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THE RELATIONSHIP BETWEEN RHEOLOGICAL PROPERTIES, COLOR AND STRUCTURAL CHARACTERIZATION OF TOMATO PASTE (COLD-BREAK) DURING PROCESSING

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ABSTRACT

The relationship between rheological and pectin fractions contents and between lycopene, total carotenoids contents and Hunter color parameters of tomato paste during processing were studied. During concentration of tomato juice to paste, rheological values (apparent viscosity, yield stress, consistency coefficient), pectin fractions, lycopene and total carotenoids contents increased significantly, while lightness (L^*), redness (a^*) and yellowness (b^*) values decreased.

The results showed a well positive correlation between rheological properties especially, apparent viscosity and oxalate-soluble, acid-soluble, total pectins contents. There was a good relation between L^* value and concentration of lycopene and total carotenoids. The obtained correlations can be used in controlling and understanding many problems arising during processing of tomato paste, especially in the flow behavior and color attributes.
Keywords*:* Tomato paste, rheological properties, color, lycopene, carotenoids, pectin.

INTRODUCTION

Tomato (*Lycopersicon esculentum)* is one of the most popular of vegetables, used as a salad, in food preparations and juice (Kaur *et al*., 2008). The annual production of tomato in Egypt is about 7.55 million tons (FAO, 2009); a small portion of this sum is processed (~1%) into paste (Shatta, 2000). While, a large part of the world tomato crop is processed into tomato paste, to be used in preparing some food products as soups, sauces and ketchup (Valencia *et al.,* 2003).

One of the main quality attributes is viscosity that should be considered to determine the overall quality and consumer acceptability of many tomato products. Furthermore, the flow properties are decisive to assess control and optimization of the unit operations related to the manufacture of different tomato products, i.e. mixing, pumping, filling, ...etc. Different empirical models have been used to characterize the flow behavior of tomato concentrate. Many of them relate to solid concentration, particle size and processing conditions, like breaking temperature, finishing, concentration and homogenization of both tomato juice and tomato paste (Xu *et al.,* 1986; Sharma *et al.,* 1996 and Yoo and Rao, 1996). In fact, these processing conditions have an indirect effect on the apparent viscosity and flow parameters, by influencing the physicochemical characteristics of the water insoluble solids particles and serum viscosity. Several researchers have shown that difficulties in quality control arise from the great variation in flow behavior in commercial tomato paste caused by different agronomical and processing conditions (Sánchez *et al.,* 2002 and Thybo *et al.,* 2005). A number of studies have been conducted on the rheological behavior of tomato products at low concentrations. However, for concentrated tomato products such as tomato paste, few studies are available, probably due to a number of measurement problems that occur because of the high concentration of large particles. Moreover, tomato paste exhibits complex rheological behavior, i.e. it is a non-Newtonian, shear-thinning and time dependent fluid that shows an apparent yield stress (Lorenzo *et al.,* 1997; Abu-Jdayil *et al.,* 2004 and Bayod *et al.,* 2008).

Color is another important quality factor in processed tomato concentrates, since it influences consumer acceptability. Many reactions can take place during thermal processing and affect color. Among them, the most common are pigment degradation, especially lycopene and browning reactions such as the Maillard reaction and oxidation of ascorbic acid (Barreiro *et al.*, 1997). Lycopene is the principle carotenoid, causing the characteristic red hue of tomatoes. Tomato lycopene content varies considerably, reflecting the influence of variety, maturity and both agronomic and environmental conditions during growing (Shi and LeMaguer, 2000; George *et al.,* 2004 and Kaur *et al.,* 2006).

The aim of this work was to study the relationship between some rheological properties (apparent viscosity, yield stress, consistency coefficient) and pectin fractions, as well as the relation between the Hunter color parameters and lycopene content of tomato paste during the processing.

MATERIALS AND METHODS

1. Materials

Tomato juice from Castle rock variety was processed into paste in Ismailia National Company for Food Industries (Foodico) using the cold-break method. Samples from the juice, each of the three stages of concentration and after pasteurization were collected in polyethylene bags and transferred to the laboratory to analyze.

2. Methods

Preparation of Tomato paste

The tomatoes were crushed and extracted at 60°C and strained by three refiners with diameters of 1.2, 0.8 and 0.4 mm, followed by holding for periods ranging from seconds to minutes during which the enzymes liberated as result of crushing catalyzed the breakdown of pectins. The concentration process passed through three stages, the first at 55-60°C, the second at 65-75°C, the last at 75-80°C under vacuum, followed by flash pasteurization at 105-110°C and filling in aseptic bags (Gould, 1974). The final concentration reached about 36 °Brix.

2.1. Chemical analysis

Moisture content, total soluble solids (TSS), pH value, titratable acidity (as citric acid) and total pectins (water-soluble, ammonium oxalate 0.2% and 0.05 N HCl fractions) were determined according to the AOAC (1990). Carotenoids were assayed and calculated according to the method described by Wettestein (1957) and lycopene content was determined as described by Ranganna (1977).

2.2. Color attributes measurements

Color attributes; lightness (L^*), redness (a^*) and yellowness (b^*) of tomato juice and paste were measured in a cylindrical sample cup (5-cm diameter × 2-cm high) filled to top using a Labscan Model LSXE (Hunter Associates Laboratory, Reston, VA, USA). Standard color plate No. 400 with reflectance values of L^* = 25.70, a^* = 33.60 and b^* = 14.70 was used as a reference. The tomato paste samples were diluted to 12 °Brix before measuring (Gomez *et al.,* 1998). The red-yellow ratio (a^*/b^*) was reported to indicate the redness of tomato paste (Min and Zhang, 2003).

2.3. Rheological measurements

Rheological properties of tomato juice during concentration were determined by the Brookfield digital rheometer model DV-III+ (Brookfield Engineering Lab., INC., Middleboro, USA) at 20 °C. The Brookfield small sample adapter and Sc_{4-14}, Sc_{4-21} spindles were used. The data were analyzed using the Bingham plastic and Power law mathematical models (Hegedusic *et al.,* 1995). These models are:

$\tau = \tau_o + \eta\gamma$ and $\tau = k\gamma^n$, where: τ = shear stress (N m^{-2}), τ_o = yield stress (N m^{-2}), η = plastic viscosity (mPa s), γ = shear rate (s^{-1}), k = consistency coefficient (mPa s^n), n = flow behavior index (dimensionless). The apparent viscosity (mPa s) was measured at 100 rpm at 20 °C.

2.4. Statistical analysis

Analysis of variance (ANOVA) was performed using CoStat under windows program (CoStat program ver. 6.311, 2005). Duncan's multiple range test was used to establish the multiple comparisons of the mean values at p = 0.05.

RESULTS AND DISCUSSION

1. Physical and chemical characteristics

Some physico-chemical characteristics of tomato juice during concentration are shown in Table (1). Upon concentration from 4.80 to 35.93 °Brix, the moisture content decreased significantly from 93.92 to 63.93 g $100g^{-1}$. The pH values and titratable acidity contents increased significantly during paste processing from 4.02 to 4.28 and from 0.506 to 2.986 g $100g^{-1}$, respectively. These results are within the limit specified by Egyptian companies and the results obtained by Shatta (2000).

Table (1): Some characteristics* during tomato paste (cold-break) processing

Item	Moisture (g 100 g^{-1})	TSS (°Brix)	pH	Titratable acidity (g 100 g^{-1}, as citric acid)
Tomato juice	93.92 ^{a}	4.80 ^{e}	4.02 ^{b}	0.506 ^{e}
First stage	91.81 ^{b}	7.15 ^{d}	3.88 ^{c}	0.576 ^{d}
Second stage	88.61 ^{c}	10.05 ^{c}	4.08 ^{b}	0.785 ^{c}
Third stage	63.98 ^{d}	35.65 ^{b}	4.27 ^{a}	2.917 ^{b}
After pasteurization	63.93 ^{d}	35.93 ^{a}	4.28 ^{a}	2.986 ^{a}

*** Means of ten replicates**

Means having the same letter within each property are non significantly different at p≤ 0.05

2. The relationship between rheological properties and pectin fractions

The consistency of tomato products (i.e. paste) refers to their viscosity and the ability of their solid portion to remain in suspension throughout the shelf life of the product. It is strongly affected by the composition of the pectins. Controlling the breakdown or retention of the pectins is great importance during processing (Hayes *et al.,* 1998).

Table (2) shows that the apparent viscosity (η) of the tomato juice, being 265.0 mPa s increased significantly with processing to 11731.5 mPa s for the pasteurized paste (35.93 °Brix). The yield stress (τ_o) is defined as the minimum stress required by a material to initiate flow. This parameter is related to the structure of the suspensions. The yield stress (τ_o) value was significantly affected by concentration it increased significantly from 2.48 N m^{-2} for the juice to 448.48 N m^{-2} for the pasteurized paste. The consistency coefficient (k) values increased significantly from 188.45 mPa s^n for the juice to 46628.50 mPa s^n for the paste. These results are in agreement with those obtained by Juszczak and Fortuna (2003), Sharoba (2004), Shatta (2006), Bayod *et al.* (2008) and Hsu (2008).

Table (2): Rheological properties and pectin fractions contents* during tomato paste (cold-break) processing

Item	Apparent viscosity (η, mPa s)	Yield stress (τ_o, N m^{-2})	Consistency coefficient (k, mPa s^n)	Pectin (g 100 g^{-1})			
				Water-soluble	Oxalate-soluble	Acid-soluble	Total
Tomato juice	265.0 ^{d}	2.48 ^{c}	188.45 ^{d}	2.26 ^{b}	5.91 ^{d}	1.91 ^{d}	10.08 ^{d}
First stage	286.3 ^{d}	3.17 ^{c}	238.10 ^{d}	2.11 ^{c}	5.92 ^{d}	2.06 ^{c}	10.08 ^{d}
Second stage	537.5 ^{c}	8.98 ^{c}	707.65 ^{c}	1.48 ^{d}	6.73 ^{c}	2.09 ^{c}	10.29 ^{c}
Third stage	9050.0 ^{b}	397.95 ^{b}	43049.50 ^{b}	2.24 ^{b}	7.29 ^{b}	2.55 ^{b}	12.07 ^{b}
After pasteurization	11731.5 ^{a}	448.48 ^{a}	46628.50 ^{a}	2.92 ^{a}	8.25 ^{a}	3.07 ^{a}	14.23 ^{a}

*** Means of ten replicates**

Means having the same letter within each property are non significantly different at p≤ 0.05.

Data in Table (2) shows the total and pectin fractions contents. The oxalate, acid soluble and total pectin contents increased significantly during tomato paste production. The water soluble pectin content varied significantly during concentration from 2.26 for the juice to 2.92 g 100 g^{-1} for the paste.

Pectin significantly influences the textural and rheological properties of tomato products, because of its great thickening and gel-forming capabilities. Many investigators proved that the colloid materials i.e. pectins were the main constituents affecting the rheological behavior of tomato juices. With this in view it could be expected that the higher the pectin the higher the rheological values (MacDougall *et al.,* 1996; Sharma *et al.,* 1996 and Narayanan *et al.,* 2002).

Figure (1) shows that the rheological parameters of tomato juice during concentration had a positive correlation with the pectin fractions contents. Linear was the arithmetic relationships between the water-soluble (WSP), oxalate-soluble (OSP), acid-soluble (ASP), total pectin (TP) contents and apparent viscosity (η), yield stress (τ_o), consistency coefficient (k) values as shown from Fig (1) and the following equations:

η = 7969 (WSP) - 13174 r^2= 0.536
τ_o = 314.74 (WSP) – 520.84 r^2= 0.479
k = 32943 (WSP) - 54379 r^2= 0.492

η = 5235.8 (OSP) - 31334 r^2= 0.863
τ_o = 210.24 (OSP) – 1261.6 r^2= 0.803
k = 22102 (OSP) - 132572 r^2= 0.818

η = 11325 (ASP) – 22082 r^2= 0.931
τ_o = 454.41 (ASP) – 889.29 r^2= 0.882
k = 47764 (ASP) – 93415 r^2= 0.866

η = 2965.5 (TP) – 29285 r^2= 0.931
τ_o = 118.63 (TP) – 1174.3 r^2= 0.877
k = 12459 (TP) – 123252 r^2= 0.859

In fact, as shown from the above equations, the highly positive correlation was between rheological properties and oxalate, acid and total pectin contents, where the correlation coefficient (r^2) values exceeded 0.80. A very well correlation was between the apparent viscosity and pectin fractions. Apparent viscosity is measured at the factories using Bostwick instrument, this means that Bostwick readings can be used to predict the content of pectins in tomato paste.

3. The relationship between lycopene, total carotenoids contents and Hunter color parameters

Maintaining the natural color in processed and stored foods has been a major challenge in food processing (Ihl *et al.,* 1998). Factors such as non-enzymatic and enzymatic browning, and process conditions like acidity, oxidation, time and temperature are responsible for the loss of pigment and color during processing of foods (Ahmed *et al*., 2002). In the case of tomato products (i.e. paste), an important reaction is the degradation of the red pigment lycopene, originally in the *trans* form, that isomerizes to the *cis* structure during heating, resulting in changes of color (Rodrigo *et al.,* 2007).

The results in Table (3) show that the lycopene and total carotenoids contents of the tomato juice were 1.785 and 0.978 mg 100 g^{-1}, respectively. Lycopene and total carotenoids contents increased during the concentration process to 3.742 and 4.918 mg 100 g^{-1} in the pasteurization paste, respectively. These results are in agreement with those reported by Marković *et al*. (2006).

Hunter color parameters; lightness (L^*), redness (a^*) and yellowness (b^*) decreased significantly during processing from 27.12, 27.26 and 14.16 for the juice to 22.85, 25.95 and 13.61 for the paste, respectively. The red-yellow (a^*/b^*) ratio, indicates the redness of tomato products. An a^*/b^* ratio of 1.90 or greater represents a first quality product in terms of color and an a^*/b^* ratio of less than 1.80 means that the tomato products may be unacceptable for inclusion in the products, where a^* bright red color is desired (Hayes *et al.,* 1998). A low a^*/b^* value (orange to brown color) is a result of the breakdown of lycopene and formation of Maillard reaction products by the intensive heat treatment (Krebbers *et al.,* 2003 and Hsu, 2008). The a^*/b^* value of the tomato juice was 1.93 decreased non-significantly to 1.91 for the paste, but still above 1.90, indicating a first quality product.

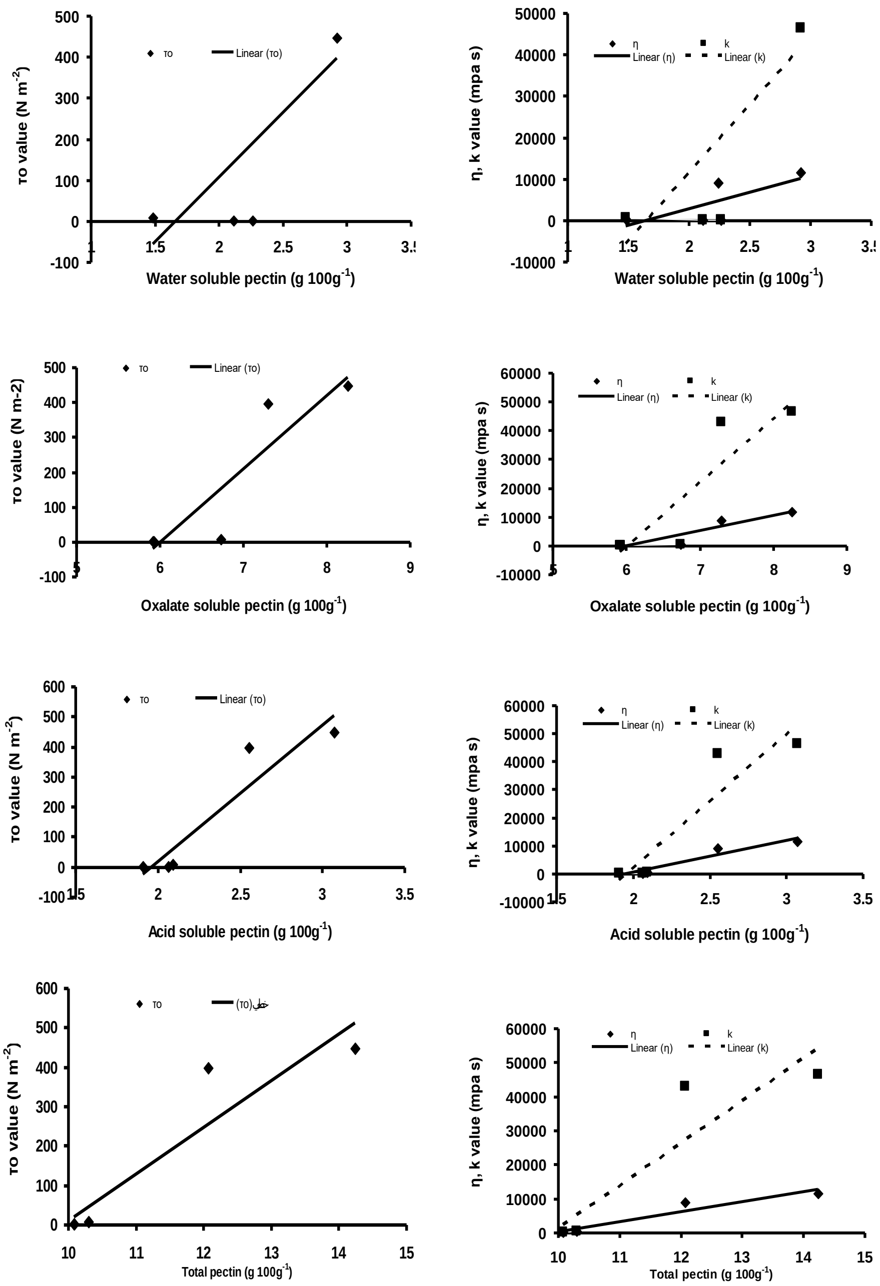

Figure (1): The relationships between the η, k, τ_o values and pectin fractions contents

Table (3): Lycopene, total carotenoids contents* and color attributes during tomato paste (cold-break) processing

Item	Lycopene (mg 100 g^{-1})	Total carotenoids (mg 100 g^{-1})	L^*	a^*	b^*	a^*/b^*
Tomato juice	1.785 ^{d}	0.978 ^{e}	27.12 ^{a}	27.26 ^{ab}	14.16 ^{b}	1.93 ^{a}
First stage	1.906 ^{c}	1.150 ^{d}	26.63 ^{a}	27.32 ^{ab}	14.61 ^{a}	1.87 ^{a}
Second stage	2.265 ^{b}	1.332 ^{c}	26.29 ^{a}	28.44 ^{a}	14.88 ^{a}	1.91 ^{a}
Third stage	3.723 ^{a}	3.686 ^{b}	23.86 ^{b}	27.15 ^{ab}	14.13 ^{b}	1.92 ^{a}
After pasteurization	3.742 ^{a}	4.918 ^{a}	22.85 ^{c}	25.95 ^{b}	13.61 ^{c}	1.91 ^{a}

*** Means of ten replicates**
Means having the same letter within each property are non significantly different at p≤ 0.05.

The relationship between lycopene, total carotenoids contents and L^*, a^*, b^* values are shown in Figure (2). Apparently, lycopene and total carotenoids contents well correlated with Hunter color parameters, indicating that the contents of these pigments significantly influenced the color of tomato paste (Patras *et al.,* 2009). The arithmetic relationships between lycopene (Lyco), total carotenoids (Caro) contents and Hunter color parameters were linear as seen from the following equations:

L^* = - 1.8939 (Lyco) + 30.434 $\quad$ r^2= 0.962
a^* = - 0.5389 (Lyco) + 28.671 $\quad$ r^2= 0.353
b^* = - 0.3339 (Lyco) + 15.174 $\quad$ r^2= 0.443

L^* = - 1.0482 (Caro) + 27.879 $\quad$ r^2= 0.989
a^* = - 0.3753 (Caro) + 28.129 $\quad$ r^2= 0.575
b^* = - 0.2172 (Caro) + 14.802 $\quad$ r^2= 0.629

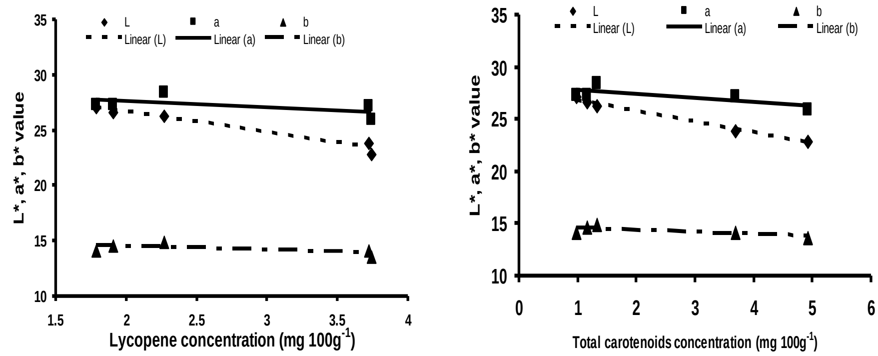

Figure (2): The relationships between the lycopene, total carotenoids and Hantur color parameters

Arias *et al.* (2000) reported that the L^* or a^* value well related to lycopene concentration; however, the ratio of a^*/b^* provided the best relation. While the lycopene concentration increased, L^* value decreased and the color changed from light to dark as shown in Table (3). However, this effect was not consistent and it appears that a more complex mechanism may be required to explain variations in instrumental color parameters for the tomato products.

Conclusion

The rheological properties and Hunter color parameters of tomato juice during processing to paste had good correlations with pectin fractions contents and pigments concentration, such as lycopene and total carotenoids. Tomato paste processing can be controlled by these correlations and understanding many problems arising during processing in the flow behavior or the color.

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العلاقة بين الصفات الريولوجية، اللون والخصائص التركيبية لعجينة الطماطم (المصنعة بالطريقة الباردة) خلال عملية التصنيع.

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تم دراسة العلاقة بين الصفات الريولوجية والمحتوى من شقوق البكتين وكذا العلاقة بين تركيز الليكوبين، الكاروتينيويدات وقيم اللون لعجينة الطماطم أثناء تصنيعها بالطريقة الباردة.
أوضحت النتائج أنه أثناء تركيز عصير الطماطم ازدادت قيم كل من اللزوجة الظاهرية، إجهاد الخضوع ومعامل القوام، كما ازداد المحتوى من شقوق البكتين وصبغات الليكوبين والكاروتينيويدات، بينما انخفضت قيم سطوع اللون (L^*) ودرجة الاحمرار (a^*) والاصفرار (b^*).

كما أوضحت النتائج وجود علاقة ايجابية بين قيم الصفات الريولوجية المدروسة، خصوصا اللزوجة الظاهرية وكل من محتوى البكتين الذائب فى الاوكسالات، والذائب فى الحامض والبكتين الكلى. كما وجدت علاقة جيدة بين تركيز كل من الليكوبين والكاروتينيويدات وقيم سطوع اللون (L^*).

يمكن استخدام العلاقات المتحصل عليها فى التحكم وفهم وإدراك العديد من المشكلات التى تحدث أثناء تصنيع عجينة الطماطم خصوصا تلك المتعلقة بسلوك الانسياب وخصائص اللون.