crude protein content

Dumas method was used to determine the crude protein content of red pepper powder (L17.00–18 2013-18 213–08, Federal Office for Consumer Protection and Food Safety of Germany). Briefly, 1.0 g of sample was weighed in a metal vial and combusted at 900°C using Vario MAX CN (Elementar analysensysteme GmbH, Langenselbold, Germany) equipped with thermal conductivity detector. *L*-glutamic acid (Merck KGaA, Germany) and pork meat with 12 g/100 g protein was used as reference material and quality control, respectively.

Crude fat content

Crude fat content was determined by Caviezel method using Turnkey fat determination system with Gas Chromatography (GC, BÜCHI fat determination B-820; Autosampler, BÜCHI fat determination B-821, Germany) (DGF CIII 19 (00), German Society for Fat Science). About 3 g of red pepper powder was weighed in a digestion beaker and mixed with 0.2 g of tridecanoic acid (98%, abcr GmbH, Germany) internal standard (IS), 1.5 g of potassium hydroxide pellets (Merck KGaA, Germany) and 45 mL of 1-butanol (VWR chemicals, France). Digestion was done at 200°C for 40 min with multiple heating magnetic stirrer (VELP Scientifica, Italy) connected to reflux condenser. After 30 min of extraction, 40 mL of sodium dihydrogen phosphate (650 g, 99–101.0%) and formic acid (86 mL, 85%) solution (ApliChem, Germany) was added and stirred for another 3 min. The solution was allowed to stand until the aqueous phase was separated from the organic phase. Pork fat (0.7 g, 99.8%) (Hänseller, AG, Switzerland) was used as a reference material. The organic phase that contain the IS and the fatty acids was injected into the GC. GC conditions were: carrier gas H_2, pressure 56 kPa, flow rate 6 mL/min, oven and column temperature 130°C, injection volume 2 μL, injection temperature 220°C, glass column, FID detector at 260°C. After GC separation, the peak areas from the IS and fatty acids were used to estimate the fat content and a pre-determined factor was used to automatically convert the fat content to triglycerides.

Crude fiber content

The crude fiber content of red pepper powder was determined using the methods of Prosky, Asp[37] and Lee, Prosky .[38] Duplicate samples (1.0 g each) were weighed and 40-mL buffer (Tris (Hydroxymethyl) aminomethane and 2-morpholinoethanesulphonic acid monohydrate, TRIS-MES, pH 8.2) (Merck KGaA, Germany) was added into each beaker with magnetic stirrer. It was stirred until the sample was optically completely dispersed. After complete dispersion, 50 µL heat-stable α-amylase solution (200 A, Megazyme, Ireland) was added while stirring. Beakers were covered with aluminum foils and heated at 98–100°C in a shaking water bath and continuously agitated for 30 min. The beakers were taken out of the hot water bath and cooled to 60 ± 1°C. Afterward, 100 µL protease solution (200 A, Megazyme, Ireland) was added and again incubated for 30 min in the bath at 60 ± 1°C. The pH was adjusted to 4.5 using 0.561 N HCl (Honeywell | Fluka, Germany). About 200-µL amyloglucosidase solution (200 A, Megazyme, Ireland) was added while stirring and incubated at 60 ± 1°C for 30 min in the bath with continuous agitation. It was filtered in a fiber filter bag (C. Gerhardt GmbH & Co. KG, Germany) and the residue was washed twice with four volumes of 95% ethanol (TH.Geyer, Germany) preheated at 60°C and with 10-mL distilled water preheated to 70°C. The residue on a crucible was dried overnight at 103°C and cooled in a desiccator for 1 h. One sample residue was analyzed for protein using Kjeldahl method (factor: N × 6.25) and the other duplicate was analyzed for ash content based on oven drying method at 550°C for 5 h. Crude fiber content was calculated from the differences of protein and ash contents.

Ash content

Ash content was determined based on the standard procedure of the Federal Office for Consumer Protection and Food Safety of Germany (L53.00–4). Briefly, 5 g was weighed in a dry crucible. Pre-ashing of the samples was carried out in a muffle furnace (Nabertherm P330, Germany) by a temperature program, changing from start temperature (<150°C) to end temperature (550°C) heated up linearly within 10 h. The incineration took place over 4 h at the final temperature of 550°C and was later on cooled in a desiccator for 1.5 h. Milk powder was used as a control.

Carbohydrates content

Utilizable carbohydrates were calculated by difference using Eq. (1):

$$Utilizable carbohydrate(g/100) = 100 - [\mathrm{moisture(g/100g) + crudeprotein(g/100g) + crudeash(g/100g) + crudefat(g/100g) + crudefiber(g/100g)}] \quad \text{Equation(1)}$$

Total phenols content

Folin-Ciocalteu (F-C) colorimetric method was used to determine the content of total phenols in red pepper powder. Briefly, 2 g of the sample and 20 mL of extraction solvent (70-mL methanol (99.9%, Merck KGaA, Germany) + 2-mL formic acid (99–100%, VWR, Germany) + 28-mL H_2O) were mixed in a beaker with magnetic stirrer for 2 h and incubated overnight in a refrigerator at 10°C. About 2 mL of the mixture was centrifuged (Universal 320 R, Hettich Zentrifugen, Germany) at 21,380 × g for 15 min. The supernatant (0.2 mL) was mixed with 1 mL of F-C reagent (Merck KGaA, Germany) and allowed to stand for 6–8 min. Then, aqueous Na_2CO_3 (800 µL, Merck KGaA, Germany) was mixed with the extract using vortex. After 2 h, the absorbance was read at 760 nm with spectrophotometer (SPECORD 40, Analytik Jena AG, Germany). *L*(+)-ascorbic acid (AppliChem, Germany) and Gallic acid (98%, Acros Organics, Germany) were used as a standard and quality control, respectively. Total phenols content was expressed as mg of gallic acid equivalents (mg GAE/100 g).

Carotenoids content

Carotenoids content of red pepper powder was determined using photometric methods. About 1 g of sample was mixed with 20 mL of methanol (99.9%, Merck KGaA, Germany) and shaken for 10 min (250 shakes/min) with shaker (SM-30, Edmund Bühler GmbH, Germany). The mixture was subsequently centrifuged (Universal 320 R, Hettich Zentrifugen, Germany) at 8,965 × g for 10 min at 20°C. The supernatant was decanted into a volumetric flask (100 mL). The procedures were repeated with 20 mL, 15 mL, 15 mL, 10 mL, 5 mL and marked with methanol up to 100 mL level. The extract was filtered with 0.45-μm membrane filter and absorbance was read at 470 nm with spectrophotometer (SPECORD 40, Analytik Jena AG, Germany). Carrot juice was used as a control. Carotenoid contents were expressed as mg β-carotene (mg βc/100 g).

Antioxidants activity

The antioxidants activity of red pepper powder was determined using Trolox equivalent antioxidant capacity (TEAC). A sample of about 2 g was mixed with 20 mL of extraction solvent (70-mL methanol (99.9%, Merck KGaA, Germany) + 2-mL formic acid (99–100%, VWR, Germany) + 28-mL H_2O) and stirred in a beaker with magnetic stirrer for 2 h. The extract was centrifuged (Universal 320 R, Hettich Zentrifugen, Germany) at 21,380 × g for 15 min and the supernatant was decanted. About 10 μL of supernatant and 1 mL of $ABTS^{\bullet +}$ (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)) (≥98%, HPLC grade, Sigma Aldrich, Germany) was mixed into the cuvette and absorbance was read at 734 nm with spectrophotometer (SPECORD 40, Analytik Jena AG, Germany). Trolox ((±)-6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) and *L*(+)-ascorbic acid (AppliChem, Germany) (Sigma Aldrich, Germany) was used as a standard and quality control, respectively. Results were expressed as μmol Trolox equivalent per g (μmol TE/g) of sample.

Color value

The color value of red pepper sample was determined according to Li, Zhao.[39] About 6 g of sample was distributed uniformly in a cuvette and color was determined at multiple locations (n = 10) based on CIELab color space system using spectrophotometer (CM-600d, Konica Minolta, Japan) in reflectance mode. The measurements were conducted at viewing angle of 10° and CIE standard illuminant D65 at room temperature (20 ± 2°C). Color was expressed as L^*, a^*, b^* average values, where the lightness value L^* defines black to white (0–100), the a^* axis represents the green-red opponent color (negative values toward green, and positive toward red) and b^* axis defines yellow-blue opponents (negative values toward blue and positive toward yellow).[40]

pH value

The pH value of red pepper powder was determined according to Choi and Lee.[41] A 45 mL of distilled water was added to 5 g of sample and homogenized for 1 min. The solution was kept for 1 h at ambient temperature and the pH value of the supernatant was determined by using a pH meter (Mettler Toledo, China).

Water activity

The water activity (a_w) of red pepper powder was determined using water activity meter (SE a_w Lab Schulz Elektronik, Hohenkirchen, Germany) at room temperature. The a_w value represents the ratio between the vapor pressure p of the water-containing medium and that of the pure water p_o. In practical terms, this means measuring the relative air humidity (*RH*) which is established as a state of equilibrium over the water-containing substance in a closed room at a defined temperature.

Bulk and tapped densities

Bulk density of the red pepper powder was measured by a funnel method according to Meghwal and Goswami.[42] The powder was poured into a measuring cylinder (volume 100 mL, height to diameter ratio of 2.5:1) using a conventional funnel and the top layer of the powder was carefully flattened with a strip of iron. The weight and volume of the powder in the cylinder were recorded and Eq. (2) was used to calculate the bulk density of the powder.

$$\rho_b = m_p / V_p \qquad \text{Equation(2)}$$

where, ρ_b is bulk density (kg/m^3), m_p is mass of the powder (kg), V_p is volume of the powder (m^3). The tapped density was measured using the same method with bulk density, but manually tapping the cylinder vertically until the height of powder in the cylinder does not change.[43] The tapped density of red pepper powder was calculated according to Ghodki and Goswami[44] using Eq. (3):

$$\rho_t = m_t / V_t \qquad \text{Equation(3)}$$

where ρ_t is tapped density (kg/m^3), m_t is tapped mass of the powder (kg), V_t is tapped volume of the powder (m^3).

Porosity

Porosity reflects the number of pores in the bulk material and was measured as described by Mohsenin.[45] Mean values of tapped density and bulk density were used to calculate the porosity (ε (%)) of red pepper powder using Eq. (4):

$$\varepsilon(\%) = \left[1 - \frac{\rho_b}{\rho_t}\right] \times 100 \qquad \text{Equation(4)}$$

Particle size distribution and specific surface area

Particle size distribution of red pepper powder was determined using laser diffraction particle size analyzer (Mastersizer 2000; Malvern Instruments Ltd., Worcestershire, UK) according to the method described by Sun, Zhang.[46] The powder was dispersed in air (ISO 13320–1) and in water (ISO 13320–1) for the paste. In particle size distribution curve, D_{10}, D_{50}, and D_{90} representing 10%, 50%, and 90% were used to describe the volume of particles undersize, respectively. The volume distribution was also used to determine the volume weighted mean ($D_{[4,3]}$) and the specific surface area (m^2/g).

Hausner ratio (Hr) and Carr's index (CI)

Hausner ratio (Hr) and Carr's index (CI) are commonly used parameters to determine the flowability of food powders.[47] Both Hr and CI were calculated by taking the tapped density and bulk density of red pepper powder using Eq. (5) and (6), as described by Meghwal and Goswami[42] and, [48] respectively:

$$Hr = \rho_t / \rho_b \qquad \text{Equation(5)}$$

$$CI = (\rho_t - \rho_b) * 100 / \rho_t \qquad \text{Equation(6)}$$

Angle of repose

Angle of repose for red pepper powder was determined using a cylinder (height to diameter ratio: 0.8:1.0) placed in a plexiglass tube (cylinder diameter to inside diameter of the tube: 0.8: 1.0; height of cylinder to height of tube: 1.0:3.0) and positioned in the middle. About 50% of the plexiglass tube was filled with the powder and the tube was slowly removed (n = 5) and the powder forms a cone on the cylinder end face. The angle of repose (α) of the red pepper powder was estimated according to Meghwal and Goswami[42] from the radius and height of the cone using Eq. (7):

$$\alpha = tan^{-1}[r/h] \qquad \text{Equation(7)}$$

where r is radius of cylindrical base (mm), h is height of the conical pile of the powder (mm).

Emulsifying capacity

Suspension of red pepper powder and water (1:3, w/v) was prepared and kept for 2 h contact time. About 50 g of the water phase was filled into a cylindrical plastic tube and dispersed using Ultra-Turrax (n = 11,000 min^{-1}, IKA Staufen, Germany) with an addition of predetermined quantity of sunflower oil within 30 s. The mixture was mixed (n = 13,000 min^{-1}) for 1 min at 25 ± 2°C. The amount of oil was quantified based on a visible film or stability after 30 min. If there was a visible oil film after 30 min, the oil quantity was reduced; or, if the emulsion was stable after 30 min, the oil quantity was increased. Emulsifying capacity was the highest percentage of oil which enabled an emulsion without visible oil layer.

Oil and water absorption capacities

For determination of oil and water absorption capacities, red pepper powder was mixed with sunflower oil (1:3, w/v) and kept for 2 h for swelling. The suspension was filled in 15 mL plastic tubes and centrifuged using Sorvall RC 6+ (Thermo Fisher Scientific, Waltham, USA) at different accelerations (1000, 2500, 5000, 7500, 10000, 12500, 15000 × g) for 10 min at 25 ± 2°C. The mass of the supernatant from each centrifugation step was measured. Oil absorption capacity is the function of remaining oil depending on centrifugal acceleration. The same procedures were followed for determination of water absorption capacity, except water was used instead of the oil.

Thermal properties

Thermal properties of the powder and the paste were analyzed using Differential Scanning Calorimeter, DSC 250 (TA Instruments, New Castle, USA) according to Noda and Tsuda.[49] A sample of 10 mg was weighed into aluminum pan, it was hermetically sealed with Tzero Press (TA Instruments, New Castle, USA) and kept at room temperature for 1 h before heating in DSC. Indium was used to calibrate the analyzer and an empty pan as a reference. Sample pans were heated from 25°C to 95°C at the rate of 2.5°C/min with modulation of 0.4°C/min and the change in heat capacity was tracked with the changes in the heat flow. The heat flow was measured as the energy required to maintain a zero temperature difference between the sample and the reference material. Thermal properties, such as onset (T_o), peak (T_p), end points (T_e) of glass transition temperature (T_g) and enthalpy were analyzed and recorded.

Oxidative stability

Oxidative stability was performed using a rancimat test in which 1 g of powder and 3 g of paste samples were subjected to accelerated oxidative conditions using 892 Professional Rancimat (Metrohm AG, Herisau, Switzerland). The oxidative stability was investigated up to 120°C with airflow rate of 20 L/h. Measuring vessels were filled with 60 mL of deionized water to monitor electrical conductivity. Electrical conductivity (μS/cm) was potted against time (h) to determine the induction period (IP) by tangent method at the inflection point.

Rheological properties

Rheological properties were assessed using Rapid Visco Analyzer (RVA) (AR 2000, TA Instruments, New Castle, USA) based on the method described by Chen and Tong.[50] Parallel plate geometry (40 mm), both cross-hatched with 500 µm slit, was used for oscillatory and steady shear measurements at 25°C. Steady shear tests were carried out with shear stress ranging from 0.01 to 100 Pa and shear rate range of 1–1000 s^{-1}. Rheological parameters including storage modulus (G′), loss modulus (G″), complex viscosity (η*) and loss factor (tan δ) were measured for the red pepper paste. The frequency sweep tests were performed in the frequency range of 1–50 rad/s at a constant stain of 3%.

Experimental design and data analysis

The experiment was designed in a Completely Randomized Design (CRD) fashion for two products, powder and paste. All experiments and analyses were done at least in triplicates, except DSC measurements done in duplicate. Regression analyses were carried out using Microsoft Excel 2010. Results are presented as the mean value of replicates.

Results and discussion

Physicochemical properties

The physicochemical properties consisting of moisture, crude protein, crude fat, crude fiber, ash and utilizable carbohydrate contents of red pepper powder are presented in (Table 1). The crude protein, crude fat, crude fiber and ash contents of red pepper powder in this study appeared higher than the reported values for dried *C. annuum* L. by FAO.[51] Similar results for red pepper were reported by earlier studies.[6,52,53] The variations in the proximate compositions could be due to the growing conditions, variety, season, differences in production and processing, and storage practices or analytical methods used. The red pepper powder had a slightly acidic pH of 5.62, and a_w of 0.263, the latter being an intrinsic factor that influences the shelf life of agricultural commodities such as spices, and often is an indicator of quality, [54] as free water will be less available for biochemical deteriorations. In this study, the moisture content of the red pepper powder is within the range of most food powders, commonly about 5% or lower.[40] According to Tuyen, Nguyen, [55] dried food powders (a_w <0.6) are less susceptible for microbiological and biochemical deteriorations during storage.

Table 1. Physicochemical properties of red pepper powder.

Parameters	Values
Moisture content [g/100 g]	3.12 ± 0.02
Crude protein [g/100 g]	16.17 ± 0.06
Crude fat [g/100 g]	14.50 ± 0.13
Crude fiber [g/100 g]	44.00 ± 1.15
Ash [g/100 g]	7.57 ± 0.16
Utilizable carbohydrates [g/100 g]	14.65 ± 1.41
Total phenols [g GAE/100 g]	1.04 ± 0.03
Carotenoids [mg βc/100 g]	374 ± 3
Antioxidants activity [µmol TE/g]	38.61 ± 0.42
Color	*L**: 44.46 ± 0.22 *a**: 17.79 ± 0.28 b*: 13.92 ± 0.28
pH	5.62 ± 0.03
a_w at 20°C	0.263 ± 0.003

Total phenols, carotenoids and antioxidants activity

The total phenols, carotenoids and antioxidants activity of the red pepper powder were 1.04 g GAE/100 g, 374 mg βc/100 g and 38.61 μmol TE/g, respectively (Table 1). Previous reports on phytochemical composition of other red pepper varieties included content of total phenols of 495.26 mg/100 g, [56] 0.842 mg GAE/kg, [57] 2.35 to 2.75 g/100 g, [58] 568 mg to 1032 mg GAE/100 g[59]; carotenoids content of 133.65 mg/100 g[56]; and antioxidant activity of 34.44 ± 0.43 μM TE/g .[60] These variations might be associated with different factors such as the type and physical form of the sample, genetics, environmental conditions and analytical methods.

There is a significant positive correlation between total phenolics and antioxidant activity of fruits and vegetables.[61] Antioxidants have a key physiological function in biological processes. Proteins, lipids or nucleic acids can be oxidized by free radicals and reactive oxygen species (ROS) and initiate many types of degenerative diseases. Food containing antioxidative compounds can reduce lipid oxidation, thus decreasing the risk of potential oxidative stress-based diseases.[62–64] In our current study, high antioxidant activity was determined in the red pepper powder comparable to several other fruits and vegetables.[65] Differences in antioxidants activity as measured in our study and compared to values reported in the literature, can be attributed to differences in the presence of other antioxidant substances including tocopherols and ascorbic acid.

Color

Color of red pepper products is the most vital quality attribute that determines the overall quality and subsequently the final market price.[66] In our study, the red pepper powder had color value of L^* as +44.46, a^* (+17.79) and b^* (+13.92), indicating the dominance of the bright red color with tendency to yellow (Table 1). The red color of red pepper is due to the occurrence of carotenoid pigments like capsanthin, capsorubin, β-carotene, cryptoxanthin, violaxanthin, zeaxanthin, etc. [58] These substances can be easily degraded under certain conditions of processing and storage, thus resulting in the deterioration of the typical red pepper color and with that related quality and market value.

Traditionally in Ethiopia, red pepper fruits are sun dried and can be stored for several months, ground to powder or flakes. Once dried and ground, stability of the carotenoids in the red pepper powder is usually reduced.[67,68] This loss of color was attributed to the degradation of carotenoids during drying and storage.[69] The stability of carotenoid pigments depends on cultivars, initial concentration of carotenoids, residual water activity, endogenous antioxidants and enzyme activity, but also on drying and processing.[70]

Bulk and tapped densities

The bulk density and tapped density of the red pepper powder were 395.1 kg/m^3 and 583.4 kg/m^3, respectively (Table 2), similar to the results reported in previous studies.[71,72] The porosity (ε) of the powder before tapping was 32.3%. High bulk density is desired, as it is related to lower packaging, storage, and transportation costs.[73] Lower bulk density and higher tapped density indicate the development of inter-particulate interactions (increased cohesiveness), which suggest the enhancement of compressibility of the powder. This creates additional voids in the bulk during pouring of powder and helps particles to keep around free spaces, thus increasing the volume.[48] Particle size reduction could contribute to lower bulk density. However, the action of tapping brings extra force to overcome cohesive attractions and cause particles to fall toward void spaces, thereby decreasing the volume of powder.

Table 2. Functional properties of red pepper powder.

Parameters	Values
Bulk density [kg/m^3]	395.10
Tapped density [kg/m^3]	583.38
Hausner ratio [Hr]	1.48
Carr's index [CI, %]	32
Porosity [ε, %]	32.3
Angle of repose [α, °]	45

Particle size distribution and specific surface area

The particle size distribution of cumulative volume undersize centiles (D_{10}, D_{50}, and D_{90}) for red pepper powder and paste are shown in Figure 1. The volume weighted mean ($D_{[4,3]}$) of the powder and the paste were 262.20 and 201.46, respectively. In all of the measurements, the volume undersize and weighted mean of the powder was higher than that of the paste due to the swelling and increase of particle size as a result of water absorption.

On the other hand, the specific surface areas of the powder and the paste were 0.0612 m^2/g and 0.213 m^2/g, respectively. With the increasing surface area, the probability of formation of inter-particle bonding tends also to increase, as a result of improved accessibility of the binding sites. Thus, particle size has a significant impact on absorption of moisture and resulting parameters like texture and viscosity.[74] Moreover, the finer particle-sized powders have more ability and stability for mixing with other spices or ingredients .[75]

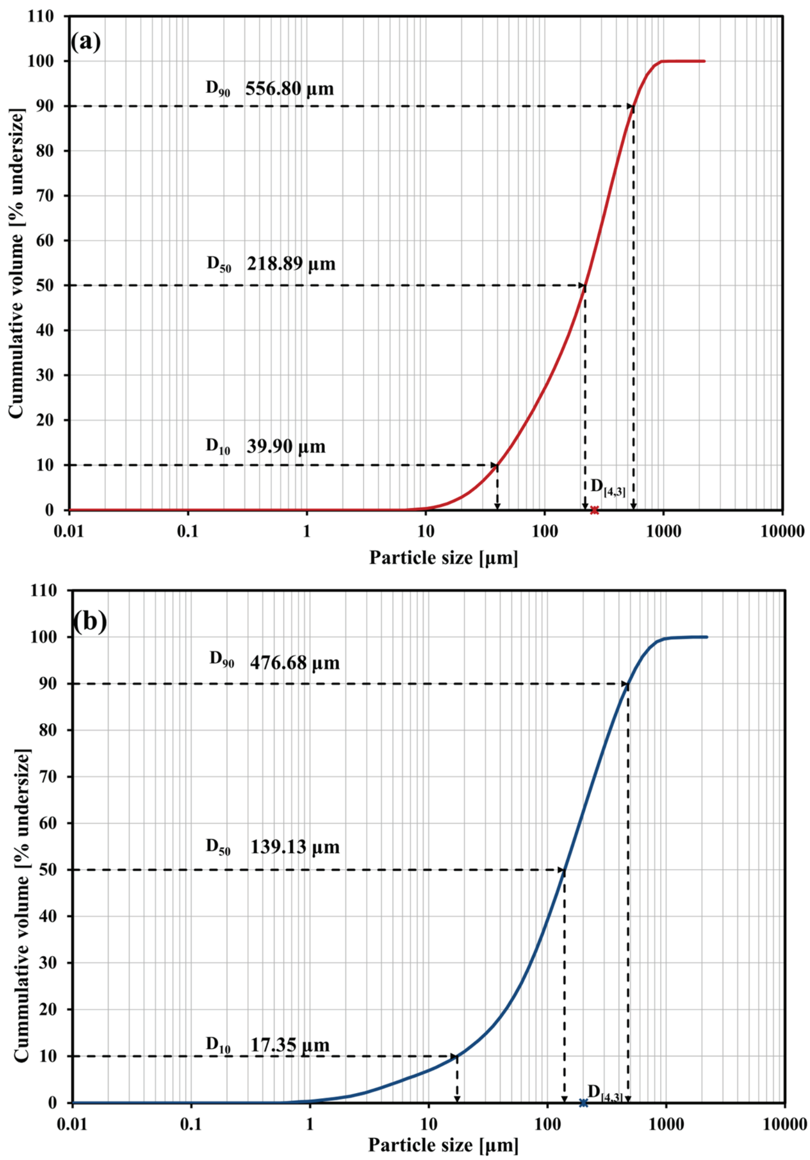

Figure 1. Particle size distribution curve for: (a) red pepper powder and (b) paste.

Flowability

Flowability is one of the key food powder properties that indicates their free flow during handling, processing, transportation and application. Flowing properties can be expressed as Hausner ratio (HR) and Carr's index (CI).[76] The powders having a HR greater than 1.34 and CI greater than 25% can be considered as 'poor' in flowability. Similarly, angle of repose (AoR, α) can be used to estimate the flowability of food powders, in which powders with α between 45° and 55° can be considered as 'cohesive'.[77] In our current study, HR and CI for red pepper powder were 1.48 and 32%, respectively (Table 2). Measurement of angle of repose of red pepper powder was found to be at α = 45° (Figure 2). Hence, the values of CI, Hr and AoR demonstrated that the red pepper powder was less able to flow freely. Powder flowability can be directly related to the particle size, [78] as particles having more uniform size enable improved flow and adhesion properties compared to non-uniform particle size.[79] These properties are useful in commercial applications when designing and manufacturing systems for handling, processing, storage, transportation as well to avoid major issues like sticking and agglomeration.[12,13]

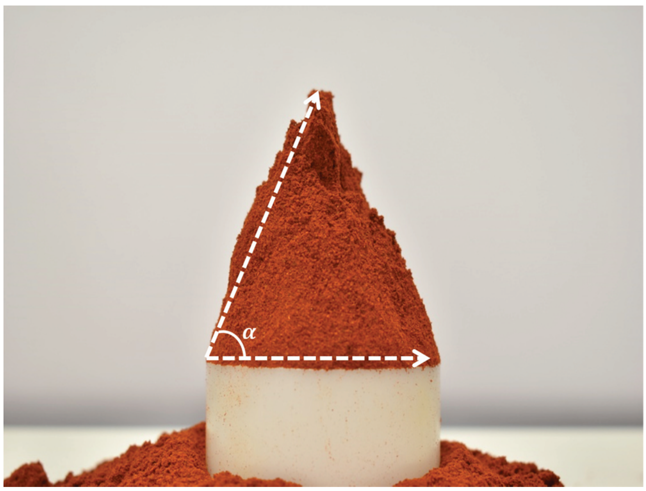

Figure 2. Angle of repose (α) of red pepper powder using cylinder method.

Emulsifying capacity

The emulsifying capacity of the red pepper powder increased progressively with the increasing amount of oil and decrease of the water phase (Figure 3). However, a reduction of emulsifying capacity was observed when the amount of oil increased to 50% and 60%. The maximum emulsifying capacity was recorded when there was no breaking point between the two mixtures. Thus, the highest percentage of oil which enabled the emulsion without visible oil layer was 47.5% with the corresponding water phase of 52.5%.

Emulsifying capacity can be influenced by the amount of proteins present in the sample and increased hydrophobicity.[80] It could be also attributed to the capacity of some proteins to reduce the interfacial surface tension involving water and oil in the emulsion.[80] The shear force applied during the assessment could also have impact on reduction of oil droplets, thus increasing the surface area depending on the amount of protein.

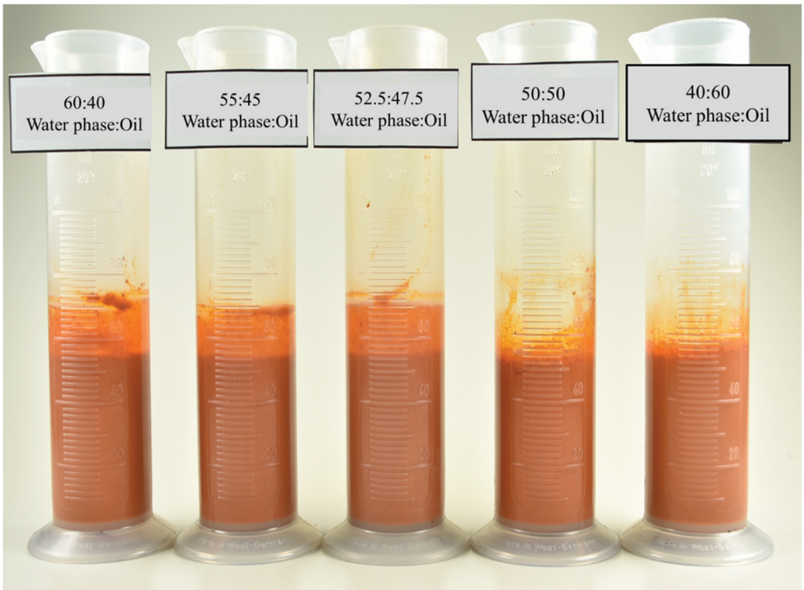

Figure 3. Measurement of emulsifying capacity ad different proportions of water phase to oil.

Oil and water absorption capacities

Oil absorption capacity (OAC) at different levels of centrifugal accelerations ranged from 1.406 to 1.733 g/g, and water absorption capacity (WAC) ranged from 0.859 to 2.290 g/g of initial weight of the red pepper powder (Figure 4). With increasing centrifugal acceleration, there was no significant change in the OAC, except at the beginning of the centrifugation process. In contrast, water absorption decreased progressively with observed stability at the highest centrifugal acceleration. In the literature, it was suggested that the lower OAC of powder could be explained by the limited amount of nonpolar protein side chains, that would bind the side chains of hydrocarbons of the oil.[81] The increased WAC of the powder could be attributed to the swelling of fibers and other carbohydrates.

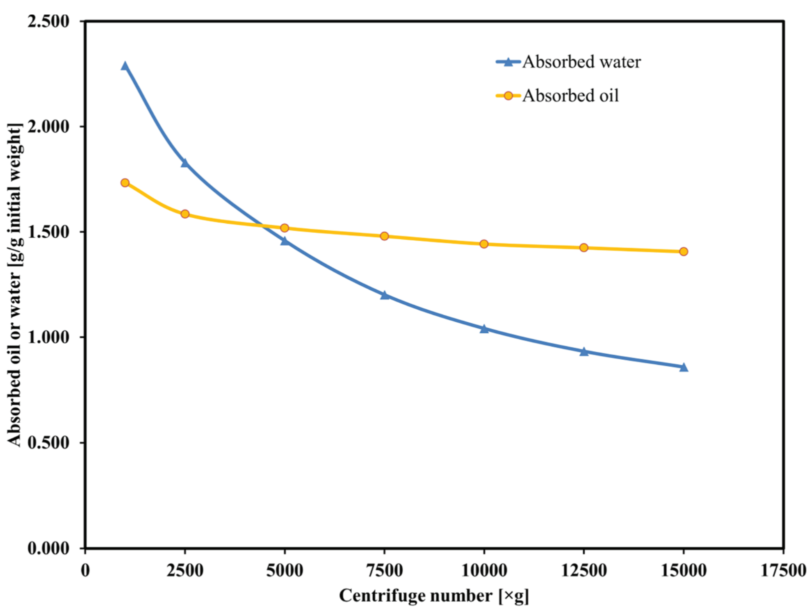

Figure 4. Oil and water absorption capacities of red pepper powder at various levels of centrifugal accelerations.

The smallest particle-sized powder may have the largest surface area and more hydrophilic groups of the powder exposed, causing an easier interaction of powder with water .[75] It has been reported that OAC can have an impact on the texture and sensory properties of some foods .[82]

Thermal properties

The thermal properties of red pepper powder and paste are presented in Figure 5. By analyzing the thermogram, the glass transition temperatures T_g of the powder were determined at T_o = 42.85°C, T_m = 62.54°C and T_c = 82.22°C with peak temperature (T_p) at 63.14°C. Whereas, the glass transition

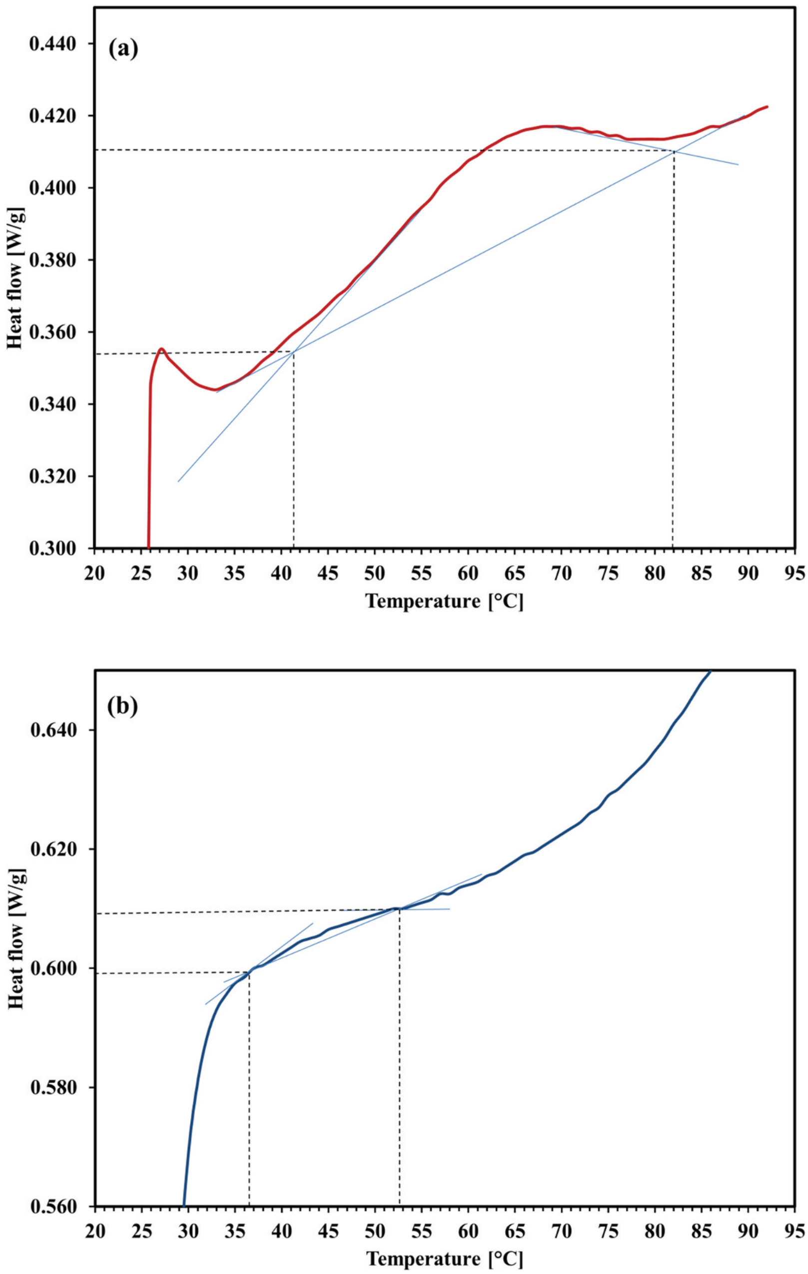

Figure 5. Glass transition temperatures of: (a) red pepper powder and (b) paste.

temperatures T_g of the paste were T_o = 37.70°C, T_m = 45.64°C and T_c = 53.58°C with T_p at 47.63°C. Although there are onset, mid- and end-point temperatures, several studies considered the mid-point temperature of a thermogram as the glass transition temperature.[83] Enthalpies of the powder and the paste at the onset temperatures were 4.44 J/g and 0.10 J/g, respectively. The glass transition temperature for the paste was lower compared to the powder, within the tested range of temperature.

The low glass transition temperature T_g implies potential weak molecular interactions in the red pepper paste. As the red pepper powder is subjected to the glass transition temperature T_g, it changes its state from amorphous to crystalline (or vice versa). Moreover, the sample becomes brittle below glass transition temperature range by converting the amorphous phase into crystalline, which might also result in smaller particles. The reason for this kind of behavior can be that, above the glass transition temperature T_g the molecules could move more freely.

Oxidative stability

The oxidative stability was measured by monitoring the electrical conductivity under accelerated oxidation conditions. The changes in the electrical conductivity during the test are shown in Figure 6. As it can be seen from the figure, there was no significant change in the conductivity up to the inflection point of the curve. However, significant increase was observed in the second stage of oxidation, considering the described two-stage oxidation, [84] where the first stage is the initiation phase (low-slope) and the second stage is the propagation phase (higher-slope).

Induction period (IP) is used to indicate the stability described at the maximum derivative of the electrical conductivity of water. The IP value was considerably higher for the powder than that of the paste, which was 5.2 h versus 3.2 h. This implies that the powder was more stable against oxidation, compared to the paste. The higher the IP value, the more stable is the food product under similar Rancimat conditions.[85] The relatively higher oxidative stability of the powder could be ascribed to the low a_w of the powder, where water is tightly bound to the surface of food and as such is less available for further reactions.

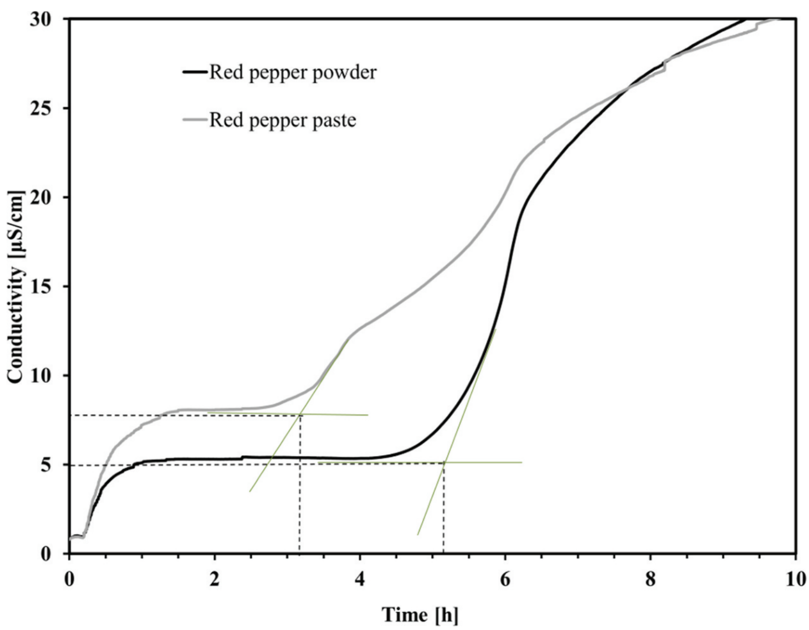

Figure 6. Oxidative stability of red pepper powder and paste.

Rheological properties

Time-dependent flow behavior: The relationship between shear stress and shearing time was determined for red pepper paste only. A characteristic viscoelastic behavior was observed, consisting of the onset of shear and the maximum shear stress (stress buildup region), and the equilibrium stress value (stress decay region) (Figure 7). As it can be seen, from the figure, there was a rapid decrease of shear stress but gradually slower until it reached equilibrium. This decrease is a typical behavior of time-dependent suspensions that might be attributed to destabilization of colloidal particles, and alignment or loss of solids structure due to the applied shear force.[86]

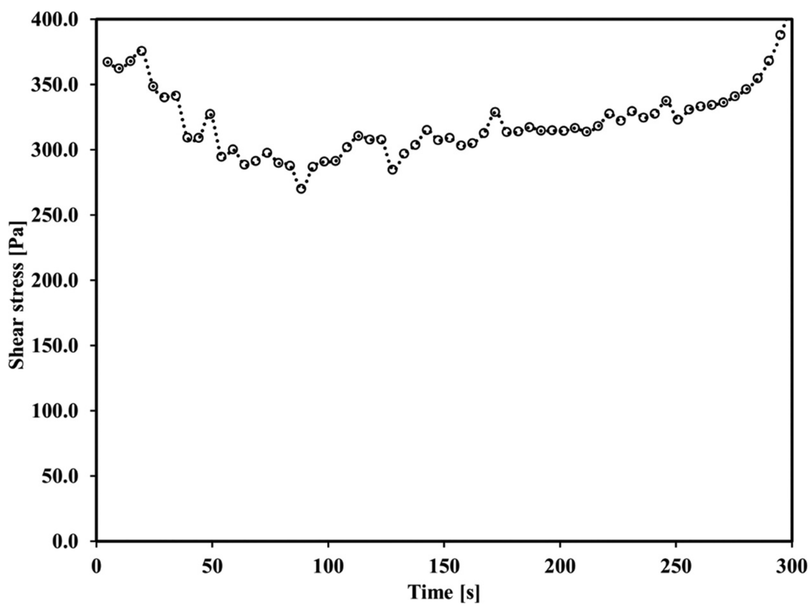

Figure 7. Time dependency curve for red pepper paste.

Dynamic shear properties: Frequency sweep tests were conducted to evaluate storage modulus (G′), loss modulus (G″) and complex viscosity (η^*) of red pepper paste. The ratio of G″ to G′ was used to estimate the loss factor (tan δ), which describes the viscoelastic behavior. Figure 8 depicts changes in G′, G″ and η*, as a function of angular frequency (ω) measured at 25°C. With an increase in ω, the magnitude of G′ as well as G″ increased, where the values G′ were considerably higher than that of G″ for the corresponding values of ω, indicating dependency of frequency. Moreover, it was observed that the paste exhibited weak gel-like behavior, related to the greater magnitudes of G′ (1826–2720 Pa), compared to G″ (558–1070 Pa) in the frequency range of 1–50 rad/s.

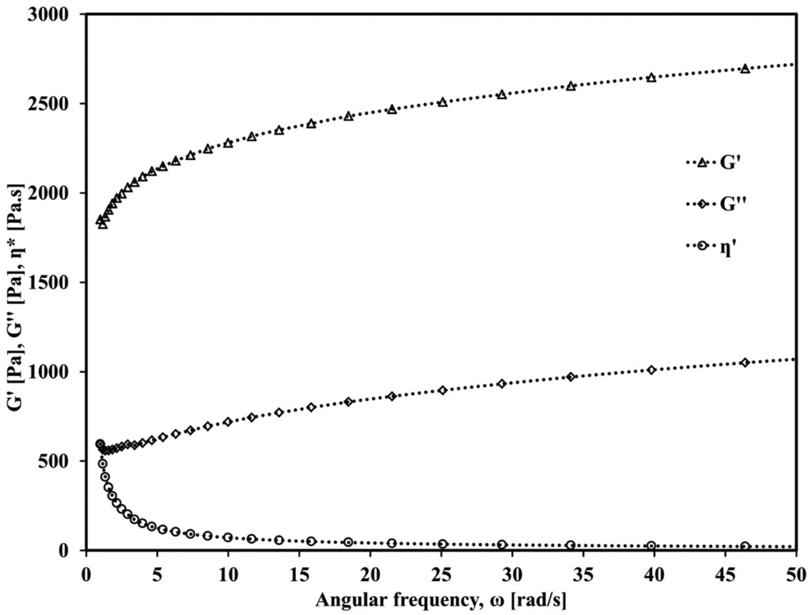

Figure 8. Dynamic shear properties of red pepper paste.

Values of tan δ also indicated that elastic properties of red pepper paste were dominant over viscous ones in the values ranging from 0.29 to 0.39 (Figure 9). Increase in the tan δ values with the corresponding frequency indicated the proportional increase of loss modulus, G″. The dominant elastic function offers enhanced retention of shape during handling and cooking suggesting matrix structure is not weak and easily deformable. Further, linear regression analysis was carried out for the dynamic rheological data plotted ln (G', G") against ln ω (rad/s) (Figure 10). According to Ross-Murphy, [87] true gels have zero and weak gels have positive slopes zero and positive slopes in the same plot.

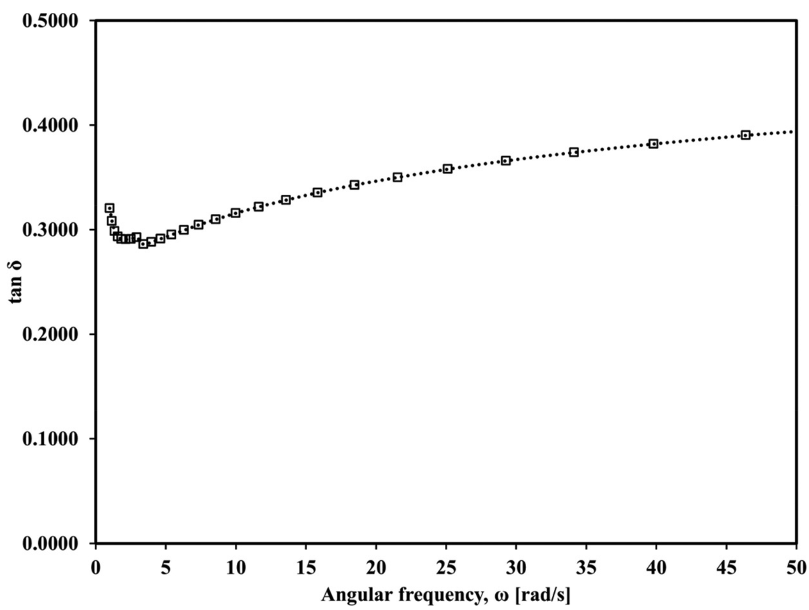

Figure 9. Viscoelastic property of red pepper paste.

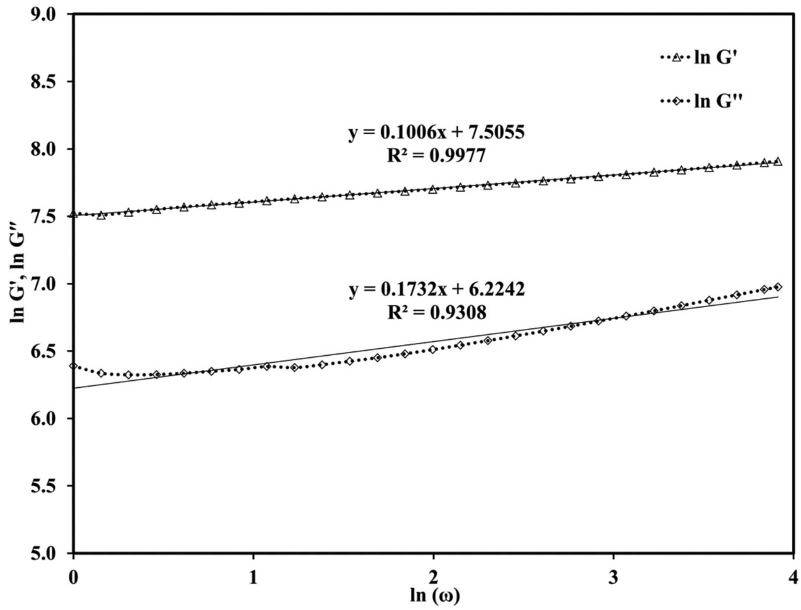

Figure 10. Frequency dependency on red pepper paste properties.

Rheological properties, in particular apparent viscosity, can be used as a reference for estimating the performance during food processing.[88] The relationship between results of viscosity and shear rate revealed that viscosity of red pepper paste decreased with increasing shear rate indicating shear-thinning behavior (Figure 11). Due to the adoption of actual processing conditions, our findings on rheological properties would be valuable for processing and developing red pepper composites for new food product formulations. Shear-thinning behavior of a product has also certain benefits in food processing, related to–price efficiency and energy consumption during mixing and pumping.[89]

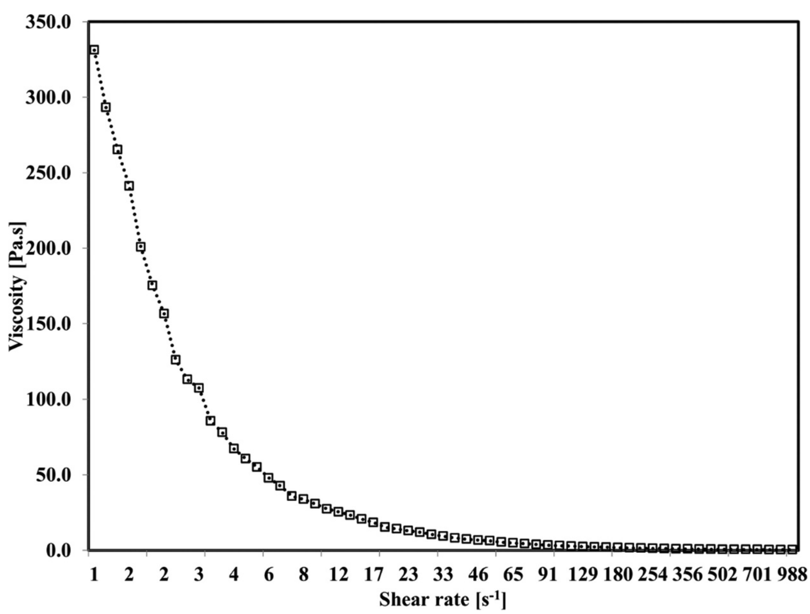

Figure 11. Shear-thinning behavior of red pepper paste.

Conclusion

The physicochemical, functional, thermal, oxidative stability and rheological properties of Ethiopian red pepper powder and paste were determined. The results demonstrated that the red pepper is rich source of nutrients, and possess phytochemicals which can further be exploited for food formulations. Red pepper had also valuable features that could bring many functional roles and enhance the textural integrity of food products. Generally, understanding the properties of red pepper powder and paste can lead to better quality control during processing and using in different applications. In conclusion, the results indicated that red pepper could be used as a source of essential nutrients and bioactive substances while improving the functional properties of food formulations. Further, complementary studies on the effect of ripening degree, different drying processes and related pre-treatments, storage, pre-processing and conditioning on the qualities of red pepper would be valuable.

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