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Viscoelastic Properties of Mixed Flour Gels

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ABSTRACT The effects of filler substitution on the viscoelastic properties of mungbean starch gels were studied. The particulate fillers, namely, corn flour, tapioca starch, brown rice flour, okara and mungbean malt were substituted (in mass fractions ranging from 0 to 0.3 of total solid) to the primary mungbean starch gels containing 15% total solid (w/v). The results indicated that substitution with particulate fillers had antagonistic effects on shear stress and strain. The substituted gels became weaker and less cohesive than the mungbean starch gels. Principal Component Analysis indicated that 3 types of mixed gel with different viscoelastic properties could be generated by changing the types of filler and substitution levels. This approach to food polymer science can help in designing starch-based food products with desirable textural properties

KEYWORDS: food polymer, flour, gel, mungbean.

INTRODUCTION

Food is a complex system where food constituents, ie, proteins, carbohydrates, minerals, vitamins, etc, interact in an aqueous environment. The complex chemical and physical interactions arising during processing and storage are the main factors determining the heterogeneous structure and texture of foods. Recent studies have been carried out by integrating the relationships between chemical components and structures to predict and understand the functional properties of food constituents in mixed systems.[1,2,3] This is because the textural properties of foods result from the formation of rigid structures in relation to the fluid ones. Therefore, changing the formulation, either for cost reducing or nutritional purposes, can alter the chemical and physical interactions responsible for the viscoelastic and, hence, textural properties.

A gel is defined as a three-dimensional network holding a large quantity of solvent (ie, aqueous phase) and showing mechanical rigidity. It is the basic structure in many food products, such as cheese, sausage, tofu, cake, bread and so on. At least three types of gels could be formed in a mixed gel system, ie, filled gels, complex gels and interpenetrating polymer networks[4,5]. Filled gels are those with additional component(s) interspersed throughout the primary gel network. Complex gels are formed when interactions among the components (known as co-polymerization) occur, leading to the association of each component. In interpenetrating gels, the networks of each component are physically compatible and penetrate each other to form mixed structures. These structures are responsible for the textural properties in sensory terms (eg tough, brittle, rubbery, mushy, etc).

The roles of particulate fillers on viscoelastic properties of flour gels were investigated in this study. This is because particulate fillers are responsible for textural characteristics of many foods by embedding in the starch gel matrix. The entire study was based on macroscopically heterogeneous gel structures, representing the multi-phase food systems. This is different from biopolymer viewpoints. The mixed gels were heterogeneous and polydisperse, composed of partially solubilized amylose, amylopectin and remnants of starch granules from different sources. The study was carried out by adding particulate fillers to alter the interfacial interactions between the primary gel matrix of mungbean and particulate fillers and, hence, viscoelastic properties of the primary mungbean starch gel matrix. The gel characteristics in this study were manipulated by: (a) decreasing the strength of network using malt enzyme hydrolysis, (b) increasing the molecular entanglement using tapioca starch and corn flour, (c) decreasing the fluidity of the network by restricting the swelling of physicochemically modified brown rice flour filler and (d) increasing the fluidity of the gel network by enhancing the swelling of okara (soybean residue from soy milk production) filler. Apart from the fillers' characteristics described, the mass fraction of the primary structure was also diluted by substitution method. The primary mungbean gel network thus had decreasing continuity and connectivity, resulting in diverse gel types. The information obtained could help to elucidate the roles of food ingredient interactions and their contribution to food texture.

Materials and Methods

Particulate fillers

Food grade mungbean starch, corn flour and tapioca starch were purchased from the local supermarket. Mungbean malts with different malting times were prepared by soaking mungbeans in tap water for 14 and 36 h, drying in a cabinet tray dryer at 55 °C to reduce the moisture content to approximately 10%, grinding to a particle size $\leq$ 1 mm using the hammer mill and storing at –40 °C. Okara, or soybean residue (10.3% moisture, 37.6% protein, 19.22% fat and 3.2% ash[6]), were prepared by soaking the soybeans in tap water for 16 h and grinding with water to obtain soy milk slurries. The soybean residue was separated from the soy milk by filtration, dried and ground in the same manner as the mungbean malt. Physicochemically modified brown rice flour was prepared by milling brown rice (9.6% moisture, 9.4% protein, 5.4% fat and 0.2% ash[6]) to a particle size $\leq$ 1 mm using a hammer mill, conditioning with a distilled water, whey suspension (13 % total solid) or whey yogurt aged 4 h (13 % total solid) to obtain a moisture content of 30%, storing at 10 °C for 16 h, and drying in a cabinet tray dryer at 55 °C for 1 h to induce Maillard reactions[7]. This resulted in Maillard products coated on the surface of the brown rice flours.

Sample preparation

Mixed gels were prepared in two separate trials using different lots of filler preparation. Mixed flour suspensions of 15% w/v total solid substituted with mass fractions of filler ranging from 0 to 0.3 were prepared in distilled water unless specified otherwise. The suspensions were heated in a water bath until the temperature reached 75 °C and held for 5 min, filled in polycarbonate tubes (20 mm in diameter), left at room temperature (30 °C) for 3 h and incubated at 25 °C for 1 h prior to the analyses.

Fracture properties

Cylindrical gel sections (20 mm diameter x 10 mm long) were compressed between the lubricated stationary bottom plate and a moving upper plate on a Lloyde Texture Analyzer (Series 500, Fareham, UK) at the rate of 10 mm/min until they fractured.

Assuming that a specimen is practically incompressible, shear stress (σ) can be calculated as[8]:

$$\sigma = \frac{F(L-\Delta L)}{\pi r^2 L}$$

where F is the compressive force at the moment of failure, L is the original sample length, ΔL is the corresponding deformation at failure, and r is the original radius. Shear strain was calculated as Hencky strain (ε):

$$\varepsilon = -\ln [1 - \frac{\Delta L}{L}]$$

Stress relaxation behaviour

Gels were cut into 10 mm long cylinders and compressed at a rate of 60 mm/min. The specimens were compressed to 80% of their original height (*ie*, 20% deformation) for 1 min using a stress relaxation test. The initial force load before relaxation, end force load after relaxation for 1 min and percent stress relaxation were collected.

Fatigue test

The 10 mm long cylindrical gels were compressed to 60% of their original height twice at the rate of 100 mm/min for both first and second compression cycles to evaluate the cohesiveness of the heterogeneous network. The cohesiveness is defined as the ratio of positive force area during the second compression to that during the first compression.[9,10]

Statistical analyses

Data from two separate trials were analyzed using the Statistical Analysis System (SAS Institute, NC) with the ANOVA procedure. The multivariate analysis PRINCOM procedure was further applied to the dataset to summarize the viscoelastic data into two uncorrelated dimensions.

Results and Discussion

Statistical analyses indicated that there was no significant difference between the trials. Increasing substitution levels significantly affected the viscoelastic properties, namely, stress and strain at failure, initial load, end load, percent stress relaxation and cohesiveness ($p<0.05$). However, the fillers used in this study affected the viscoelastic properties differently.

The maximum stress and strain at failure in large deformation test can help elucidate the strength and ultimate extensibility of the three-dimensional gel network. Figure 1 (a-h) summarizes the influences of the level of substitution and filler type on stress and strain at fracture. The primary mungbean gel exhibited higher shear stress and strain than the substituted ones, indicating tougher texture. The increase in substitution level towards 4.5% in total solid reduced stress and strain, suggesting that the structure was weaker, less cohesive and more mushy in sensory terms.[9-11] However, the substitution of mungbean starch with okara and 36 h malt at 4.5% affected the primary gel structure differently. Increasing their substitution level did not significantly affect shear strain but reduced shear stress. Considering both the stress and strain values, the results suggested that the mixed structures were more rubbery than the primary structure of mungbean starch gels.

The measurement of stress relaxation after compression can be used to indicate viscoelastic behaviour of foods.[12] Presented in Figures 2 and 3, the substitution of primary structure with 1.5% particulate fillers slightly decreased the initial load, end load and percent stress relaxation values, with the exception of the values obtained from the gels substituted with 36 h malt (36M). However, when 4.5% particulate fillers were substituted into the primary mungbean starch gel network (MB), the presence of filler decreased the initial and end load values dramatically. Samples substituted with fillers relaxed more than the mungbean starch gel, resulting in a much lower end load value after 1 min of deformation. Although the mixed structure from the mungbean-tapioca blend (T) can form gels, the gels were too weak and tended to collapse due to the gravity; thus, they were not evaluated in this test. The viscoelastic mungbean starch gels substituted with 36 h malt relaxed to the highest extent (Figure 3c). Similar to mungbean-36 h malt gels, the mungbean-okara gels (O) showed low initial and end load values. The extent of stress relaxation of both gels was in good agreement with stress and strain at failure results (Figure 1). However, the mixed gels containing brown rice flour (BR), brown rice flour coated with whey (BRW), brown rice flour coated with whey yogurt (BRWY) and 14 h malt (14M) showed slightly different relaxation behaviour (Figures 2 and 3), since their initial and end load values were much higher than the mungbean-okara (O) and mungbean-36h malt (36M) gels. It appeared that the influences of different fillers on deformation mechanisms differed from each other.

The sensory cohesiveness can be assessed objectively by the fatigue test.[10] The gels were compressed twice to imitate mastication and areas under the peak during first and second compression cycles were calculated. Results in Figure 4 are in good agreement with those of the failure test and stress relaxation test, which were performed using a single compression cycle. Increasing levels of substitution reduced the cohesiveness of mixed gel and the degree of cohesiveness also depended on the types of filler ($p<0.05$).

The rheological properties of a food material can be correlated to the sensory characteristics (eg, mushy, brittle, rubbery, tough).[9,10] Stress relates to sensory hardness and strain to sensory cohesiveness.[9-11] In this study, different particulate fillers were embedded in primary mungbean starch gel matrices. The rheological properties of mixed gels, therefore, were governed by the fraction of primary network and interfacial interactions within the matrices.[1] Overall, the substitution of the primary network showed antagonistic effects to the mixed structure, particularly shear stress. In the case of tapioca starch and corn flour substitution, the dilution of the primary starch concentration from 15% to 13.5% resulted in the lowering of stress at failure. However, the dilution had limited effect on strain. At low level of substitution, the stress at failure of samples containing tapioca starch is higher than that containing corn flour. However, when more tapioca starch was substituted to the primary structure (ie, above 1.5%), the long paste characteristics of tapioca may have induced weakness and adhesiveness to the mixed gels. Therefore, self-supporting mixed gels could not be formed. Note that the forces/interactions stabilizing both gels are H-bonds and the molecular entanglement. The high MW tapioca amylose molecules, released from starch granules during gelatinization, might be responsible for a higher degree of molecular entanglement within the structure compared to corn amylose.

The hydrolytic activity of particulate malt fillers affected the primary structure. However, the effects of substitution with 14 h malt were different from those with 36 h malt. Changes in the continuity and connectivity of the primary structure resulted in the changes of stress and strain at failure. Substitution of 36 h malt up to 4.5% appeared to have a synergistic effect to the network strain; ie, the mixed structure had low stress but remained high strain.

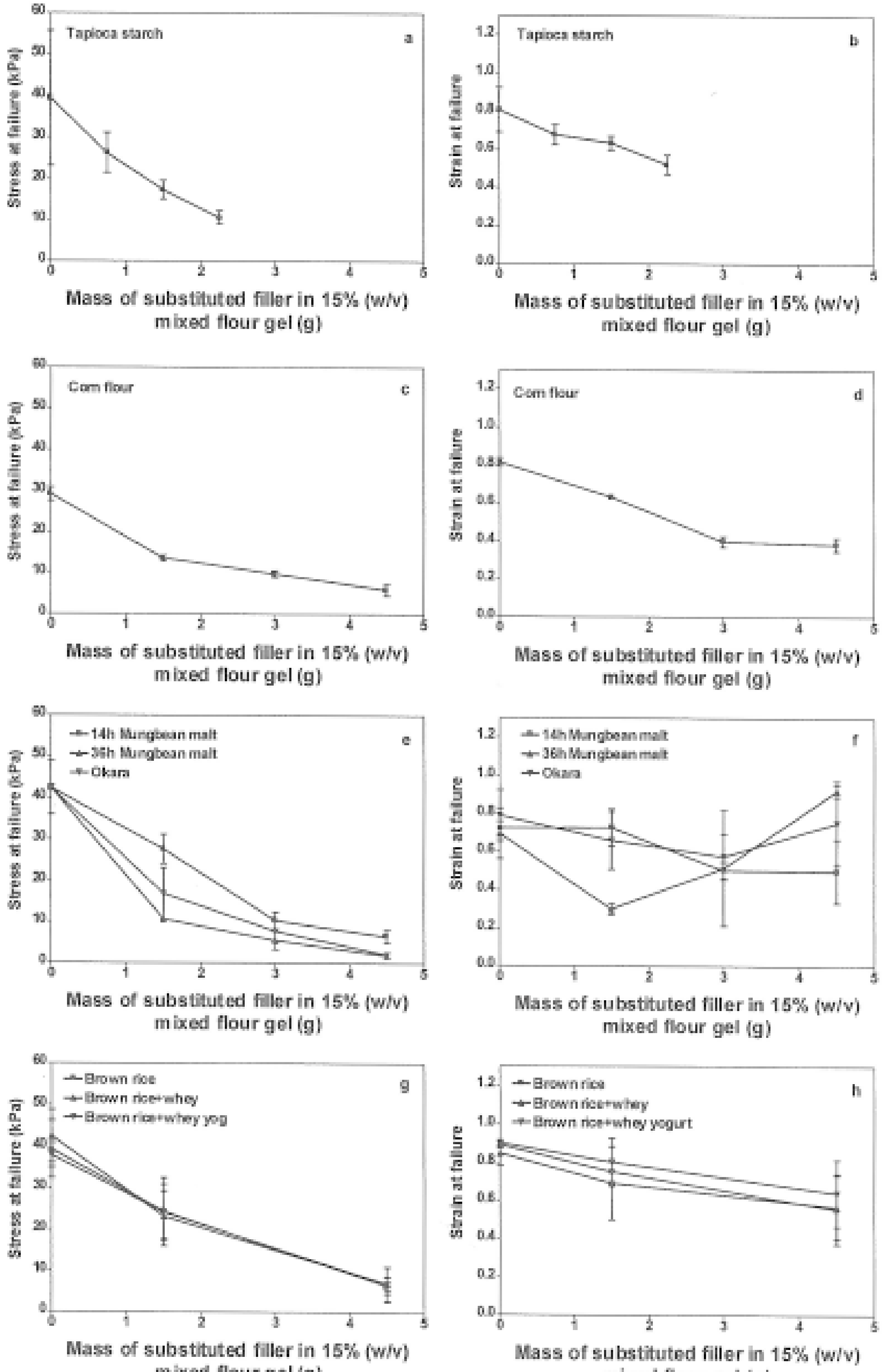

Fig 1. Stress and strain at failure of mixed flour gels containing mungbean starch as the primary network and substituted with tapioca starch (a, b), corn flour (c, d), okara and malt flour (e, f) and coated and uncoated brown rice flour (g, h). Bars represent standard deviation.

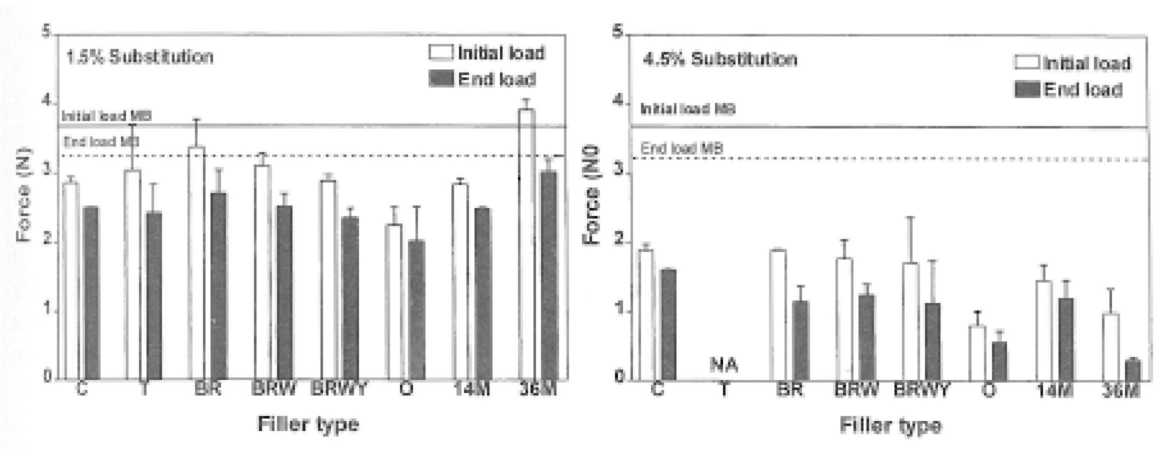

Fig 2. Effects of filler types and substitution levels on initial force load and end force load after 1 min of compression at constant strain: (a) 1.5% substitution and (b) 4.5% substitution. Mixed flour gels (15% total solid) contained mungbean starch (MB) as primary network and substituted with corn flour (C), tapioca starch (T), brown rice flour (BR), brown rice flour coated with whey (BRW), brown rice flour coated with whey yogurt (BRWY), okara flour (O), 14 h mungbean malt (14M) and 36 h mungbean malt (36M). Bars represented standard deviation.

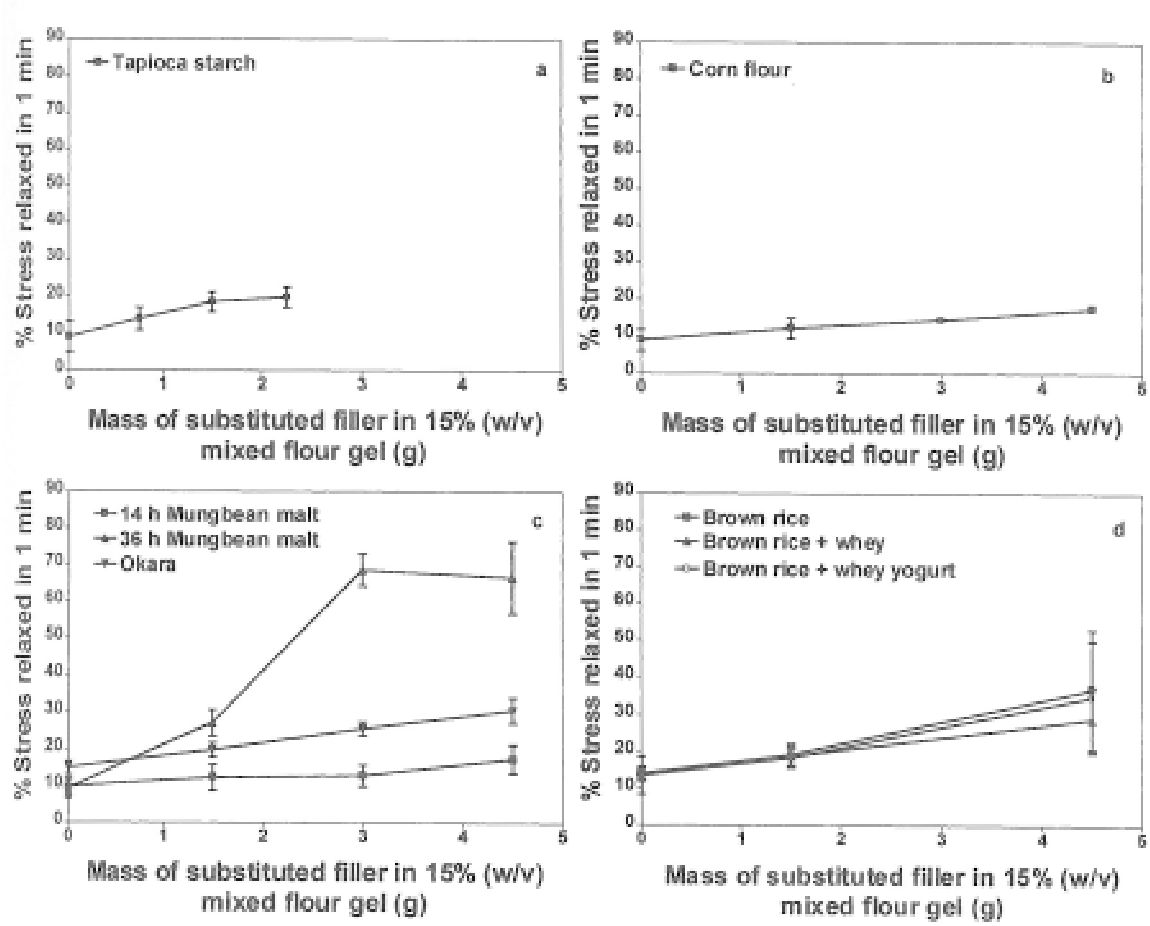

Fig 3. Effects of filler types and substitution levels on percent stress relaxation of mixed flour gels containing mungbean starch as the primary network and substituted with tapioca starch (a) corn flour (b), okara and malt flour (c) and coated and uncoated brown rice flour (d). Bars represent standard deviation.

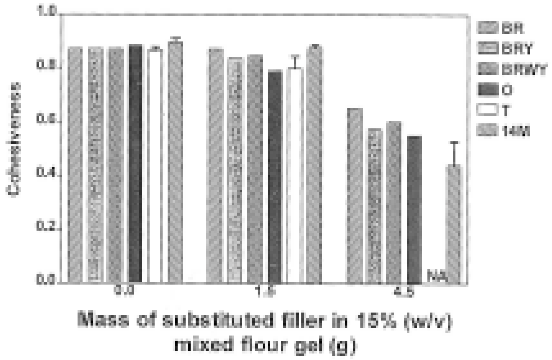

Fig 4. Effects of filler types and substitution levels on cohesiveness of mixed flour gels containing mungbean starch as the primary network. Bars represent standard deviation.

This is probably because the hydrolytic products, particularly starch hydrolysates, are more polar and hydrophilic than high MW starch, resulting in good water holding capacity and hence, the fluidity of the mixed structure.[2] Similar results were obtained when okara was substituted up to 4.5% (O). The excellent water holding capacity of okara[13] could also help increase the fluidity behaviour of the mixed structure.

However, the mechanisms involved in the network stabilization of the mixed structure containing 36 h malt and that containing okara might not be explained by the increase in the fluidity of the mixed structure alone. Note that the okara contains fairly high content of insoluble fiber.[13] It is likely that the mixed gels contained mungbean starch network, interpenetrated with fiber and embedded with particulate okara filler could have been compatible. Therefore, the synergistic effect of increasing okara level was seen as an increase in strain at failure.

The substitution of primary network by 36 h malt and okara appeared to have different effects from brown rice flours and 14 h malt, particularly at high level of substitution. The weaker structure of mixed gels, compared to the mungbean starch gels, was probably due to the dilution of the mungbean starch concentration. The substitution also affected the continuity of the network. Maillard intermediates induced during the preparation of brown rice flour coated with whey or whey yogurt could reduce water absorption into the fillers; thus, lowering the degree of gelatinization of fillers embedded in the mungbean gel network. Consequently, the ratio of crystalline to amorphous structures of the mixed gel structure was higher than that in the primary network.[14-18]

Principal Component Analysis (PCA) was used to statistically summarize the results. To describe the influences of filler types and levels of substitution on the viscoelastic properties which were determined at different degrees of deformation and test speeds, the data on stress and strain at failure (Figure 1), as well as percent stress relaxation (Figure 3) were grouped into two uncorrelated dimensions, namely, principal components (PCs). Table 1 shows that two PCs (of which the eigenvalues were higher than 1.0) provided a good summary of the gel characteristics. These two PCs accounted for 92.28% of the standardized variance.[19] The PC1 accounted for the largest amount of the total variation in the data set; and the PC2 was a weighed linear combination of the observed variables not correlated with PC1. The eigenvectors of each component (Table 2), which were the sums of the squares of the factor loadings computed for the original variables, represent the contributions of each original factor to the total variance. Results show that the PC1 is a measurement of stress (high positive loading) and inversely correlated to percent stress relaxation. This component is likely related to the mass fraction of the primary network. The second eigenvector had high positive loading on strain and percent stress relaxation. It is possible that this component relates to the flexibility of the network.

Figure 5 shows that three types of mixed flour gels can be generated by altering the types and levels of fillers, which, in turn, change the rigidity/fluidity ratio within the mixed structure. The first type was hard and flexible (positive PC1 and PC2; defined as tough gel).[9-11] The second type was weak but flexible (negative PC1 and positive PC2; defined as rubbery gel[9-11] and the third type was weak and not flexible (negative PC2; defined as mushy gel).[9-11] At low substitution levels, the characteristics of the primary

Table 1. Eigenvalue, proportion and % cumulation of total variance accounted for by each Principal Component derived from the Principal Component Analysis.

Principal Component	Variance explained: Eigenvalue	Proportion	% Cumulation
PC1	1.6407	0.5469	54.69
PC2	1.1276	0.3759	92.28
PC3	0.2317	0.0772	100.00

Table 2. Factors loading for Principal Components (PCs) with eigenvalues exceeding 1.0.

Original variables	Eigenvector: PC1	PC2
Stress at failure	0.7369	0.0592
Strain at failure	0.3608	0.8080
%Stress relaxation	-0.5717	0.5862

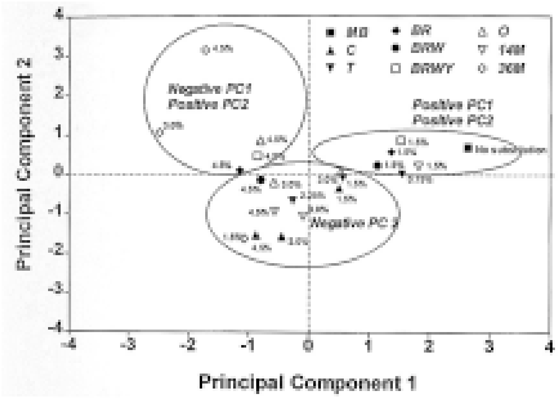

Fig 5. Plots between Principal Component 1 and Principal Component 2 of mixed flour gels containing mungbean starch (MB) as the primary network and substituted with corn flour (C), tapioca starch (T), brown rice flour (BR), brown rice flour coated with whey (BRW), brown rice flour coated with whey yogurt (BRWY), okara flour (O), 14 h mungbean malt (14M) and 36 h mungbean malt (36M).

structure of mungbean starch gels were predominant, resulting in a tough gel texture. When the substitution level increased, the characteristics of mixed gels depended on the type of particulate fillers. The critical level of substitution determining whether the mixed structure is going to be rubbery or mushy is likely dependant on the characteristics of the fillers. For example, the presence of tapioca above 0.75% in the mixed gels resulted in a mushy texture while the presence of okara above 3.0% resulted in a rubbery texture.

In summary, this study demonstrates that the viscoelastic properties of mixed gels can be altered by changing the levels and types of ingredient. Understanding the contribution of food ingredient characteristics in the formula can help in designing products with desirable texture. For example, the rubbery texture of okara-containing mixed flour has been used to modify flow properties in heat-stable, high energy, high protein liquid emulsions requiring low yield stress and shear thinning characteristics, while the tough texture from rice flour has been under investigation for its potential use in the solid foam structure of bakery products in our laboratory.

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