Physicochemical, morphological and rheological properties of canned bean pastes “negro Querétaro” variety (*Phaseolus vulgaris* L.)

A. H. Martínez-Preciado · Y. Estrada-Girón ·
A. González-Álvarez · V. V. A. Fernández ·
E. R. Macías · J. F. A. Soltero

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Abstract Proximate, thermal, morphological and rheological properties of canned “negro Querétaro” bean pastes, as a function of fat content (0, 2 and 3 %) and temperature (60, 70 and 85 °C), were evaluated. Raw and precooked bean pastes were characterized by scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). Well-defined starch granules in the raw bean pastes were observed, whereas a gelatinized starch paste was observed for the canned bean pastes. The DSC analysis showed that the raw bean pastes had lower onset peak temperatures (79 °C, 79.1 °C) and gelatinization enthalpy (1.940 J/g), compared to that precooked bean pastes (70.4 °C, 75.7 °C and 1.314 J/g, respectively) thermal characteristics. Moreover, the dynamic rheological results showed a gel-like behavior for the canned bean pastes, where the storage modulus (G') was frequency independent and was higher than the loss modulus (G''). The non-linear rheological results exhibited a shear-thinning flow behavior, where the steady shear-viscosity was temperature and fat content dependent. For canned bean pastes, the shear-viscosity data

followed a power law equation, where the power law index (n) decreased when the temperature and the fat content increased. The temperature effect on the shear-viscosity was described by an Arrhenius equation, where the activation energy (E_a) was in the range from 19.04 to 36.81 KJ/mol. This rheological behavior was caused by gelatinization of the starch during the cooking and sterilization processes, where starch-lipids and starch-proteins complex were formed.

Keywords Canned bean pastes (*Phaseolus vulgaris* L.) · Fat content · Temperature · Rheology · Morphology

Introduction

Beans (*Phaseolus vulgaris* L.) are an important food in the traditional Mexican diet. This dried seed has excellent nutritional properties protein, fiber, vitamin B-complex, iron and calcium, as well as low content of fat (Zamindar et al. 2011). Hulling, pre-cooking, canning, dehydration and extrusion are some of the technologies used to process beans (Echavarría and Velasco 2010; Güzel and Sayar 2012).

At present, there are a number of studies that address processing of beans and the effects on their nutritional and sensory properties. The post harvest storage of beans at different conditions of temperature, time and humidity may cause hard-to-cook phenomenon, starch gelatinization, loss of nutrients, change in polyphenols of the seed coat, and decrease of the antioxidant activity (Beninger et al. 2005; Machado et al. 2008). Several authors have reported that the processing condition of beans modifies their nutritional and textural properties. Candela et al. (1997) reported that cooking produced a decrease in carbohydrate and amino acid contents, and increases in the protein content of kidney

A. H. Martínez-Preciado · Y. Estrada-Girón ·
A. González-Álvarez · E. R. Macías · J. F. A. Soltero (✉)
Departamento de Ingeniería Química, Universidad de Guadalajara,
Blvd. M. García Barragán # 1451,
Guadalajara, Jal. 44430, Mexico
e-mail: jfasmm@hotmail.com

J. F. A. Soltero
e-mail: armandosolteros@yahoo.com

V. V. A. Fernández
Departamento de Ciencias Tecnológicas,
Universidad de Guadalajara,
Av. Universidad # 1115,
Ocotlán, Jal. 47810, Mexico

beans. Martín-Cabrejas et al. (2006) demonstrated that the dehydration process in legumes changes the content of insoluble fiber and decreases the α -galactosides content.

On the other hand, the rheological properties of semi-solid legumes pastes are associated with the structure and composition of proteins and carbohydrates. Liu and Hung (1998) reported that the chickpea protein dispersion exhibited Newtonian behavior at low protein or salt concentrations. Ahmed et al. (2006) studied the thermorheological characteristics of soybean protein isolate. They found that increasing the amount of soybean protein and the processing temperature causes that the proteins behaved like a rigid gel. Moreover, Gerschenson and Bartholomai (1986) reported that the changes in the viscosity of canned beans, produced by the heating process, causes protein solubilization. Franco et al. (1998) analyzed the viscoelastic behavior and the changes in texture of lupin protein-stabilized emulsions. They concluded that an increase in the energy input during the emulsification process decreased the droplet diameter of the emulsion; however, it increased the rheological and textural parameters. Furthermore, Revilla and Vivar-Quintana (2008) studied the effect of the canning process on the texture of faba beans. They found that the heat-treating conditions affected the external skin texture of beans; however, the addition of chelating agents to the brine did not affect the textural parameters.

Some studies only address the changes in the rheological properties of beans in terms of the viscosity, but they do not explore, to a profound extent, the behavior of bean pastes in the linear and non-linear viscoelastic region. Therefore, it is important to investigate the rheological properties of different formulations of bean pastes, with the aim of evaluated the changes in their structure.

The present study was undertaken to investigate the effect of canning, sterilization and temperature processing and the fat content in the microstructural, thermodynamical and linear and non-linear rheological properties of bean pastes of “negro Querétaro” var. In order to study this effect, raw, precooked and canned bean pastes were analyzed by differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and rheometry.

Materials and methods

Materials

Black beans (*Phaseolus vulgaris* L.), “negro Querétaro” variety, used in this work were provided by the Verde Valle Company (Mexican beans processor). Corn oil was purchased at the local market. To obtain beans flour, beans were ground using a MiniThomas mill (Thomas Scientific Co., NJ, USA), until passing through a 0.5 mm mesh.

Proximate chemical analysis of the beans flour was performed according to the AOAC methods (1995): moisture (925.19), ash (923.03), total lipids (920.85), proteins (960.52), and crude fiber (962.09). The total carbohydrates were calculated as the difference from the other components.

Canning

The bean pastes samples were prepared by weighting 250 g of bean flour. In order to adjust the moisture content at 75 % (w/w), and oil content to 0, 2 and 3.0 % (w/w), were added 800 g, 780 g and 770 g of bidistilled water, and 0 g, 20 g and 30 g of corn oil respectively. The moisture content was established according to the Mexican standard, NMX-F-478-NORMEX-2005 (Ministry of Economy, Mexico 2005) The mixture was precooked at 93 °C for 10 min at atmospheric pressure (627.3 mm de Hg). Then, 200 g of precooked paste was placed into a polymeric-lined steel can (2.6×3.0 in), which was sealed and sterilized in an autoclave (Felisa) (FELI Co., Jalisco, México) at 121 °C at a pressure of 2.5 kg/cm² during 15 min. The cooked bean pastes were cooled to room temperature and stored at 4 °C until further analyses.

Thermal properties

Differential Scanning Calorimetry (DSC) measurements were conducted to investigate starch retrogradation temperatures and enthalpy of raw, precooked and canned bean pastes. Thermograms were obtained with a Q2000 differential scanning calorimeter (TA Instruments Co., DE, USA) that was previously calibrated with indium, water and n-octane standards. All scans were performed with heating rates of 1 °C/min. Hermetical aluminum pans (TA Instruments Co., DE, USA) were used to minimize losses by evaporation. Samples in the sealed pans were weighted before and after each test. Results from samples that lost weight were discarded. The enthalpic changes were determined by measuring the area under the curve of the thermograms using the Universal software version V4.5A of TA Instruments.

Morphological properties

Scanning Electronic Microscopy (SEM) was used to determine the microstructural characteristics of the starch granules and changes of the bean pastes due to the sterilization processes. A JEOL (5400 LV) scanning electron microscope (JEOL, Tokyo, Japan) was used for this study. An electron beam with accelerating voltage of 20 kV was used on each sample. The samples were prepared as follows: approximately 5 g of raw, precooked or canned bean pastes were dried in a

vacuum oven (Precision) (GCA Co., IL, USA) at 50 °C and 15 kg/cm², until the sample reached constant weight. Then, 1 cm² of dried sample was placed in a brass sample holder and coated with a thin gold film to enhance image resolution. This was made using an EMS-76 Sputter coater (Ernest F. Fullam Co., CA, USA), with an applied current of 5 KV, 69 mA for 3 min.

Rheological properties

Temperature ramp, oscillatory and steady simple-shear experiments were performed in an ARES 22 rotational strain-controlled rheometer (TA Instruments Co., DE, USA) with a cone-and-plate geometry, with a cone angle of 0.1 rad, 25 mm in diameter and with a cone truncation gap of 0.053 mm. A humidification chamber was set around the geometry to minimize water evaporation from samples. Temperature was controlled within ± 0.1 °C during measurements. For each test, approximately 0.5 g of well-mixed sample was carefully transferred to the rheometer plate to minimize possible destruction of the sample. Measurements were carried out at 60, 70 and 85 °C. All rheological measurements were performed at least three times. Frequency sweeps were made at an oscillatory strain deformation range of 0.1 to 0.4 %, which were within the linear viscoelastic region (LVR). LVR is defined as the region where the storage (G') and the loss (G'') moduli are strain independent. Simple shear measurements were made under steady state conditions. Temperature ramp measurements from 40 to 90 °C were applied to study the gelatinization temperatures of raw and precooked bean pastes. The measurements were fixed at a constant frequency of 10 rad/s, a constant deformation of 5 % and a ramp rate of 1 °C/min.

The steady simple-shear viscosity was fitted using a power law equation applied to the shear-thinning region (Rao 1999):

$$\sigma = K \dot{\gamma}^{n-1} \quad (1)$$

Where σ is the shear stress (Pa), K the consistency index (Pa sⁿ), $\dot{\gamma}$ the shear rate (s⁻¹) and n is the power law index.

Results and discussion

Proximate analysis

Proximate analysis of the bean flour var. “negro Querétaro” is shown in Table 1. As observed, the bean flour has a low content of total lipids; however, is rich in proteins and carbohydrates, mainly starch. The moisture content of “negro Querétaro” beans was similar (8.35 %) to that found for four varieties of Negro beans (8.87–9.19 %) (Carmona-

Table 1 Proximate chemical analysis of “negro Querétaro” (*Phaseolus vulgaris* L.) bean flour (%wwb)

Components	
Moisture	8.35 $\pm$ 0.24
Ash	3.62 $\pm$ 0.02
Total lipids	5.07 $\pm$ 0.59
Starch	53.84 $\pm$ 1.54
Sugars	3.44 $\pm$ 1.80
Crude fiber	2.32 $\pm$ 0.38
Protein (Nx6.25)	23.36 $\pm$ 1.70

(mean $\pm$ standard deviation, $n=3$)

García et al. 2007). Sammán et al. (1999) found that the moisture content of Argentinean black beans ranged from 11.78 to 13.37 %. The protein content was also similar to that for beans var. Mayocoba (23.41 $\pm$ 0.49 %) (Osorio-Díaz et al. 2005), and for four varieties of black beans (18.9 % and 24.2 %) (Vargas-Torres et al. 2004). The total lipids content was higher to that reported for some authors. Osorio-Díaz et al. (2005) reported a lipid content of 1.98 $\pm$ 0.29 % for Mayocoba bean, Vargas-Torres et al. (2004) reported values of 1.26 to 2.8 %, for different black bean varieties. The lipid content in beans is important because of the amylose-lipid complex, which is formed when beans are cooked. This complex modifies the product texture, rheological properties, digestibility and storage stability (Kaur and Singh 2000). The ash content for the samples analyzed in this work (3.62 %) was similar to that reported elsewhere for different varieties of Argentinean black beans (Sammán et al. 1999). Hence, the black bean flour, obtained from the Negro Querétaro variety used in this study constitutes a healthy food product, that combined with cereals like maize (*Zea mays*), rich in sulfur amino acids, may produce a nutritional food with a good energy balance (Pachón et al. 2009).

Morphological properties

SEM images of the vacuum-dried raw, precooked and canned bean pastes with different fat content are depicted in Fig. 1. In this Figure, columns 1 and 2 show the microstructure of the bean pastes with a fat content of 0 and 3 % (w/w), respectively. Raw beans paste with 0 % (w/w) of fat content (Fig. 1a) shows irregular oval-shape starch granules with sizes of 10–40 μ m in length and 10–25 μ m in width as well as small spherical shape granules of 10 μ m. It can be noticed that the starch granules have well defined shape and no damage. The size and shape observed in this sample is characteristic of starch granules reported elsewhere (Kaur et al. 2011; Sudha and Leelavathi 2011). On the other hand, the raw beans paste, with a 3 % (w/w) of fat content (Fig. 1b), show a plasticized surfaced with few interconnected starch granules, with sizes of 10–40 μ m in length, and 12–30 μ m in width. It is well known that the addition of water, or other plasticizers (such as oil), enables the starch to obtain

homogeneous smooth surfaces, which considerably reduces flow properties and degradation of starch (Sudha and Leelavathi 2011).

Figures 1c and d show the microstructure of bean pastes with a fat content of 0 and 3 % (w/w), respectively. Figure 1c reveals swollen starch granules with irregular shape and size; between 10–40 μm in length, and 10–25 μm in width. Clearly, the starch granules were damaged by the precooking process, which causes the amylose release from the granule (Biliaderis et al. 1980). Increasing the fat content to 3 % (w/w), a complete plasticized surfaced is produced, where all the starch granules are integrated to the paste (Fig. 1d). Figures 1e and f show the canned bean pastes with a fat content of 0 and 3 % (w/w), respectively. In both figures, a gelatinized starch paste is observed, indicating that a starch retrogradation occurred as a consequence of the heating process, leading to a total disruption of granules. The starch retrogradation is related to a structure ordering where the starch chains reassociate with the amylose molecules (Tester and Debon 2000). Besides, the granule disruption, with the consequently starch dissolution, is known as pasting, and is associated with the increase of viscosity (Douzals et al. 1996).

Thermal properties

DSC thermograms of raw, precooked and canned bean pastes with 0 % (w/w) of fat content are shown in Fig. 2. As can be noticed, an endothermic transition is observed for the raw bean paste in the temperature range where starch gelatinization process occurs. The whole raw bean paste showed an onset temperature (T_o), a mean peak temperature (T_{max}) and a completion temperature (T_e) of 79.01, 79.12 and 81.20 $^{\circ}\text{C}$, respectively. Moreover, the change of enthalpy or enthalpy of gelatinization (ΔH_{gel}) was found to be 1.940 J/g. This transition is due to the starch gelatinization, which has been well documented by DSC studies of starch based food systems (Biliaderis et al. 1980). The ΔH_{gel} provides information of the energy changes during the melting of recrystallized amylopectin (Karim et al. 2000). Precooked bean paste showed a long endothermic transition, where the values of T_o , T_{max} and ΔH_{gel} were 70.39, 75.68 $^{\circ}\text{C}$ and 1.314 J/g, respectively. The reduction in T_o of ca. 8.6 $^{\circ}\text{C}$ is attributed to a gel fusion in the crystallized starch (Biliaderis et al. 1980). After cooling down the gelatinized bean paste, starch retrogradation occurs leading to a reassociation process (hydrogen bonding between starch chains) that causes crystallization (Hoover 2001). Sasaki et al. (2000) attributed the reduction on the temperature gelatinization and ΔH_{gel} of retrograded starches to a weaker starch crystallinity. For canned bean pastes, the transition temperature was not detected in the temperature range studied, indicating that the starch was completely gelatinized.

These results corroborate the morphology observed by SEM images (Fig. 1e), where a total starch granules disruption was observed for canned pastes. The differences in transition temperature and transition enthalpy may be attributed to the differences in shape and size of starch granules, amylose content, internal molecular arrangement of starch fractions within the granule, and different botanical starches sources and proteins (Yáñez-Farías et al. 1997). On the other hand, the influence of oil content on the gelatinization and melting parameters was not significant, remaining barely identical. Increasing the amount of oil (3 % (w/w)), T_{max} , T_o and T_e , slightly shift to higher temperatures; meanwhile, ΔT , defined as ($T_e - T_o$) remained constant (data not shown). Moreover, ΔH_{gel} remained unchanged considering the error bars of ± 1 J/g. Results obtained in this study show that the gelatinization process is controlled by the high amount of moisture (75 % (w/w)), which were similar with previously reported results (Kaur and Singh 2010).

Pasting properties

Gelatinization and retrogradation of the starch are important physicochemical properties considered in the food industry (Olayinka et al. 2011). The gelatinization properties of the raw and precooked bean pastes were analyzed using a rotational rheometer, which allows the continuous assessment of dynamic moduli at different temperatures and frequencies. In typical rheological experiments, the storage modulus (G') measures the energy stored in the material per cycle of deformation, meanwhile the loss modulus (G'') measures the energy lost per cycle of deformation (Steffe 1996). The ratio of loss modulus to storage modulus for each cycle of deformation is defined by loss tangent ($\tan \delta = G''/G'$), which is another rheological parameter used to characterize the viscoelastic properties of materials. $\tan \delta < 1$ indicates a predominantly elastic behavior, meanwhile $\tan \delta > 1$ indicates a predominantly viscous behavior. These types of tests are important because these make possible to determine the gel-type behavior of materials.

Figure 3 shows the effect of temperature on G' and $\tan \delta$ for raw and precooked bean pastes for 0 and 3 % (w/w) of fat content. For the raw bean paste with 0 % (w/w) of fat content (open circles), G' increases at 60.3 $^{\circ}\text{C}$, and continues increasing as the temperature rises, reaching a maximum (G'_{max}) at 82.05 $^{\circ}\text{C}$ (Fig. 3a). This is related to the gelatinization temperature, or the temperature at which the maximum moduli is reached. The initial increase in G' is attributed to the degree of starch granular swelling (Eliasson 1986) and the intergranule contact, which creates a three-dimensional network of the swollen granules (Sankarakutty et al. 2010). With further temperature increase, G' decreases, indicating that the gel structure is destroyed. For

Fig. 1 Scanning electron microscopy (SEM) images of raw (a), precooked (b) and canned (c) of bean pastes with 0 % (w/w) (column 1) and 3 % (w/w) (column 2) of fat content

the raw bean paste, the $\tan \delta$ vs. temperature curve (Fig. 3b) exhibits a broad peak between 67.5 and 75.9 °C. The molecular relaxation observed around 75.9 °C may be reflected in the significant drop of G' induced by the structure destruction in this temperature range.

Fig. 2 Thermograms of bean pastes with 0 % (w/w) of fat content

Moreover, for the raw bean paste with 3 % (w/w) of fat content (open squares), G' shows a $G'_{\max}$ of 80.95 °C (Fig. 3a), and the initial increase of G' is shifted to lower temperatures (60 °C). Besides, it can be noticed that $\tan \delta$ (Fig. 3b) presented a narrow peak between 63.9 to 68.2 °C. The $\tan \delta$ values are higher compared with those of the raw bean paste with 0 % (w/w) of fat content indicating that samples with 3 % (w/w) of fat are more viscous. On the other hand, the precooked bean paste with 0 % (w/w) (closed circles) and 3 % (w/w) (closed squares) of fat content showed significant differences compared with the raw bean pastes. For instance, in both types of bean pastes, G' increases progressively as temperature increases (Fig. 3a), however, $G'_{\max}$ was not detected. Meanwhile, $\tan \delta$ peaks were shifted to lower temperatures; the bean pastes with 3 and 0 % (w/w) of fat content presented a temperature shift of 60 and 66.5 °C, respectively. It can be noticed, that the precooked bean pastes (0 and 3 % (w/w) of fat content) had lower $\tan \delta$ values, which means that they were more structured and more solid-like (elastic) compared with the raw bean pastes (Fig. 3a). These results suggest that the precooked bean pastes are partially gelatinized, which is an indication of a stronger gel structure, with a more solid-like behavior. On the other hand, the pasting temperature

Fig. 3 Temperature ramp test for storage modulus (G') (a) and $\tan \delta = G''/G'$ (b), of raw (open symbols) and precooked (closed symbols) “negro Querétaro” bean pastes at different percentages of fat content (% (w/w)): (○) 0; (□) 3. Inset: Heating and cooling kinetics curves of raw and precooked bean paste with (○) 0 and (□) 3 % (w/w) of fat content. The solid line is the applied temperature ramp

reduction and the increase of $\tan \delta$ are attributed to the oil and proteins presented in beans pastes. During cooking, the proteins are denatured and the starch is gelatinized, leading to the formation of complexes between starch and lipids and between proteins and lipids (Ho and Izzo 1992). Both phenomena affect the pasting properties. The lipids contained in beans, either those naturally present in the grain or those added during the process, could form an amylose-lipid complex. However, the triglycerides contained in corn oil are reported as not complex-forming because of their sterically hindered structure, the monoglycerides formed during heating can be capable of forming complexes, as well as, monoglycerides naturally present in the beans flour. The origin of the starch-lipid complex is due to the ability of the amylose fraction of starches to bind fatty acids or linear alcohols, which are hosted in the helical cavity of amylose (Nuessli et al. 2003). Fanta et al. (2002) have attributed the complex formation to the transfer of the guest molecules

from water to a less polar environment within the amylose helix. The amylose ability to form complexes with organic compounds has been used to fractionate amylose from amylopectin. Some authors have reported an affection in pasting properties of starch pastes by the complex formation (Singh et al. 2002). Other authors however, have reported that by increasing the protein content of rice starch pastes, the viscosity decrease meanwhile the pasting temperature increases (Lim et al. 1999). Inset in Fig. 3 shows the heating and cooling kinetics-pasting curves for raw and precooked bean pastes with 0 and 3 % (w/w) of fat content. During heating, $\tan \delta$ increases progressively, and increases with the fat content. It can be observed that for the raw bean paste with 3 % (w/w) of fat content, the $\tan \delta$ peak shifts to higher time and the area under the peak increases as well, compared to the 0 % (w/w) sample. Hence, the paste stability improved, not only due to the friction of the starch granules that have swelled, but also by the starch-lipid complexes formed during the heating. Then, it is assumed that the increased stability of the starchy paste with the oil was also due to the formation of crystalline amylose-lipid complexes, which form a shear resistant network. On the other hand, cooling the samples to 30 °C produced the decrease of $\tan \delta$ in raw bean pastes, where the retrogradation process is the cause of the decrease in viscosity.

Dynamic shear rheological properties

Figure 4 shows graphs of frequency sweeps as a function of temperature for canned bean pastes with 3 % (w/w) of fat content. For all canned bean pastes studied, a solid-like response is observed, where the storage modulus was higher than the loss modulus ($G' > G''$) (Figs. 4a and b). Moreover, both moduli show a small oscillation frequency (ω) dependence (Fig. 4a), without crossover of G' and G'' throughout the frequency range studied. These results indicate that their rheological behavior seems to be a *weak gel-like behavior* (Rao 1999).

On the other hand, $\tan \delta$ values for all canned bean pastes decreased as the oscillatory frequency increased, and they were smaller than unity, which indicate a predominantly elastic behavior (Fig. 4c). This type of behavior was similar to that reported by Puppo and Añón (1998). In this study, a dependence of the linear viscoelastic properties on temperature is evident where both types of moduli increased when the temperature increased from 60 to 70 °C (see Fig 4). At 70 °C the storage and loss moduli exhibited a maximum, which is an indication of a stronger gel structure, compared with the canned bean at 60 °C. Furthermore, when increasing the temperature at 85 °C, G' and G'' decreased even more than those of bean pastes at 60 °C. These results suggest that the bean gels are affected at high temperatures, where their cross-links densities decreased. At high

Fig. 4 Frequency sweep test for storage modulus (G') (a), loss modulus (G'') (b) and $\tan \delta = G''/G'$ (c), for canned “negro Querétaro” bean paste with 3 % (w/w) of fat content measured at different temperatures (°C): (□) 60; (○) 70; (△) 85

temperatures, the gel structure is destroyed during prolonged heating. This destruction is due to the melting of the crystals present in the gel, which deforms and loosens the structure, causing the decrease of elasticity (Eliasson 1986).

Figure 5 shows the variation of G' , G'' and $\tan \delta$ vs. frequency for canned bean pastes measured at 60 °C for the fat contents selected in this study. It is evident that, G' decreased as the fat content increased (Fig. 5a), meanwhile, the G'' increased (Fig. 5b). Moreover, similarly to Fig. 4c, $\tan \delta$ values were smaller than unity, indicating a predominantly elastic behavior (Fig. 5c). However, the bean paste with a 3 % (w/w) of fat content presented the highest value, indicating that this type of paste is less elastic than pastes with 2 and 0 % (w/w) of fat content. This behavior was expected because it is well known that fat acts as a plasticizer, which reduces the elasticity. Also, the glass-rubber transition shifts to a lower temperature reducing the network elasticity. This plasticizing effect on starch is similar to that reported elsewhere (Sankarakutty et al. 2010). Moreover, as it was discussed before, the amylose-lipid complex formation affects the network elasticity. Singh et al. (2002)

Fig. 5 Frequency sweep test for storage modulus (G') (a), loss modulus (G'') (b) and $\tan \delta = G''/G'$ (c) for canned “negro Querétaro” bean paste with 60 °C at different percentages of fat content (% (w/w)): (□) 0; (○) 2; (△) 3

reported that the amylose-lipid complex formation occurring during gelatinization of corn starch decreased G' and G'' .

From these observations, it can be concluded that the rheological response is attributed to the gelatinized starch and their relationship with proteins contained in the bean pastes. During thermal processing such as cooking and sterilization, a softening of legumes caused by the gelatinization and hydrolysis of starch, leads to rupture of the starch, where the amylose simultaneously leached out from the granule (Revilla and Vivar-Quintana 2008). Therefore a three dimensional network is formed when gelatinization occurs, mainly because the amylose leached out from the starch granules (Tester and Morrison 1990). The dynamic rheological measurements of canned bean pastes were similar to those reported by Franco et al. (1998). They reported that isolated lupin protein pastes had a predominantly elastic behavior ($G' > G''$), due to the formation of a structural network between oil, water and lupin protein. Apichartsrangkoon (2002) studied the dynamic properties of gluten/soy protein gels. Prior to the rheological measurements, the system was heated to 90 °C for different periods of time. This author found that an increase in the heating time also increases the dynamic

moduli. Moreover, the gluten/soy protein paste presented a weak-gel behavior. Additionally, Ahmed et al. (2006) reported that different concentrations of isolated soybean protein diluted in water, had an elastic behavior.

Steady shear rheological properties

Steady shear viscosity (η) vs. shear rate ($\dot{\gamma}$) as a function of temperature for canned bean pastes with 0, 2 and 3 % (w/w) of fat content is presented in Figs. 6a, b and c, respectively. All samples showed a shear thinning behavior at all shear rates studied. Shear thinning behavior is characterized for a viscosity decrease with increasing shear rate due to a structure alignment or destruction, and is followed by the most non-Newtonian foods (Rao 1999). Some authors have reported shear-thinning behavior on several starch based pastes (Achayuthakan and Supphantharika 2008).

Solid lines in Fig. 6 are the best fit of the power law (Eq. 1), which is applied at the shear-thinning region, the values of which are disclosed in Table 2. The power law is an important model for understanding the flow behavior of many types of foods, which indicates the extent of shear-thinning behavior as it deviates from 1. It was found that the

Fig. 6 Shear viscosity for canned bean pastes with 0 (a), 2 (b) and 3 (c) of fat content (% (w/w)) as a function of temperature (°C): (□) 60; (○) 70; (△) 85. The solid lines are the best fit with the Eq. (1)

flow behavior index value is less than 1 ($n < 1$), indicating that the canned bean pastes behave like a shear-thinning fluid (Rao 1999). The bean pastes exhibited a decrease in the power law index (n), as the temperature and the fat content increased. Similar results have been reported for starch pastes elsewhere. Liu and Hung (1998) studied the flow properties of chickpea protein. They also found a non-Newtonian behavior when increasing protein or salt concentration. Some authors have found an n value for waxy corn starch pastes at 25 °C of 0.51, and for mixtures of waxy corn starch with guar and xanthan gums of 0.52 and 0.36, respectively (Achayuthakan and Supphantharika 2008). Yoo et al. (2005) reported n values for rice starch dispersion and rice starch dispersion containing guar gum at 20 °C of 0.24 and 0.18, respectively.

Effect of temperature and fat content on relative viscosity

Figure 7 depicts the average relative viscosity (η_r) dependence with temperature obtained under steady shear rate measurements for canned bean pastes with different fat contents. η_r is defined as the shear viscosity measured at a fixed shear rate, and here η_r was selected at $\dot{\gamma} = 10 \text{ s}^{-1}$. As can be noticed, a linear dependence with temperature is observed, where η_r decreases for all bean pastes. The effect of temperature on viscosity is very important in the evaluation of foods properties that will be subject to varying processing temperatures, which could impact during storage and consumption (Rao 1999). The viscosity reduction may be explained in terms of a freer molecule-to-molecule interaction caused by the increase in temperature (Adebowale and Sanni 2011). During heating, the intermolecular forces of the bean pastes are broken, producing in the samples less opposition to the shear. These results are in good agreement with those reported by Gerschenson and Bartholomai (1986). They found that increasing the temperature and decreasing the content of soluble solids in beans flour, a decrease in viscosity was observed.

The inset in Fig. 7 shows a η_r vs. inverse temperature graph obtained from the bean pastes. The temperature effect on bean paste viscosity follows an Arrhenius type equation, which indicates a thermal activated process that follows the equation:

$$\eta(T) = \eta(T_0) \exp\left(\frac{E_a}{RT}\right) \quad (2)$$

where, R is the gas constant, and E_a is the activation energy and $\eta(T_0)$ is a coefficient depending on the nature of the material. E_a is the energy barrier that must be overcome before the elementary flow process could occur (Chun and Yoo 2004). The values of the activation energy, calculated from the inset in Fig. 7 are reported in Table 3 as a function

Table 2 Power Law parameters for canned “negro Querétaro” beans pastes

T (°C)	Content of fat (% (w/w))								
	0			2			3		
	K^*	n^{**}	R^2	K^*	n^{**}	R^2	K^*	n^{**}	R^2
60	224	0.3015	0.997	221	0.1715	0.99	193	0.0335	0.997
70	136	0.3138	0.998	138	0.1263	0.99	136	0.0194	0.998
85	97	0.2572	0.99	120	0.0382	0.98	127	−0.0788	0.999

*Consistency index (K in Pa s^n) /**Power law index (n)

of fat content. Good agreement (R^2) with linearity was found. It was found that the activation energy of bean pastes is dependent with their fat content. Higher E_a means higher viscosity dependence on temperature changes (Rao 1999). Some authors have reported an Arrhenius temperature behavior for modified corn starch (Park et al. 2004), rice flour dispersion (Chun and Yoo 2004), and a rice starch-xanthan gum mixture (Kim and Yoo 2006). The values of E_a for the bean pastes studied here are lower than those found in other starch pastes. Kim and Wang (1999) reported an E_a value of 57.1 KJ/mol for waxy corn starch pastes. Moreover, η_r decreases as the fat content augments. As was discussed above, the viscosity reduction on pasting properties is attributed to a complex formation between oil and starch. However, in steady state-shear experiments, the η_r reduction is attributed to the oil, which acts as a plasticizer. This reduced the glass-rubber transition temperature (T_g) of the crystallized starch, which is similar to that observed in semicrystalline

polymers. The decrease of T_g depends on the amount of the plasticizer, and its compatibility with the polymer.

Conclusion

A full study of the proximate, morphological, thermal, pasting and rheological properties of bean pastes var. “negro Querétaro” (*Phaseolus vulgaris* L.) was reported. Morphological characteristics, such as shape and size of the starch granules exhibit significant differences. Raw bean pastes showed oval-shape starch granules with sizes of 10–40 μm in length and 10–25 μm in width. Whereas, precooked bean pastes showed swollen and damage starch granules with irregular shapes and similar sizes to those observed for the raw bean pastes. On the other hand, the canned bean paste showed a complete gelatinized starch paste. Gelatinization temperatures determined by the thermograms (T_o , T_{max} and T_c) and (ΔH_{gel}), of raw and precooked bean pastes differ significantly. ΔH_{gel} of raw bean paste were higher (1.940 J/g) than that obtained for the precooked bean paste (1.314 J/g), as well as T_{max} . These reductions are attributed to the partially retrograded precooked bean pastes. The pasting properties were modified by the addition of oil to the bean pastes, which suggest that a starch-lipid complex was formed. The rheological response was caused by gelatinization and hydrolysis of the starch during the cooking and sterilization processes. The dynamic rheological characterization showed that the canned bean pastes, behave like “weak-gels”, with a predominating elastic behavior ($G' > G''$). The predominating elastic behavior is associated to the formation of a starch-protein-fat network. Moreover, the

Fig. 7 Relative shear viscosity (η_r) measure at shear rate ($\dot{\gamma}$) of 10 s^{-1} vs. temperature for canned bean pastes at different percentages of fat content (% (w/w)): ($\square$) 0; ($\circ$) 2; ($\triangle$) 3. The solid lines are aide to the eye. Error bars indicate standard error. Inset: Arrhenius plot of the relative shear viscosity for canned bean pastes at different percentages of fat content (% (w/w)): ($\square$) 0; ($\circ$) 2; ($\triangle$) 3. The solid lines are the best fit with the Eq. (2)

Table 3 Activation energy values for canned “negro Querétaro” beans pastes

Fat (% (w/w))	$\eta_{(T_0)}$	E_a^a (KJ/mol)	R^2
0	7.505e-5	36.81	0.975
2	4.98e-5	36.86	0.862
3	1.17e-2	19.04	0.96

^a Activation energy (E_a)

canned bean pastes exhibited shear-thinning flow behavior; where the Power Law parameter is dependent on temperature and fat content. The effect of temperature on η_r of the canned bean pastes was described in terms of an Arrhenius type equation with good correlations values (R^2). E_a values were lower than those reported in the literature for starch dispersions. In general, the presence of oil and temperature in the canned bean pastes modified the steady and dynamic shear rheological properties, as well as their morphology and pasting properties.

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