Textural characterization of foxtail millet gels: effect of cations and hydrocolloids

P. Nagaprabha¹ · Sila Bhattacharya¹

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Abstract Foxtail millet (*Setaria italica*) is traditionally cultivated in mainly dry land areas and has nutritional importance. The textural characteristics of gels, formed with foxtail millet flour at different concentrations (9–13 %, dry solid basis) along with selected cations and hydrocolloids, were determined. Different concentrations of monovalent (NaCl) and divalent (CaCl_2 and FeSO_4) cations, and hydrocolloids such as gelatin, gellan, starch, xanthan and agar were incorporated in gels. The gel forming ability markedly improved with an increase in the concentrations of CaCl_2 and FeSO_4 , while NaCl had a marginal effect. Gels prepared with 11 % of foxtail millet alone were found to sensorially acceptable while addition of 0.5 % CaCl_2 or 0.2 % FeSO_4 respective with 10 % foxtail millet also resulted in acceptable gels. Among the hydrocolloids, starch and gellan had marked effects on gel formation, and textural and sensory attributes. The principal component analysis (PCA) plot showed that concentration of foxtail millet formed a cluster with sensory hardness, springiness, cohesiveness, and instrumental peak stress, fracture strain and compression energy indicating that these attributes

were interrelated to each other. Stickiness and gelling time formed a cluster on the other side of the axis indicating inversely related. Foxtail millet has a good potential for development of new ranges of gelled health benefiting convenience products with nutraceutical property, and the addition of cations helps to achieve acceptable structural integrity.

Keywords Foxtail millet · Texture · Cation · Hydrocolloid · Sensory

Introduction

Gel is a substantially diluted system which exhibits no steady state of flow (Renard et al. 2006). A liquid (or sol) is converted into a solid (or gel) through the process of sol–gel transition. Available food gels are mainly prepared by using a protein or hydrocolloid, possessing different texture, taste and flavour, they are viscoelastic substances with high moisture content. The semi-solid state of these products is the major factor for consumer acceptance and convenience. Factors responsible for gel formation include the type and concentration of hydrocolloid, temperature, pH, presence of cations, and co-solutes such as sugar; the effects of these factors are frequently determined using rheological data. In case of starch gel, the amount and type of amylose and amylopectin present, the interaction between these two components, rate of heating, time and temperature are also related to gel formation (Liu et al. 2006). The addition of cations (both monovalent and divalent) is responsible for gelation phenomenon and the quality attributes of the formed gels (Laplante et al. 2005).

Millet based gels are not available as a commercial product, though millets are rich in dietary fibre, minerals, vitamins and antioxidants. Millet consumption in diet has been claimed to reduce the risk of cancer, cardiovascular disease, tumor, blood

Research highlights

1. A minimum concentration of 11 % foxtail millet (FM) flour was required to obtain a gel
2. Starch and gellan had marked effect on FM gel textural and sensory attributes
3. Gel forming ability of FM markedly improved with increase in concentration of CaCl_2 and FeSO_4
4. Cation addition on FM gel formation closely related with peak stress and syneresis

✉ Sila Bhattacharya
silabhat@yahoo.com

¹ Grain Science & Technology Department, Central Food Technological Research Institute, Council of Scientific & Industrial Research, Mysore 570020, India

pressure and heart diseases (Truswell 2002). Among the millets, foxtail millet is an important dry land crop in North China (Sampath et al. 1989), Italy and India. Processing of millets includes dehulling, soaking and cooking to reduce the antinutrients such as polyphenols and phytates, and thus improves iron and zinc bioavailability (Pawar and Machewad 2006). Foxtail millet may also be used in the preparation of noodles (*lajia* noodles) by stretching the dough continuously (Lu et al. 2005). Popping and malting quality of foxtail millet varieties were conducted by Choudhury et al. (2011) and hydration characteristics by Vasudeva et al. (2010). However, scope exists to develop and popularize various foxtail millet products as health benefitting foods.

The present study thus enables the concept of gel formation using foxtail millet (FM) flour. Gels, being convenient to use and transport, are more preferable to consumers than liquid based food products. Cereal based gels are mainly prepared from hydrocolloids like isolated starches while the use of whole grain is rather rare. Preparation of millet based gels can thus offer a specialty health food. Hence, there is a need to study the process of gel formation using millet flour and the attributes of the gels including sensory acceptance of the product. Further, gels are usually sensitive to the presence of cations and hydrocolloids (Arendt et al. 2008). It is also desirable to investigate their effects on the attributes of the gels particularly texture and syneresis.

The objective of the present work is to study the gel forming ability and characteristics of the gels formed using foxtail millet flour at different concentrations along with the effect of (a) cations like NaCl, CaCl₂ and FeSO₄, and (b) hydrocolloids such as gelatin, gellan, starch, xanthan and agar.

Materials and methods

Materials

Foxtail millet (PS4 variety) was procured from a nearby farm of Mysore, Karnataka, India. These grains were dehulled in a laboratory model centrifugal sheller, debranned in a cone polisher and ground to fine flour employing a laboratory model dry grinder (model # M20 IKA-WERKE, Germany) with cooling arrangement by using a water jacket in addition to cooling the raw material to about 4 °C prior to grinding. The grinding operation was conducted below 40 °C to minimize the chance of gelatinization of starch. The flour thus obtained was passed through a 150 µm aperture British Standard (BS) sieve, and only the fine flour passing through this sieve were used for the study. All solvents/chemicals and hydrocolloids used were of analytical grade, and were obtained from Merck, Mumbai, India. Corn starch was procured from a local supermarket.

Proximate composition and water holding capacity

The proximate composition of foxtail millet (FM) flour was determined following AOAC (2002) methods, was 10.0 % moisture, 10.5 % protein ($N \times 6.25$), 2.1 % fat, 1.1 % ash and 76.3 % carbohydrate (by difference). Water holding capacity (WHC) of flour was determined by following the method of Elhardallou and Walker (1993). The results for WHC were expressed as g of water absorbed per g of dry flour; it was 1.54 ± 0.12 g/g based on the measurements of triplicate samples.

Gel preparation

Foxtail millet flour dispersions at different concentrations of 9, 10, 11, 12 and 13 % (dry solid basis) were prepared by dispersing the powdery material in deionised water by continuous stirring in a mechanical stirrer for 30 min to avoid the formation of any lump while hydrating the particles. The range of concentration was selected based on the preliminary studies to examine the formation or the setting of a gel. Different cations such as NaCl, CaCl₂ and FeSO₄, and hydrocolloids such as xanthan, gellan, gelatin, agar and cornstarch were used to prepare gels having different concentrations of FM flour. All these hydrocolloids were hydrated for 30 min at room temperature (about 25 °C) with constant stirring as mentioned earlier. Effect of cations on gels was also studied by following the above mentioned procedure. Gels were prepared by heating the flour dispersions in a water bath, maintained at a temperature of 95 °C for 45 min (Kapri and Bhattacharya 2008) with constant stirring followed by cooling for 1 min and then transferred to petri plates (35 mm diameter, 10 mm depth). The process of gel formation was repeated twice.

Texture of gel

A texture measuring instrument (Model #TAHD, Stable Microsystems, Surrey, UK) was used to determine the compressive textural attributes of ten gels. The crosshead speed employed was 1 mm s^{-1} while using a 100 mm diameter flat surface compression probe up to 80 % strain. Fracture strain, peak stress and energy for compression were the instrumental textural parameters determined for the developed FM gels by analyzing the force-deformation curves. The maximum force, obtained as the peak force during the compression cycle, was divided by the initial area of the gel to calculate the peak stress. The point of fracture was identified from the compression curve as the position where there was a sudden decrease in force values due to the fracturing of the sample. Fracture strain was thus calculated as the ratio of deformation at fracture and the initial height of the sample, and was expressed as per cent basis. The total area under the positive force-deformation curve was reported as the total compression work or energy for compression, which indicates the quantity of energy required to achieve 80 % strain in the gel.

Syneresis

Syneresis of the gels was determined by employing the method of Verbeke et al. (2006). Five gel samples were allowed to be formed in centrifuge tubes, and were then refrigerated for 48 h. The tubes were then centrifuged in a laboratory model centrifuge and the water expelled from the samples was drained and noted. The difference in mass obtained compared to initial mass of gel gave syneresis, and was expressed as per cent basis.

Sensory assessment

Sensory assessment was performed using a 9-point hedonic scale. The various sensory attributes determined were the time of gelling (1–most quickly forming, 9–most slowly forming), hardness (1–extremely soft, 9–extremely hard), stickiness (1–least sticky, 9–extremely sticky), cohesiveness (1–least cohesive, 9–extremely cohesive), springiness (1–no springiness, 9–extremely springy) and overall acceptability (1–dislike extremely, 9–like extremely). The overall acceptability of these gels was also reported by the panelists considering their general appearance, extent of setting and textural features. Time taken to form a gel is the gel forming ability (Daubert et al. 1998) or the rate of gel formation. The attributes like stickiness and cohesiveness were expressed according to Kälviäinen et al. (2000). Ten trained panelists from the Institute performed the sensory evaluation of these gel samples using the method of descriptive sensory analysis. For evaluation, coded gel samples were served on white porcelain dishes. The panelists had the opinion that the minimum stickiness with good integrity (cohesiveness) was the most desirable feature. Sensory assessment of these gel samples was repeated twice.

Experimental design and statistical analysis

Foxtail millet gels were prepared with solid concentrations of 9, 10, 11, 12 and 13 % (*w/w*). The independent variables for the gel formation were the various concentrations of hydrocolloids such as xanthan (0.1, 0.2 and 0.3 %), gellan (0.1, 0.3 and 0.5 %), gelatin (0.1, 0.3 and 0.5 %), agar (0.010, 0.015 and 0.020 %) and cornstarch (0.5, 1.0 and 1.5 %) (according to GRAS limit) and cations such as NaCl (0.5, 1.0 and 2 %), CaCl₂ (0.1, 0.3 and 0.5 %) and FeSO₄ (0.1, 0.2 and 0.3 %). The experimental design consisted of one variable at-a-time approach. These levels have been selected based on preliminary trials considering the development of a well-set gel. It was observed that FM flour without any hydrocolloid or cation offered a very weak gel when FM concentration was 9 %, while a very hard gel resulted with 13 % FM solid. Hence, the effect of hydrocolloid and cations was judged with FM concentration of 10, 11 and 12 % (Table 1). The principal

component analysis (PCA) was employed for interrelating data on independent and dependent variables by using the statistical software Statistica[®]99 (StatSoft, Tulsa, OH, USA).

Results and discussion

Texture

The texture of a product affects the consumer acceptability of a food product. The effect of the concentration of FM solid (without any additive) on three instrumental textural parameters (peak stress, compression energy and fracture strain) is shown in Fig. 1. An increase in FM concentration shows an increasing trend on these three textural indices. However, the high value of fracture strain (>50 %) is a serious limitation of gels as these samples appear to be too tough and do not fracture easily. Hence, the effect of different additives (hydrocolloids and cations) on different textural parameters and sensory attributes has been investigated. Peak stress indicates the maximum stress that a gel can offer during compression in the instrument or inside the mouth. A very low value is associated with soggy mouth feel while an extremely high value means difficulty in biting, fracturing and/or chewing. This is also true for the compression energy which indicates the amount of energy to be spent while eating by repeated biting, compression and fracturing. The fracture strain is an indicator of the brittleness and a low value means a ductile material. Being rich in starch, gel formation from FM flour is expected to occur mainly due to swelling, hydration of starch granules and gelatinization and affects the amorphous region of starches. The strength of the formed gel depends on intragranular binding forces within swollen starch granules following treatments such as heat, moisture and annealing, structural reordering, and realignment of amylose and amylopectin (Adebawale et al. 2005).

Effect of hydrocolloids

The effect of gellan (0.1–0.5 %) on different textural attributes is shown in Fig. 2a. An increase in the concentration of FM and/or gellan increases peak stress and compression energy indicating the development of tough products. The change of coil-to-helix or disordered to ordered transition of gellan gum during heating in aqueous system has been observed by Godard et al. (1980). During the gelation of foxtail millet (FM) flour, the starch present in it has a prominent role while the hydrocolloids can reinforce the gels in terms of structural integrity and increased hardness. Sworn (2004) has also observed that the use of deacylated gellan gum improves the storage stability in puddings.

The fracture strain of these gels is also high (>40 %) meaning that these gels do not get easily fractured when

Table 1 Effect of different hydrocolloids on sensory assessment and syneresis of foxtail millet gels

Concentration of foxtail millet (%)	Time of gelling	Hardness	Stickiness	Cohesiveness	Springiness	Comment on gel	Overall acceptability	Syneresis (%)
9	7.5±0.3d	4.1±0.2b	7.2±0.2d	3.1±0.3b	3.1±0.5b	Poor setting, soft	4.0±0.2a	1.16±0.05 g
10	5.5±0.5c	5.2±0.3c	4.0±0.2c	5.8±0.4c	6.0±0.4c	Good	6.1±0.2b	1.14±0.03 g
11	5.4±0.4c	5.4±0.5c	4.1±0.3c	6.0±0.3c	6.1±0.4c	Best	8.0±0.3c	1.0±0.02f
12	2.7±0.2b	7.2±0.3d	3.1±0.4b	7.4±0.4d	7.5±0.2d	Hard	7.4±0.3c	0.96±0.02f
13	1.5±0.5a	8.2±0.4e	1.4±0.2a	8.4±0.3e	8.6±0.2e	Too hard	6.2±0.5b	0.85±0.04d
With 0.1 % gellan								
10	5.8±0.3c	5.2±0.2c	4.2±0.4c	6.6±0.3c	6.9±0.1c	Good	8.1±0.3c	0.99±0.05f
11	5.8±0.2c	5.5±0.4c	4.1±0.3c	6.4±0.2c	6.8±0.2c	Best	8.5±0.2c	0.64±0.03c
12	2.7±0.2b	7.2±0.1d	3.0±0.3b	7.6±0.2d	7.3±0.3d	Hard	7.3±0.3c	0.44±0.05b
With 0.3 % gellan								
10	5.7±0.2c	5.3±0.4c	3.9±0.3c	6.7±0.2c	6.7±0.2c	Best	8.4±0.2c	0.69±0.04c
11	5.8±0.4c	5.7±0.3c	3.9±0.3c	6.7±0.1c	6.6±0.2c	Best	8.5±0.3c	0.42±0.03b
12	2.6±0.1b	7.2±0.2d	3.1±0.3b	7.4±0.3d	7.4±0.1d	Hard	7.2±0.2c	0.36±0.05b
With 0.5 % gellan								
10	5.6±0.2c	5.4±0.2c	3.8±0.3c	6.8±0.3c	6.6±0.2c	Best	8.5±0.2c	0.67±0.02c
11	5.5±0.3c	5.8±0.4c	3.8±0.2c	6.5±0.3c	6.5±0.2c	Best	8.4±0.3c	0.47±0.04b
12	2.6±0.1b	7.1±0.3d	3.0±0.2b	7.2±0.2d	7.5±0.1d	Hard	7.1±0.2c	0.39±0.03b
With 0.1 % gelatin								
10	5.2±0.2c	5.1±0.2c	3.8±0.2c	6.3±0.3c	6.3±0.1c	Best	8.2±0.2c	0.79±0.02d
11	5.4±0.4c	5.2±0.2c	3.9±0.1c	6.1±0.1c	6.1±0.2c	Best	8.5±0.3c	0.63±0.06c
12	2.8±0.1b	7.1±0.3d	3.2±0.2b	7.4±0.4d	7.4±0.3d	Hard	7.2±0.2c	0.47±0.05b
With 0.3 % gelatin								
10	5.1±0.5c	5.3±0.2c	3.7±0.1c	6.1±0.1c	5.9±0.1c	Best	8.3±0.2c	0.46±0.03b
11	5.2±0.3c	5.3±0.3c	3.8±0.2c	5.9±0.3c	5.6±0.2c	Best	8.3±0.3c	0.33±0.05a
12	2.7±0.1b	7.2±0.2d	3.1±0.2b	7.7±0.1d	7.1±0.3d	Hard	7.1±0.2c	0.30±0.02a
With 0.5 % gelatin								
10	5.5±0.4c	5.2±0.4c	3.9±0.3c	5.8±0.2c	5.5±0.2c	Best	8.4±0.2c	0.35±0.04a
11	5.2±0.3c	5.4±0.5c	3.8±0.2c	5.7±0.3c	5.4±0.1c	Best	8.5±0.3c	0.24±0.05a
12	2.6±0.1b	7.1±0.3d	3.0±0.2b	7.6±0.2d	7.4±0.2d	Hard	7.1±0.3c	0.21±0.03a
With 0.1 % xanthan								
10	5.1±0.3c	5.1±0.4c	3.8±0.3c	5.7±0.2c	5.5±0.3c	Best	8.2±0.2c	1.35±0.02 h
11	5.0±0.3c	5.3±0.3c	3.9±0.3c	5.5±0.1c	5.3±0.3c	Best	8.3±0.3c	1.13±0.03 g
12	2.7±0.2b	7.3±0.2d	3.0±0.2b	7.2±0.3d	7.5±0.3d	Hard	7.2±0.2c	0.94±0.04f
With 0.2 % xanthan								
10	5.4±0.4c	5.2±0.5c	4.0±0.3c	5.8±0.3c	5.1±0.4c	Best	8.3±0.2c	0.62±0.02c
11	5.6±0.4c	5.3±0.2c	4.0±0.3c	5.7±0.2c	5.2±0.8c	Best	8.3±0.3c	0.61±0.02c
12	2.6±0.7b	7.3±0.2d	3.1±0.4b	7.1±0.1d	7.5±0.2d	Hard	7.3±0.3c	0.55±0.03c
With 0.3 % xanthan								
10	5.7±0.3c	5.9±0.4c	4.2±0.4c	5.9±0.2c	4.8±0.3c	Best	8.4±0.2c	0.65±0.03c
11	5.5±0.2c	5.8±0.3c	4.2±0.3c	6.0±0.2c	4.9±0.2c	Best	8.5±0.3c	0.63±0.05c
12	2.5±0.4b	7.2±0.3d	3.0±0.4b	7.7±0.1d	7.5±0.2d	Hard	7.2±0.3c	0.61±0.04c
With 0.5 % corn starch								
10	5.1±0.3c	6.0±0.2c	4.1±0.4c	5.8±0.3c	4.7±0.3c	Best	8.3±0.2c	0.87±0.02e
11	5.3±0.2c	6.1±0.3c	4.1±0.3c	5.7±0.2c	4.6±0.4c	Best	8.5±0.3c	0.60±0.03c
12	2.5±0.4b	7.3±0.4d	3.2±0.2b	7.6±0.2d	7.3±0.1d	Marginally hard	8.4±0.2c	0.56±0.04c
1.0 % corn starch								
10	5.0±0.3c	6.2±0.2c	4.2±0.4c	5.5±0.2c	4.6±0.1c	Best	8.5±0.2c	0.88±0.05e
11	5.4±0.2c	6.2±0.3c	4.1±0.3c	5.6±0.1c	4.4±0.3c	Best	8.6±0.2c	0.55±0.02c

Table 1 (continued)

Concentration of foxtail millet (%)	Time of gelling	Hardness	Stickiness	Cohesiveness	Springiness	Comment on gel	Overall acceptability	Syneresis (%)
12	2.6±0.3b	7.2±0.3d	3.2±0.4b	7.6±0.2d	7.5±0.1d	Marginally hard	8.5±0.3c	0.33±0.02a
1.5 % corn starch								
10	5.8±0.3c	6.1±0.4c	4.2±0.2c	5.5±0.1c	4.7±0.2c	Best	8.6±0.2c	0.28±0.03a
11	5.5±0.2c	6.0±0.3c	4.2±0.3c	5.6±0.2c	4.9±0.1c	Best	8.6±0.3c	0.27±0.04a
12	2.7±0.2b	7.1±0.4d	3.2±0.2b	7.6±0.2d	7.6±0.1d	Hard	8.1±0.2c	0.16±0.05a
With 0.01 % agar								
10	5.0±0.3c	6.2±0.2c	4.3±0.3c	5.8±0.1c	4.8±0.2c	Good	7.6±0.3c	0.88±0.02e
11	5.1±0.2c	6.0±0.3c	4.3±0.3c	5.6±0.2c	4.9±0.3c	Good	7.8±0.4c	0.41±0.04b
12	2.5±0.2b	7.2±0.2d	3.3±0.2b	7.5±0.2d	7.4±0.4d	Marginally hard	7.3±0.3c	0.43±0.04b
0.015 % agar								
10	5.8±0.3c	6.1±0.4c	4.3±0.2c	5.9±0.3c	4.7±0.2c	Good	7.8±0.3c	0.18±0.01a
11	5.5±0.2c	6.2±0.3c	4.2±0.3c	5.5±0.2c	4.8±0.3c	Best	8.2±0.2c	0.10±0.02a
12	2.6±0.3b	7.2±0.4d	3.1±0.4b	7.6±0.2d	7.6±0.2d	Marginally hard	7.3±0.2c	0.10±0.03a
0.02 % agar								
10	5.7±0.3c	6.1±0.4b	4.2±0.3c	5.7±0.1c	4.8±0.3c	Good	7.9±0.2c	0.21±0.02a
11	5.8±0.2c	6.0±0.3c	4.1±0.3c	5.5±0.2c	4.6±0.1c	Best	8.4±0.3c	0.15±0.03a
12	2.8±0.3b	7.2±0.3d	3.0±0.2b	7.7±0.1d	7.7±0.1d	Hard	7.5±0.1c	0.16±0.02a

Scale: 9 point hedonic scale

Time of gelling: 1 - Most quickly forming, 9 - Most slowly forming

Hardness: 1-Extremely soft, 9 - Extremely hard

Stickiness: 1- Least sticky, 9 - Extremely sticky

Cohesiveness: 1- Least cohesive, 9 - Extremely cohesive

Springiness: 1 - No springiness, 9 - Extremely springy

OA score 1- least acceptable, 9- extremely acceptable

Values with different alphabets in the same column indicate statistically different at $p \leq 0.05$

compressing in the instrument or inside the mouth; these gels show a delayed fracture at a high compressive strain. Hence, the role of gellan is not advantageous in developing acceptable FM gels. It may be mentioned here that a low fracture strain means a brittle product while a high value indicate a difficult

to break situation. However, the extent of soft/hard is dictated by the fracture force/stress and peak stress.

In the case of gelatin (0.1–0.5 %) added gels (Fig. 2b), compression energy decreases markedly when gelatin is added. The fracture strain for 10 % FM samples are low (<30 %) with gelatin at 0.1 and 0.3 % levels, indicating the formation of a desirable brittle gel under these conditions. An increase in xanthan concentration increases peak stress of gels (Fig. 2c) resulting in the formation of tough gels. In the case of the existence of a favourable interaction between the chains of two polymers (starch and hydrocolloid) connected together by intermolecular binding or two different polymers, they interact by mutual entanglements leading to an increase in the structural integrity (Sikora et al. 2008), and thus the hardness/compression energy of the gelled product increases. Marfil et al. (2012) have indicated that the introduction of gelatin and acid modified corn starch causes an increase in hardness and opacity in gummy gel preparation. Djabourov et al. (1985) have observed that during quenching and isothermal annealing of gelatin and water, gelatin chains undergo a conformational coil helix transition, and creates a network

Fig 1 Effect of concentration on textural characteristics of foxtail millet gel

Fig 2 Effect of **a** gellan, **b** gelatin **c** xanthan, **d** corn starch and **e** agar on textural characteristics of foxtail millet gel

structure which makes the system to change from a purely viscous liquid or sol to an almost purely elastic solid or gel.

The fracture strain of these gels is also high (>40 %) indicating the unsuitability of xanthan in developing acceptable gels. These samples appear to be a non-brittle gel. The presence of corn starch increases the peak stress and compression energy (Fig. 2d) as corn starch addition causes tougher gel; an increase in starch content can enhance the level of gelatinisation to offer a harder gel. The fracture strain behaves in a different manner; at 10 % FM concentration, the fracture strain reduces to as low as 25 % indicating that addition of corn starch results in gels that are tougher but brittle in nature.

Agar does not give any clear trend with respect to peak stress and compression energy (Fig. 2e). This phenomenon may be attributed to the structure of the formed gel network which in turn depends on the characteristics of the hydrocolloid undergoing sol–gel transition. However, the fracture strain increases due to the presence of agar meaning the creation of a non-brittle/tough gel. A high magnitude of fracture strain of more than 45 % in most of the agar-FM gels make agar added gel samples unsuitable as they do not break easily.

Effect of cation

The effect of using cations like NaCl, CaCl₂ and FeSO₄ on FM gels shows that NaCl up to 2 % level decreases the compression energy (Fig. 3a). It is possible that salt induces the solubilization of salt soluble proteins such that these proteins form a part of the sol and participate in the gelling process. However, the formed gels are softer while the fracture strain of these gels is above 40 % indicating the development of less brittle samples. It is possible that a monovalent cation like NaCl has less binding effect on gel formation.

The use of calcium chloride increases the peak stress and compression energy while the fracture strain is marginally affected (Fig. 3b). The fracture strain of samples increases with FM concentration and the values are more than 40 %. This means that the use of CaCl₂ improves the integrity of the samples in addition to increasing the toughness. Tang et al. (1996) have reported an increase in gellan gel strength with an increase in cation concentration up to a certain level. Gel strength of gellan-gelatin mixed gels increases with an increase in calcium ion concentration (Lai et al. 2000). The addition of FeSO₄ markedly increases the peak stress and compression energy (Fig. 3c); the fracture strain is marginally affected. The addition of 0.1 % FeSO₄, FM at 10 % solid concentration forms gels with decreased fracture strain values (~30 %).

It indicates that a low level of FeSO₄ is suitable for developing a brittle gel which is also nutritious due to the addition of divalent iron.

Syneresis

The release of water during post-gelling phase reflects the phenomenon of syneresis, and is an undesirable feature or attribute in gels. Tables 1 and 2 show the syneresis values of gels prepared with additives like different hydrocolloids and cations, respectively. An increase in FM and hydrocolloid concentrations decreases syneresis (Table 1). Sutherland (2007) has reported that hydrocolloids which are used for thickening, gelling or dispersing emulsions reduces syneresis by increasing the water retention in the system. The low values of syneresis (less than 0.25 %) are associated with FM gels in combination with 0.5 % gelatin, or 1.5 % corn starch, or with 0.015 to 0.020 % agar. Agar incorporated gels has the least syneresis compared to corn starch, xanthan, gelatin and gellan samples meaning that agar improves the shelf-stability of the gel and prevents nutrient loss in a better way than other hydrocolloids used in the present investigation.

The cations have a lesser effect on syneresis compared to hydrocolloids (Table 2). Among the cations used here, NaCl at a level of 0.5 to 2.0 % can bring down syneresis to less than 0.1 %. Other cations like CaCl₂ and FeSO₄ do not offer any significant effect on syneresis.

Sensory assessment

Tables 1 and 2 show the sensory attributes of the FM gels prepared with hydrocolloids and cations, respectively. An increase in FM concentration decreases the time of gelling and stickiness; an increase in FM concentration obviously increases the availability of more quantity of starch so that water gets enough solid in the vicinity to form the gel faster, and possibly denser. Hence, hardness, cohesiveness and springiness increase for gels made with the hydrocolloids used in the present study (Table 1).

Gel made with 11 % FM without any additive is acceptable in terms of sensory perceptions. The gels having 0.2 % CaCl₂ or 0.1 % FeSO₄ with 10 % concentration of FM can develop acceptable gels with the desirable structural integrity (Table 1). Hydrocolloids also possess a good binding property at the appropriate concentrations; 0.2 % xanthan or 0.3 % gellan or 0.5 % corn starch along with 10 % FM concentration can offer acceptable gels with respect of sensory acceptability (Table 2).

The trend of gel forming ability of various hydrocolloids is in the order of gellan>gelatin>xanthan>corn starch>agar according to sensory assessment. The addition of cations (mainly FeSO₄ and CaCl₂) and hydrocolloids at different

Fig 3 Effect of **a** NaCl, **b** FeSO_4 and **c** CaCl_2 on textural characteristics of foxtail millet gel

Table 2 Effect of different cations on sensory assessment and syneresis of foxtail millet gels

Concentration of foxtail millet (%)	Time of gelling	Hardness	Stickiness	Cohesiveness	Springiness	Comment on gel	OA score	Syneresis (%)
With 0.5 % NaCl								
10	4.2±0.3b	5.4±0.1c	4.7±0.6c	6.2±0.4c	6.3±0.3c	Best	7.6±0.2c	0.13±0.1a
11	3.8±0.4b	5.7±0.1c	4.2±0.3c	7.0±0.4c	7.3±0.1c	Best	8.1±0.1c	0.12±0.1a
12	2.8±0.1a	8.0±0.1d	3.2±0.3b	7.9±0.1d	8.2±0.1d	Hard	7.9±0.1c	0.10±0.1a
With 1 % NaCl								
10	4.0±0.1b	5.4±0.3c	4.5±0.3c	6.8±0.1c	6.5±0.2c	Best	7.2±0.1c	0.12±0.1a
11	3.8±0.1b	5.1±0.5c	4.0±0.2c	6.9±0.3c	7.3±0.2c	Best	8.2±0.1c	0.11±0.1a
12	2.7±0.2a	7.9±0.3d	3.1±0.1b	7.8±0.2c	8.2±0.1d	Hard	7.6±0.1c	0.11±0.1a
With 2 % NaCl								
10	3.9±0.1b	5.0±0.1c	4.4±0.2c	6.9±0.1c	6.6±0.1c	Best	8.2±0.1c	0.89±0.1j
11	3.9±0.2b	5.1±0.1c	3.9±0.4c	7.0±0.4c	7.2±0.4c	Best	8.2±0.1c	0.93±0.1 k
12	2.6±0.1a	7.9±0.2d	3.0±0.1b	7.9±0.1d	8.0±0.1d	Hard	7.7±0.1c	0.90±0.1j
With 0.1 % CaCl ₂								
10	4.1±0.2b	5.2±0.2c	4.8±0.2c	6.7±0.1c	6.6±0.2c	Best	8.2±0.1c	0.46±0.1c
11	3.8±0.5b	5.5±0.4c	4.4±0.4c	6.8±0.2c	7.0±0.1c	Best	8.2±0.1c	0.44±0.1c
12	2.8±0.1a	7.5±0.2d	3.2±0.1b	7.8±0.2c	8.0±0.3d	Hard	7.6±0.1c	0.40±0.1c
With 0.3 % CaCl ₂								
10	4.0±0.1b	5.3±0.2c	4.4±0.1c	6.8±0.2c	6.7±0.3c	Best	8.4±0.1c	0.51±0.1d
11	3.9±0.4b	5.7±0.2c	4.3±0.3c	6.8±0.1c	6.9±0.2c	Best	8.5±0.1c	0.48±0.1c
12	2.7±0.2a	7.6±0.3d	3.1±0.2b	7.8±0.2c	8.0±0.1d	Hard	7.6±0.1c	0.43±0.1c
With 0.5 % CaCl ₂								
10	3.9±0.1b	5.4±0.1c	4.3±0.1c	6.9±0.1c	6.4±0.4c	Best	8.5±0.1c	1.04±0.1n
11	3.9±0.2b	5.8±0.1c	4.0±0.2c	7.0±0.2c	7.1±0.3c	Best	8.2±0.1c	0.87±0.1j
12	2.6±0.1a	7.7±0.4d	3.0±0.1b	7.9±0.3c	8.1±0.2d	Difficult to pour, hard gel	7.4±0.1c	0.62±0.1f
With 0.1 % FeSO ₄								
10	4.2±0.2b	5.3±0.1c	4.5±0.1c	6.9±0.1c	6.0±0.2c	Best	8.4±0.1c	1.03±0.1n
11	3.9±0.2b	5.7±0.2c	4.2±0.2c	7.0±0.1c	7.0±0.1c	Best	8.4±0.1c	0.76±0.1 h
12	2.7±0.2a	7.5±0.2d	3.1±0.2b	7.8±0.2c	8.1±0.1d	Marginally hard	7.6±0.1c	0.76±0.1 h
With 0.2 % FeSO ₄								
10	4.1±0.2b	5.2±0.3c	4.3±0.1c	6.8±0.2c	5.9±0.2c	Best	8.6±0.1c	0.40±0.1c
11	3.8±0.1b	5.2±0.2c	4.0±0.2c	7.2±0.2c	7.2±0.3c	Best	8.5±0.1c	0.38±0.1c
12	2.8±0.1a	7.6±0.3d	2.8±0.1a	8.2±0.1d	8.2±0.1d	Hard	7.5±0.1c	0.35±0.1b
With 0.3 % FeSO ₄								
10	4.0±0.2b	5.1±0.2c	4.3±0.1c	6.7±0.1c	5.8±0.2c	Best	8.6±0.1c	0.79±0.1i
11	3.9±0.2b	5.1±0.1c	3.9±0.1c	7.4±0.2c	7.3±0.3c	Best	8.4±0.1c	0.67±0.1 g
12	2.8±0.1a	7.7±0.3d	2.9±0.1b	8.2±0.3d	8.2±0.1d	Hard	7.4±0.1c	0.59±0.1e

Values with different alphabets in the same column indicate statistically different at $p \leq 0.05$

concentrations result in an improvement in gel formation with reference to structural integrity of the gel. Gellan shows a higher increase in gelation than other hydrocolloid used in the present study. The addition of agar shows the least ability in gel formation among these hydrocolloids. Harding et al. (2011) have reported that calcium salts such as calcium sulphate, calcium chloride and calcium citrate try to form crosslink in gels, and thus the textural attributes are improved.

Interrelationship

The principal component analysis (PCA) is a statistical representation to show the interrelation among the variables and the indices (both subjective and objective), and their nature as individual groups. PCA plots have been obtained separately for gels with added hydrocolloids and cations (Figs. 4 and 5). The principal components account for a total variation of 97.2 % and 93.4 % for FM gels with added hydrocolloids

Fig 4 PCA plot on the hydrocolloid effect of foxtail millet gel

and cations, respectively. The PCA plot of FM gels with added hydrocolloids having sensory and instrumental textural data shows that stickiness and gelling time are closely related being in the same quadrant (Fig. 4). The addition of agar, gelatin and xanthan along with no hydrocolloid added gels are close to each other in PC1 against PC2 plot. Springiness, cohesiveness, FM concentration and hardness of hydrocolloid added gels lie in same quadrant and are closely related. An increase in FM concentration increases the starch content to undergo gelatinisation to finally yield a gel with improved cohesion characteristics in addition to developing the solid or elastic characteristics. The addition of gellan and corn starch at different concentrations along with instrumental textural indices (fracture strain, peak stress and compression energy) are close to each other are situated in nearby locations. These scores are interrelated with overall score which is in the opposite quadrant. It means that an increase in these textural parameters decreases the overall acceptability of the formed gels. Compression energy, cohesiveness, springiness, FM concentration and hardness are close to each other in the first quadrant, which means that an increase in concentration increases instrumental and sensory attributes (Fig. 4). These indices are interrelated with overall score which is in the opposite quadrant. The effect of addition of cation on gel formation has a close relationship with peak stress and syneresis as they lie in the same quadrant (Fig. 5). It means that an increase in these textural indices decreases the overall acceptability of the formed gels.

Table 3 shows the desirability index of the additive containing FM gels. For achieving the best acceptable gel gellan at 0.3 % concentration or cornstarch at 1.0 % concentration

offers the best choice. However, sodium chloride at 1.2 % level or calcium chloride at the 0.3 % level or ferrous sulfate at the 0.3 % level can also provide excellent values for desirability index of 0.916, 0.910 and 0.900, respectively.

The common hydrocolloids like gellan gum, agar and gelatin can exhibit a coil-to-helix, or disordered to ordered transition upon cooling or gel formation (Godard et al. 1980). During the gelation of foxtail millet (FM) flour, the starch present in it has a prominent role while the three hydrocolloids can reinforce the gels in terms of structural integrity and reduced syneresis. The divalent cations are more effective in improving the gel strength in hydrocolloids than the monovalent cations (Chandrasekaran et al. 1988; Sanderson 1990; Tang et al. 1996). A minimum of 11 % FM flour is required for gel formation from foxtail millet flour without using any additive. However, at a lesser concentration of 10 %, the addition of some hydrocolloids has improved the structural integrity. This may be possible when a favourable interaction exists between the chains of two polymers connected together by intermolecular binding (Banerjee and Bhattacharya 2012) or two different polymers interact by mutual entanglements (Sikora et al. 2008). Many hydrocolloids, being hydrophilic in nature, improve the gel network formation which has also been noticed during the FM gel formation in the present investigation as being supported by improved sensory attributes and reduced syneresis values. Deacylated gellan gum has been reported to improve moisture retention, flavour release and storage stability in puddings and to reduce syneresis (Sworn 2004).

Tang et al. (1996) have studied the effect of monovalent and divalent cations on gellan gels at a low concentration of cations, and have reported an increase in gel strength with an

Fig 5 PCA plot on the cation effect of foxtail millet gel

increase in cation concentration. Calcium added gellan gels have been reported to be tougher than magnesium added gels at the optimum concentration of the ions. Lai et al. (2000) have studied the effect of calcium ions on the gel strength of gellan-gelatin mixed gels. An increase in calcium ion concentration improves hardness of these gels up to a certain level of calcium ions. There has been a reduction in hardness after crossing the critical limit of calcium ion concentration in these gels. At low concentrations of calcium ions, the brittleness, springiness and cohesiveness of the gels are less sensitive. Higher concentration of calcium ions results in increased brittleness, and less cohesiveness and springiness. In the present study, the effect of FeSO₄ and CaCl₂ is more pronounced than

NaCl on FM gels. The results also emphasize that divalent cations have more effect on gel formation compared to monovalent ion. The cations like NaCl, CaCl₂ and FeSO₄, and hydrocolloids such as agar, gelatin, gellan, corn starch and xanthan can improve the binding/cohesive characteristics of the formed gel. Thus, they reduce syneresis which in turn also decreases the loss of nutrients which is an advantageous feature for food gels. Hydrocolloids which are used for thickening, gelling, dispersing and stabilizing emulsions are reported to reduce syneresis by increasing the water retention in the system (Sutherland 2007). Marfil et al. (2012) have prepared gummy gels with gelatin and acid modified corn starch (AMCS), and have indicated that the introduction of AMCS in gelatin causes an increase in hardness and opacity, and a decrease in stringiness and adhesiveness.

Table 3 Desirability index for the additives effect on foxtail millet (FM) gels

Additive	Additive concentration (%)	Predicted overall score	Desirability index
No additives	—	8.0	0.910
Gellan	0.30	8.5	1.000
Gelatin	0.30	8.4	0.913
Xanthan	0.20	8.3	0.897
Corn starch	1.00	8.6	1.000
Agar	0.015	8.1	0.774
NaCl	1.16	8.1	0.916
CaCl ₂	0.30	8.5	0.910
FeSO ₄	0.20	8.4	0.900

Conclusions

Foxtail millet, being rich in starch (about 76 %) facilitated gel formation. The addition of cations and hydrocolloids improve the integrity and decreases syneresis. Acceptable soft gels with high sensory overall score (more than 8.0) were formed with 11 % foxtail millet concentration. The use of additives at suitable concentrations (such as 0.3 % gellan or 0.3 % gelatin or 1 % corn starch or 0.3 % CaCl₂ or 0.2 % FeSO₄) further improved the textural and sensory attributes. Thus, micro-nutrient enriched millet gels can be formulated using the under-utilized grain like foxtail millet to offer a health

promoting convenience food. Compression energy, cohesiveness, springiness, FM concentration and hardness showed close interrelationships. The effect of cation on gel formation has a close relationship with peak stress and syneresis. Stickiness and gelling time of FM gels are closely related with added hydrocolloid gels having sensory and instrumental textural data.

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Conflict of interest The authors declare that they have no conflict of interest.

References

- Adebowale YA, Adeyemi IA, Oshodi AA (2005) Functional and physicochemical properties of flours of six *Mucuna* species. *Afr J Biotechnol* 4(12):1461–1468
- AOAC (2002) Association of official analytical chemists (16th ed.) Official methods of analysis. AOAC, Washington DC
- Arendt EK, Morrissey A, Moore MM, Dal Bello F (2008) Gluten free breads. In: Arendt EK, Dal Bello F (eds) *Gluten-free cereal products and beverages*. Academic, San Diego, pp 289–319
- Banerjee S, Bhattacharya S (2012) Food gels: gelling process and new applications. *Crit Rev Food Sci Nutr* 52:334–346
- Chandrasekaran R, Puigjaner LC, Joyce KL, Arnott S (1988) Cation interactions in gellan: an X-ray study of the potassium salt. *Carbohydr Res* 181:23–40
- Choudhury M, Das P, Baroova B (2011) Nutritional evaluation of popped and malted indigenous millet of Assam. *J Food Sci Technol* 48(6):706–711
- Daubert CR, Tkachuk JA, Truong VD (1998) Quantitative measurement of food spreadability using the vane method. *J Texture Stud* 29(4):427–435
- Djabourov M, Maquet J, Theveneau H, Leblond J, Papon P (1985) Kinetics of gelation of aqueous gelatin solutions. *Br Polym J* 17(2):169–174
- Elhardallou SB, Walker AF (1993) The water-holding capacity of three starchy legumes in the raw, cooked and fibre-rich fraction forms. *Plant Foods Hum Nutr* 44(2):171–179
- Godard P, Biebuyck JJ, Barriat PA, Naveau H, Mercier JP (1980) Kinetics of the crystallization of gelatin in aqueous-solution: influence of different molecular-components. *Makromol Chem* 181(9):2009–2018
- Harding SE, Smith IH, Lawson CJ, Gahler RJ, Wood S (2011) Studies on the macromolecular interactions in tertiary mixtures of konjac glucomannan, xanthan gum and sodium alginate. *Carbohydr Polym* 83:329–338
- Kälviäinen N, Roininen K, Tuorila H (2000) Sensory characterization of high viscosity gels made with different thickeners. *J Texture Stud* 31(4):407–420
- Kapri A, Bhattacharya S (2008) Gelling behavior of rice flour dispersions at different concentrations of solids and time of heating. *J Texture Stud* 39(3):231–251
- Lai VMF, Wong PAL, Lii CY (2000) Effects of cation properties on sol–gel transition and gel properties of κ -carrageenan. *J Food Sci* 65:1332–1337
- Lapante S, Turgeon SL, Paquin P (2005) Effect of pH, ionic strength, and composition on emulsion stabilizing properties of chitosan in a model system containing whey protein isolate. *Food Hydrocoll* 19(4):721–729
- Liu HS, Yu L, Xie FW, Chen L (2006) Gelatinisation of corn starch with different amylose/amylopectin content. *Carbohydr Poly* 65:357–363
- Lu H, Yang X, Ye M, Liu KB, Xia Z, Ren X, Cai L, Wu N, Liu TS (2005) Culinary archaeology: millet noodles in late Neolithic China. *Nature* 437(7061):967–968
- Marfil PHM, Anhê ACBM, Telis VRN (2012) Texture and microstructure of gelatin/corn starch-based gummy confections. *Food Biophys* 7(3):236–243
- Pawar VD, Machewad G (2006) Processing of foxtail millet for improved nutrient availability. *J Food Process and Preserv* 30(3):269–279
- Renard D, van de Velde F, Visschers RW (2006) The gap between food gel structure, texture and perception. *Food Hydrocoll* 20(4):423–431
- Sampath TV, Razvi SM, Singh D, Bondale KV (1989) Small millets in Indian agriculture. In: Seetharam A, Riley KW, Harinarayana G (eds) *Small millets in global agriculture*. Oxford & IBH Publishing Co. Pvt. Ltd., New Delhi, pp 33–44
- Sanderson GR (1990) Gellan gum. In: Harris P (ed) *Food gels*. Elsevier Science Publishers Ltd., New York, pp 201–232
- Sikora M, Kowalski S, Tomasik P (2008) Binary hydrocolloids from starches and xanthan gum. *Food Hydrocoll* 22:943–952
- Sutherland IW (2007) Biotechnology of microbial polysaccharides in food. In: Shetty K, Paliyath G, Pometto A, Levin E (eds) *Food biotechnology*, 2nd edn. CRC Press, Boca Raton, pp 193–220
- Sworn G (2004) Hydrocolloid thickeners and their applications. In: Philips GO, Williams PA (eds) *Gums and stabilizers for the food industry*, vol 12. RSC Publishing, Oxford, pp 13–22
- Tang J, Tung MA, Zeng Y (1996) Compression strength and deformation of gellan gels formed with mono- and divalent cations. *Carbohydr Polym* 29:11–16
- Truswell AS (2002) Cereal grains and coronary heart disease. *Eur J Clin Nutr* 56(1):1–14
- Vasudeva S, Vishwanathan KH, Aswathanarayana KN, Indudhara Swamy YM (2010) Hydration behaviour of food grains and modelling their moisture pick up as per Peleg's equation: Part I. *Cereals J Food Sci Technol* 47:34–41
- Verbeken D, Bael K, Thas O, Dewettinck K (2006) Interactions between κ -carrageenan, milk proteins and modified starch in sterilized dairy desserts. *Int Dairy J* 16(5):482–488