

## MODIFICATION OF STARCH PASTING, TEXTURAL AND RHEOLOGICAL ATTRIBUTES BY BLENDING WHEAT AND CHICKPEA STARCHES

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Native starches are sometime difficult of use in products due to their inherited deficiencies like poor stability, less viscosity and higher degree of gelatinization. Starches are modified by different ways to improve their properties. Starch blending from different sources is one of the methods to improve their properties. Wheat starch (WS) and chickpea starch (CS) were blended in 100-0, 90-10, 70-30, 50-50 and 0-100 proportions, respectively. Blends were studied for their pasting, thermal, rheological and textural properties using rapid viscoanalyzer, differential scanning colorimeter, and rheometer and texture analyzer. Additive effect of both starches was observed in blends analyzed through differential scanning calorimeter. Pasting properties of blends were significantly different for all levels as compared to individual starches. Amylose lipid complex was observed in individual WS and all blends while it was not present in individual CS. Syneresis from starch gels was higher in individual CS and 50-50 blends at 0, 30 and 60 days of storage. Gel hardness values increased as the level of CS was increased in blends. All blends exhibited the pseudoplastic nature ( $n < 1$ ) when data was fitted to power law model. Overall, 50-50 blend can be a suitable choice for foods where higher temperature processing and stability is required.

**Keywords:** Wheat starch, chickpea starch, blends, pasting, texture, rheology.

### INTRODUCTION

Cereals are the significant (40-90%) starch containing sources followed by pulses/legumes (30-70%) (Biliaderis, 1991). Starches are used in different food products with different objectives. They are used as gelling, thickening and texturizing agents. The properties of starches may vary depending upon their amylose contents, chain length and granular size. Some of the starches are not preferred in particular food application due to their thermal decomposition, quick retrogradation, less viscosity and less freeze thaw stabilities (Friedman, 1995; Kokini *et al.*, 1995). Properties of native starches of different botanical origins can be modified by several means including physical, chemical and enzymatic treatments. Different types of hydrocolloids e.g guar gum, xanthane gum, Arabic gum, carragenan, okra gum are also used to modify the starch properties (Alamri *et al.*, 2012; Alamri *et al.*, 2013; Wang *et al.*, 2009; Tischer *et al.*, 2006; Rosell *et al.*, 2011). Several researches have also prepared the different types of starch blends with improved stability and functional properties. Blending of starches is considered as an economical and safe method of starch modification (Chen *et al.*, 2003; Puncha-Arnon *et al.*, 2008; Zhang *et al.*, 2011; Zaidul *et al.*, 2007). Blending of two or more starches from different botanical origin shows synergistic effect due to differences in amylose and amylopectin nature and contents (Jane and Cheng, 1992). Unmodified mixtures of starch blends can be helpful to avoid

chemical and enzymatic treatments. Obani and Bemiller (1997) have studied a starch blend that can be used as a replacement to chemically modified starch having similar pasting behavior. Acceptable stability of the starch gels can be achieved by proper blending of different starches (Bello-Perez, 2001).

Use of legume starches is preferred in high temperature extrusion (high amylose, gel elasticity and quick retrogradation) (Czuchajowska *et al.*, 1998; Betancur-Ancona *et al.*, 2001) but using individual legume starches can be a problem due to high Syneresis and poor freeze thaw stability (Alamri *et al.*, 2013). Differential scanning calorimetry, rapid visco analysis, syneresis, texture and rheological properties of starches are commonly studies to access their suitability for different food applications. Individual chickpea starch is considered to be less stable and have limited food applications. The objectives of current studies were to blend the wheat and chickpea starch at different levels and investigate their thermal, rheological, textural and functional properties.

### MATERIALS AND METHODS

**Materials:** Hard red spring wheat flour and Chickpea grains were obtained from local market.

#### Methods

**Starch isolation from chickpea and wheat:** Chickpea grains were mixed with distilled water (50/50) and blended in heavy

duty blender for 3-5 minutes. Prepared slurry was filtered through muslin cloth and then passed through 200 mesh sieve. The filtered material was centrifuged at 2300x g for 10 minutes. Supernatant was removed while precipitate was re-suspended in distilled water and re-centrifuged using same conditions. The process was repeated several times until clear white starch precipitate was obtained. Wheat starch was isolated from wheat flour according to Martin process as followed by Hussain *et al.* (2013). Flour dough with water (2:1 ratio) was kneaded and dipped in water for 30 minutes to develop gluten. Dough ball was then washed with excess amount of water by kneading on muslin cloth. Washing was performed until all the whitish milky material was extracted from dough ball. The contents were centrifuged at same conditions as mentioned above to get the clear white starch. The starches obtained from both types of botanical sources were dried using acetone and milled to fine powder using coffee grinder. The starches were stored in air tight containers at 4°C till further use.

**Preparation of starch blends:** Wheat starch (WS) and Chickpea starch (CS) were mixed in different proportions like 0CS/100WS, 10CS/90WS, 30CS/70WS, 50CS/50WS and 100CS/0WS, respectively to prepare different blends. The blends were stored in airtight glass jars at 4°C till further used in different experiments.

**Differential scanning calorimetry (DSC):** DSC analysis was conducted to determine the thermal properties of starch blends using Setaram instruments Mico Evo DSC III. Starch sample (individual or blends, 240 mg) were placed in Standard Hastelloy cell and 400 µl distilled water was added. Suitable amount of distilled water was added in other cell to use it as a reference cell. Samples were sealed, equilibrated for 1 hour and scanned at 2°C/ minute heating rate from 20-100°C. Data was recorded for different parameters like gelatinization enthalpy ( $\Delta H$  J/g), peak temperature (°C) and onset temperature for major gelatinization peak and the second peak representing amylose lipid complex.

**Rapid visco analyzer measurements (RVA):** Rapid visco analyzer (Newport Scientific, Sydney, Australia) was used to determine the pasting properties of starch blends. The blends (3 grams at 14% moisture basis) were weighed into aluminum RVA canisters. Distilled water was added to achieve a total weight of 28 grams and starch slurry was prepared. The slurry was held at 50°C for 30 seconds, heated to 95°C in 4.40 minutes (at 10.23°C/ min) and held at 95°C for 4 minutes. It was then cooled to 50°C in 2 minutes (at 22.5°C/min) and held at 50°C for 2 minutes. The paddle rotation was 960 rpm for first 10 seconds and then reduced and kept at 160 rpm throughout the remainder experiment. Thermocline window software was used to process the data.

**Texture profile analysis of starch gels:** Gels obtained from RVA experiments were poured in glass beaker (35 mm height, 30 mm internal diameter) and stored at room temperature overnight. Gels were compressed using

Brookfield CT3 Texture Analyzer (Brookfield Engineering Laboratories, Inc. Middleboro, USA) in two penetration cycles at a speed of 0.5 mm/sec to a distance of 10 mm using 12.7 mm wide and 35 mm high cylindrical probe. Gel hardness, springiness, cohesiveness and adhesiveness were recorded. The gumminess was calculated as a product of hardness and cohesiveness while chewiness as a product of gumminess and springiness.

**Syneresis from starch gels:** Starch gels prepared in RVA canisters were transferred in centrifuge bottles and frozen at -20°C in freezer. Tubes were taken out from the freezer on the following day and placed in water bath at 50° C for 30 minutes. Centrifugation was performed on gels 3000 xg for 15 minutes. Separation of water from gels was recorded and the gels were restored in freezer. Similar procedure was performed at 30<sup>th</sup> and 60<sup>th</sup> days of storage and the percent syneresis from gels after three freeze thaw cycles was reported on day1, day 30 and day 60.

**Light microscopy of starch gels:** Microstructure images of cooked starch gels placed on glass slides were taken at 40x magnification using a light microscope Model. 591300 Wolfe, Digivu, TM, CVM, Carolina Biological Supply Company, Burlington, North Carolina, USA.

**Statistical analysis:** Data obtained in triplicate from all type of experiments were subjected to one-way analysis of variance. Comparison of means was done by Duncan's Multiple Range (DMR) test at  $p \leq 0.05$  PASW® Statistics 18 software.

## RESULTS AND DISCUSSION

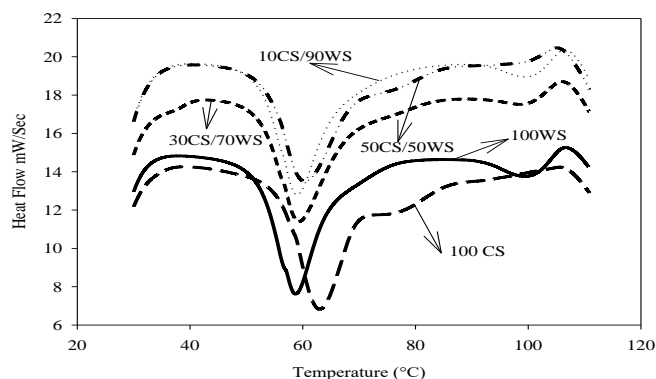
**Thermal properties:** Differential Scanning Colorimeter (DSC) thermograms of individual Wheat and chickpea starches and their blends are presented in Fig 1. The results regarding transition temperatures i.e onset temperature (OT) and peak temperature (PT) and gelatinization enthalpies ( $\Delta H$ ) of major endothermic peak representing starch gelatinization and minor endothermic peak representing amylose-lipid complex are presented in Table 1. Transition temperatures and  $\Delta H$  of individual CS were higher as compared to individual WS. Additive effect with single endothermic peak was observed in all blends. The  $\Delta H$  of 100% CS was higher ( $11.5 \pm 0.35$  j/g) as compared to  $9.75 \pm 0.75$  J/g of 100% wheat starch. More influence of WS was evident at 10 and 30 % levels might be due to smaller granular size of wheat starch effecting the gelatinization behavior of CS by competing for water. The findings are supported by Sun and Yoo (2011). Appearance of single peak in blends system is supporting the theory that the DSC thermogram is a sum of individual starches (Liu and Lelivre, 1992). It is evident from the table that onset temperature for individual and starch blends ranged from 52 to 56°C. Amylose lipid complex was not observed in individual CS. The linear decrease in the  $\Delta H$  in 100 WS and 50CS/50WS blends from  $1.27 \pm$  to  $0.23 \pm 0.08$  j/g, respectively

**Table 1. DSC parameters of starch blends**

Blend	Wheat and chickpea starch (CS)					
	$\Delta H$ J/g	P T °C <sup>1</sup>	O T °C <sup>2</sup>	ALC <sup>3</sup>	ALC <sup>4</sup>	ALC <sup>5</sup>
100WS	9.75±0.34c	58.81±0.10d	52.43±0.05e	1.27±0.13a	100.22±0.07a	93.37±0.47a
10CS/90WS	9.77±0.04c	59.11±0.06bd	53.04±0.04d	1.17±0.04a	100.28±0.30a	94.13±0.74a
30CS/70WS	9.98±0.09c	59.51±0.25c	53.41±0.04c	0.70±0.13b	100.10±0.24a	95.05±0.11a
50CS/50WS	10.55±0.06b	60.58±0.12b	53.58±0.02b	0.23±0.08c	99.77±0.24a	94.67±0.93a
100 CS	11.5±0.35a	62.9±0.14a	56.1±0.57a	-	-	-

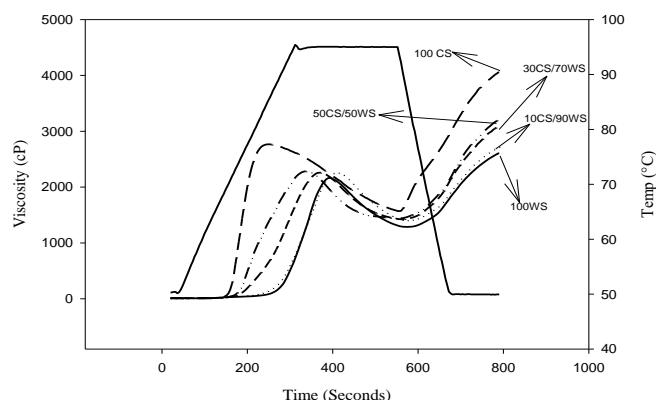
<sup>1</sup> Peak T °C, <sup>2</sup> Onset T °C, <sup>3</sup> Amylose lipid Complex  $\Delta H$  (J/g), <sup>4</sup> Amylose lipid Complex Peak T °C, <sup>5</sup> Amylose lipid Complex Onset T °C. Means carrying same letters in the columns are statistically non-significant

suggest that appearance of amylose lipid complex as native property of WS. Theoretical enthalpies and experimental enthalpies of blends are dependent on the proportional contribution of individual starches in blends system (Liu and Lilivre, 1992). The images shown in Fig. 4 also explain that different levels of two starches affected the gelatinization behavior of different blends. Smaller size starch granules generally gelatinize slowly and at higher temperatures. Similar type of phenomenon was observed in our previous studies conducted on wheat and Turkish bean starch blends (Hussain *et al.*, 2013).

**Figure 1. DSC thermograms of different starch blends**

**Pasting properties:** The pasting behavior profiles (RVA) of wheat and chickpea starches and their blends are presented in Fig. 2. The RVA properties presented in Table 2 indicate that there was a significant difference between individual wheat starch with chickpea starch while blends were non significantly different to wheat starch with respect to peak

viscosity. The final viscosity of the blends with 30 and 50% CS was more influenced by CS as compared to wheat starch.

**Figure 2. RVA profile of different starch blends**

Setback values were also higher in blends with higher levels of CS indicating that high contents of amylose (higher than 35%) in CS had more influence on SB as compared to relatively lower amylose containing wheat starch. Significant decrease ( $P \leq 0.05$ ) in the pasting temperature was observed due to addition of chickpea starch ( $69.10 \pm 0.39^\circ\text{C}$ ) in wheat starch ( $87.68 \pm 0.63^\circ\text{C}$ ). The declining effect on pasting temperature was proportionate with higher levels. Theoretically if we calculate the pasting temperature of 50CS-50WS blend, it should be around  $78^\circ\text{C}$  but the observed value is  $74.67 \pm 0.8^\circ\text{C}$ , which looks to be more influenced by CS as compared to WS at same concentration. The theory can be interpreted that larger granules of chickpea starch had more pronounced effect in starch blends and the presence of CS also hindered the pasting of wheat starch. Similar results were

**Table 2. RVA properties of starch blends**

Blend	Wheat and chickpea starch (CS)						
	Peak Viscosity	Trough	Breakdown	Final Viscosity	Set back	Peak Time	Peak Temp
100WS	2168.33±147.00b	1287.33±71.22c	881.00±76.54b	2605.00±97.25c	1317.67±36.53d	6.53±.07b	87.68±.63a
10CS/90WS	2261.00±20.66b	1404.00±26.46b	857.00±38.30b	2720.67±34.36c	1316.67±09.50d	6.82±.04a	85.50±.35b
30CS/70WS	2262.67±43.75b	1422.67±68.82b	840.00±43.14b	3085.00±97.26b	1662.33±57.68c	6.16±.10c	74.67±.08c
50CS/50WS	2284.00±75.45b	1440.33±30.02b	843.67±47.17b	3206.00±68.20b	1765.67±46.61b	5.62±.04d	72.27±.38d
100 CS	2766.33±125.03a	1568.00±77.66 a	1198.33±60.12a	4053±139.38a	2485±79.21a	4.13±.07e	69.10±.39e

Means carrying same letters in columns are statistically non-significant

**Table 3.** *n* and *K* values of starch gels

	Wheat and chickpea Starch (CS) blends				
	100WS	10CS/90WS	30CS/70WS	50CS/50WS	100 CS
Ramping up					
<i>n</i>	0.46	0.45	0.41	0.40	0.26
<i>K</i>	3.97	3.93	4.17	4.20	4.64
<i>R</i> <sup>2</sup>	0.99	0.99	0.99	0.99	0.85
Ramping down					
<i>n</i>	0.35	0.34	0.31	0.29	0.24
<i>K</i>	4.55	4.41	4.60	4.66	4.77
<i>R</i> <sup>2</sup>	0.99	0.99	0.99	0.99	0.84

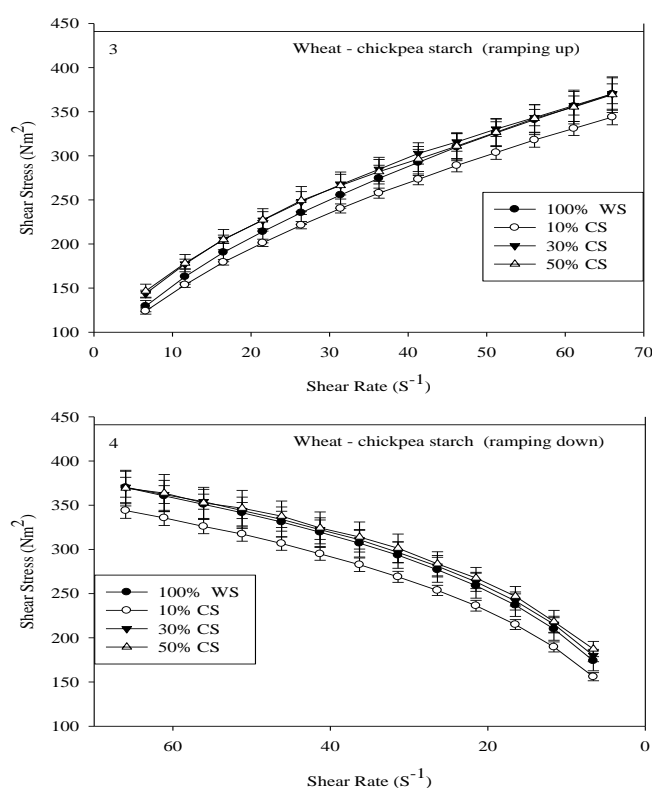
The *K* = consistency index (Pa.s) and the *n* = flow behavior index (dimensionless)

reported by Zhang *et al.* (2011). It is observed during the current studies that Final viscosity was higher at higher levels of blending. This is a positive indicator that blends having higher level of CS in WS are stable during heating and cooling cycles can perform better during agitation and shear stress. They can tolerate high temperature sterilization in contrast with some other commercial available starches which losses their consistency during processing (Villarcres and Espin, 1996; Novelco-cen and Betancur-Ancona, 2005), thus making them suitable for using in processed / cooked baby foods.

**Steady shear properties:** Steady shear flow properties of gels of individual starches and their blends are presented in Fig 3. The ramping up and down of shear rates flow curves are well fitted to the power law model for wheat starch and other blends ( $R \geq 0.99$ ). The values of flow behavior index (*n*) and consistency coefficients (*K*; Pa.s<sup>*n*</sup>) are presented in Table 3. The pseudo plasticity of all blends and individual starches is evident from the results ( $n < 1$ ). Decrease in apparent viscosity was noticed with increasing shear rate. The value of *K* in ramping down was higher as compared to ramping up in all blends and individual starches which indicates more thickening during ramping down of shear rate. The value of *n* for 100% WS was 0.46 (ramping up) and 0.35 (ramping down) which was reduced to 0.40 (ramping up) and 0.29 (ramping down) in 50CS-50WS blend. As the level of chickpea starch was increased in blend, decrease in the *n* value was noticed, which is indicative of more pseudo plasticity of the system. The results of present studies are supported by the findings of Zhang *et al.* (2011) in which they found that mixtures of potato and maize starch have more pseudo plasticity. The possible decrease in *n* value of blends with higher shear rate can be due to decrease in joint points among the starch molecules (Nurul *et al.*, 1999).

**Gel textural properties:** After RVA study, gels of WS, CS and their blends were stored for 24 h at room temperature (or 4 °C) and the texture was assessed using Brookfield Texture Analyzer. The texture data presented in Table 4 indicates measureable variations in all the studied parameters. As the starch gel presents meta-stability in its system, some

structural changes takes place during storage (Ferrero *et al.*, 1994).

**Figure 3.** Steady shear properties of starch gels

Ring *et al.* (1987) reported that initial hardness of gel instigated by retrogradation of amylose with a subsequent slow crystallization of amylopectin. In case of gel hardness the least value was observed for WS. However, with increasing the CS replacement concentrations hardness was increased with the maximum of 781 g observed for 100CS. Higher hardness of a starch-water system is directly correlated with its amylose contents. It is reported that CS has 33% amylose of the total starch (Rao, 1976) Hence, for higher CS percentage in CS: WS blends higher hardness is obvious

**Table 4. Texture parameters of starch blends**

	Wheat and chickpea Starch (CS) blends				
	100WS	10CS/90WS	30CS/70WS	50CS/50WS	100 CS
Hardness (g)	166.50±7.78c	170.50±4.95c	179.50±14.85c	235.00±15.56b	781.00±137.18a
Cohesiveness	0.56±0.16a	0.48±0.01a	0.45±0.03a	0.39±0.04a	0.47±0.02a
Springiness(mm)	10.30±0.28a	10.00±0.00a	9.20±0.00b	9.05±0.07b	8.80±0.28c
Adhesiveness (mJ)	1.50±0.12a	0.85±0.07b	0.60±0.00b	0.95±0.07b	0.00±0.00c
Gumminess (g)	93.24±21.55b	63.29±3.32b	80.76±1.61b	91.65±16.04b	363.17±47.22a
Chewiness (g)	960.37±248.12b	632.93±33.23b	743.10±14.77b	829.43±138.63b	3195.85±313.23a

Means carrying same letters in rows are statistically non-significant

**Table 5. % syneresis from gels prepared from different starch blends**

Blend	Wheat and chickpea starch (CS)		
	Day 1	Day 30	Day 60
100WS	0.00±0.00c	7.44±0.78d	5.25±0.21c
10CS/90WS	5.95±0.07b	6.50±0.47d	4.10±1.08c
30CS/70WS	5.98±1.19b	10.52±0.15c	4.10±1.08c
50CS/50WS	15.60±0.71a	15.62±0.28b	11.65±0.99b
100 CS	16.06±0.23a	17.03±1.04a	14.23±0.51a

Means carrying same letters in columns are statistically non-significant

due to the higher total amylose of the system. Similarly, a positive correlation between amylose and gel firmness has also been mentioned for chickpea (Czuchajowska *et al.*, 1998). Although, statically ( $p>0.05$ ) similar cohesiveness was seen for all the gels but WS presented the highest cohesiveness value (0.56) and that was reduced to 0.39 for 50 CS: 50WS blend. One plausible explanation might be the higher degree of polymerization of amylose in WS that rendered a more cohesive gel (Sandhu and Kaur, 2010). Springiness of gels from individual WS, CS and their blends was observed between 10.3 - 8.8 with the decreasing order of 100WS> 10CS-90WS > 30CS-70WS> 50CS-50WS> 100CS. Adhesiveness, more specifically, is a surface property and depends upon mutual effect of cohesive and adhesive forces (Huang *et al.*, 2007). A significant reduction in adhesiveness was seen by 10% CS replacement of WS. For 30CS/70WS blend less than half adhesiveness was observed compared to what was seen for 100WS. Interestingly, for 50CS/50WS the adhesiveness was just similar to 10CS/90WS, possibly suggesting the additive effect /synergy between two starches. However, above all, 100CS presented a non-adhesive nature. Gumminess of gel is a hardness and cohesiveness dependent parameter. The highest gumminess was noticed for 100CS with the least given by 10CS/ 90WS. This might be due to reason that higher amount of amylose content of chickpea starch resulted in higher hardness value and gumminess is directly influenced by the hardness of starch. It is reported that gels with more rigid and firm characteristics, as observed in our studies (50CS/50WS and 100CS), could be used in products like custard, pudding and cream (Novelo-Cen and Betancur-Ancona, 2005).

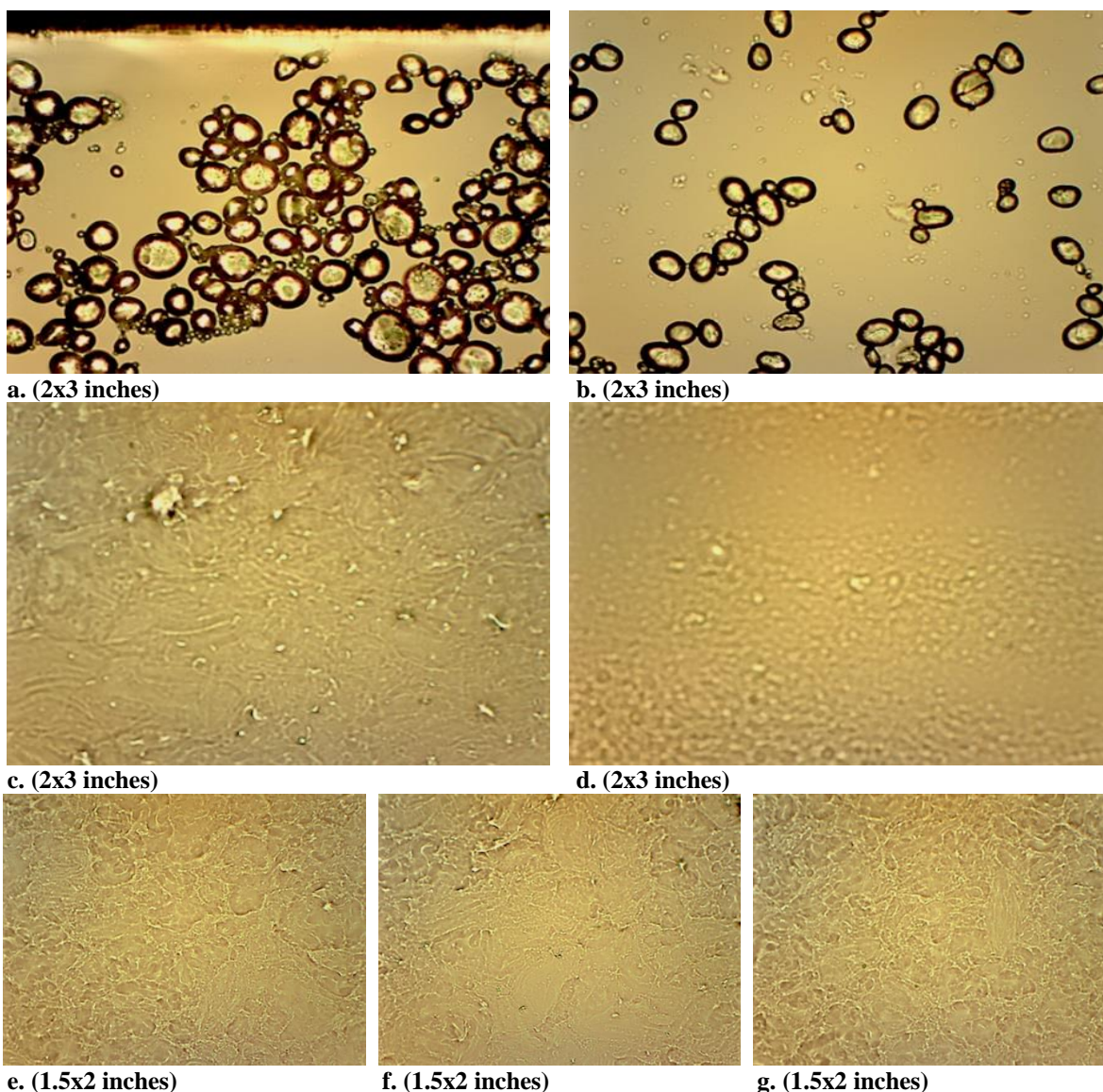
**Syneresis:** Gels obtained from the RVA experiments were poured into centrifuge tubes and stored at freezing

temperature to study the freeze thaw stability after 1, 30 and 60 days storage intervals. Freeze thaw stability of the foods containing starch is an important factor during transportation and storage. Repeated freezing and thawing cycles may lead to the development of ice crystals that ultimately affects the overall structure. Syneresis from products as a result of thawing during transportation may leave the product unfit for consumption due to safety, quality, stability and structural issues (Lewicki, 2004). Data presented in Table 5 indicates that there was a significant difference in the % syneresis from gels of individual starches and their blends. There was no syneresis in WS after day 1 but it was highest (16.06±0.23) in individual CS. Increasing the level of CS in blends resulted in increase in % syneresis from starch at all freeze thaw cycles (i.e at 1, 30, 60 days storage). Blends having lower levels of CS (10CS/90WS and 30CS/70WS) had less syneresis i.e. 5.95±0.07 and 5.98±1.19%, respectively as compared to 50CS/50WS blend (15.60±0.71). Presence of higher amylose contents in chickpea starch can be responsible for higher syneresis in blends with higher CS level as well as individual CS starch. Different researches reported that starches with higher amylose contents in blends system leads to higher syneresis. Amylose is considered to retrograde by association with other neighboring molecules which may leads to precipitation and ultimate expulsion of water from the gel system (Hussain *et al.*, 2013; Tester *et al.*, 2004). Our results are also supported by (Novelo-Cen and Betancur-Ancona, 2005); they reported that high amylose lima bean starch presence in cassava starch blends linearly increased the percent Syneresis. Total syneresis from chickpea starch during all the three free thaw cycles was much higher (47.32%) as compared to total syneresis from individual wheat starch (12.69%). Rege and Pai (1996) also reported



more than 40% syneresis from chickpea starch after five freeze thaw cycles. It is observed during the current studies that total syneresis from 50CS/50WS blend was 42.67% seems to be more influenced by CS than WS. Contrary to that, blends with 10 and 30 CS starch had lower syneresis i.e 16.55% and 20.6%, respectively. This lower syneresis could be attributed to the level dependent interaction between the differences in starch granule size of both chickpea and wheat starches. The results suggest that individual chickpea starch may not be a suitable option for the frozen foods but blending the CS with WS up to 30% level can be a suitable option from syneresis viewpoint.

**Light microscopy:** Microscopic images of individual cooked, uncooked wheat starch, chickpea starch and their blends are shown in Fig 4. Relatively more homogenous matrix was observed in the individual wheat starch gels as compared to individual CS gels. Additive effect of both the starches (i.e chickpea and wheat) can be seen in starch cooked blends. CS starch has dominated at all levels in the blends. This reflects that how significantly CS starch has influenced the pasting, thermal, rheological properties and freeze thaw stability of cooked starch blends. Similar trend was observed in the previous studies of Hussain *et al.* (2013) when wheat starch blends were prepared with Turkish bean starch.



a. Wheat Starch uncooked, b. Chickpea starch uncooked, c. Wheat Starch cooked, d. Chickpea starch cooked, e. Wheat- Chickpea starches (90-10) cooked, f. Wheat- Chickpea starches (70-30) cooked, g. Wheat- Chickpea starches (50-50) cooked

**Figure 4. Light microscopic images of starch gels (40X magnification)**

**Conclusion:** It can be concluded from the findings of current research that blends of chickpea and wheat starches had acceptable rheological, textural and thermal properties. Additive effect was noticed in blends. The blending between two types of starches helped to produce desirable gels than can be used to produce hot cooked foods, puddings and different types of baby foods. Synergy during cooking between gels mixtures was also noticed in the microscopic examinations. The blending of two starches in equal proportions can help to improve their food applications.

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