SZENT ISTVÁN UNIVERSITY

Apple pomace as a natural texture modifier in fruit products

Theses of PhD dissertation

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1. INTRODUCTION AND OBJECTIVES

In the recent decades costumers interest in quality, composition and origin of food products and also their apprehension of artificial food additives have strongly increased. As a result several studies are published investigating the possibilities for replacing all or a part of artificial additives by natural compounds. Aim of these studies were to find natural materials with high nutritive value, influencing positively food quality but not listed as food additives (ie. have no E-number).

Bakery products including fruit ingredients are popular among costumers. Fruit preparations are filled into bakery products before baking procedure therefore baking stable fruit preparations are required to be fresh, to have fruity taste and to show excellent firm texture even after baking at high temperature. Their quality is influenced by several parameters such as processing technology, fruit variety, sugar included, pH, and type of texture modifier. Most often pectin, xanthan gum and gellan gum are used for these products.

Processing of fruits and vegetables results in not only the main product but high amount of by-products. Reutilization of the latter is reasonable and important from both economic and environmental aspects.

The growth of horticulture industries worldwide has generated huge quantities of fruit wastes (25%-40% of the total fruits processed). These residues are generally a good source of carbohydrates, especially cell wall polysaccharides and other functionally important bioactive molecules such as proteins, vitamins, minerals and natural antioxidants. Apple is the third relevant fruit all over the world after banana and watermelon. "Apple pomace" is a left-over solid biomass with a high moisture content, obtained as a by-product during the processing of apple fruits for juice, cider or wine preparation. Owing to the high carbohydrate content, apple pomace is used as a substrate in a number of microbial processes for the production of organic acids, enzymes, single cell protein, ethanol, low alcoholic drinks and pigments. Recent research trends reveal that there is an increase in the utilization of apple pomace as a food processing residue for the extraction of value added products such as dietary fibre, protein, natural antioxidants, biopolymers, pigments and compounds with unique properties. Beside the bioactive components apple pomace is composed of water (76.3%) and dry solids (23.7%), and is generated from pulp and epidermis (95.5%), seeds (4.1%), and stems (1.1%). Due to high pectin content it could be used as a natural texture modifier in food products after a simple drying process.

Aim of PhD dissertation was to investigate the effect of addition of apple pomace powder produced by a simple drying method on the rheological properties of baking stable fruit preparation.

Main objectives were the following:

- to investigate whether dried apple pomace as texture modifier is suitable for replacing pectin in baking stable fruit preparations and to evaluate the differences between applied apple varieties
- to investigate the influence of apple pomace concentration on the structure and physical properties of the bakery fruit preparations
- to determine the maximum apple pomace concentration suitable for producing appropriate products considering both sensorial and technological properties
- to evaluate the texture of the heat stable fruit preparations during storage and to predict the shelf-life
- to find an appropriate analytical technique for objective measurement of texture of baking stable fruit preparations.

2. MATERIALS AND METHODS

2.1. Materials

Three apple varieties *Malus ×domestica* (Borkh.) were used in experiments for preparing apple pomace powder. One conventional (Idared) and two multiresistant apple varieties (Artemisz and Cordelia) were used. Varieties 'Artemisz' and 'Cordelia' have been developed in the apple breeding program of Szent István University and their state registration was accepted in 2011 and 2012, respectively.

Heat stable fruit preparations were produced using apple-, apricot-, sour cherry, plum and black currant puree (20-20%) (Sió-Eckes Ltd., Hungary). Apple was chopped and pressed using a stainless steel manual press. After pressing the obtained apple pomace (including skin, core and kernel) was dried at 80 °C until it reached 5% wet content. Dried apple pomace was grinded by a laboratory grinder and sieved through a 200µm sieve producing apple pomace powder and used as natural texture modifier in baking stable fruit preparations in accordance with regulation MÉ 2/601. Industrial heat stable pectin (E 440; Classic AB 401, Herbstreith & Fox) and preservative (potassium sorbate) were purchased from Pacific Óceán Ltd. (Vác, Hungary).

2.2. Experimentals

2.2.1. Preparation of dried apple pomace powder

Apple pomace was obtained from varieties Artemisz, Cordelia and Idared, 2011 by industrial apple juice technology. Apple was first washed, cut, crushed. According to the industrial method, enzymes were not applied for pectin and starch degradation. Juice was obtained by laboratory press machine.

After pressing wet apple pomace was dried in a single layer on perforated trays in an athmospheric dryer LMIM LP 232/1 (Esztergom, Hungary) at 80°C until it reached 5% wet content (approximately for 5 hours.) Finally samples were grinded by a laboratory grinder and passed through a 200 μm sieve producing apple pomace powder for the experiments.

2.2.2. Production of baking stable fruit preparation

Production of baking stable fruit preparation was performed according to Table 1. Samples were prepared in accordance with regulation MÉ 2/601.

Table 1. Ingredients of baking stable fruit preparation

Sample	Fruit content (g)	Sugar (g)	Preservative (g)	Pectin (g)	AP (g)
Control				12	0
Ar40; Co40; Id40				7,2	4,8
Ar50; Co50; Id50				6,0	6,0
Ar60; Co60; Id60	550	565	1	4,8	7,2
Ar80; Co80; Id80				2,4	9,6
Ar100; Co100; Id100				0	12,0

Ar: Artemisz; Co: Cordelia; Id: Idared; AP: apple pomace

40, 50, 60, 80, 100: apple pomace content (%)

The procedure was the following: raw materials and 90% of sugar were mixed and heated up to 80°C to obtain the complete dissolution of sugar. Pectin and apple pomace powder with a little amount of sugar (10%) were dispersed in preheated water (80 °C) and added to the preheated (80 °C) fruit pulp. Then 1% preservative (Potassium sorbate) was added to the mixture. The whole mixture was boiled until obtaining 61.1±1.0% water soluble dry material content. Then pH was adjusted into the range of 3.0-3.2 using citric acid. The final mixture was boiled for 2 min. 200 ml plastic containers were filled with the obtained fruit preparation at 80°C and closed. Total soluble dry material content of the finished baking stable fruit preparation was 61.1±1.0%, and fruit content was 55%. Storage of heat stable jams was performed at room temperature (22°C) for 12 months. Rheological measurements were carried out in every 4^{th} month (0; 4; 8; 12. month).

2.3. Applied instruments and measuring methods

2.3.1. Measurement of pectin content

Pectin content of apple varieties and apple pomace powder were determined in accordance with the method of KYRIAKIDIS & PSOMA (2001).

2.3.2. Rheological measurements

Rheological measurements (oscillation and rotational tests) were performed using a Physica MCR 51 rheometer (Anton-Paar GmbH., Graz, Austria). For the tests a plate and plate measurement system was used which consists of a P-PTD200 plate and a PP50/S (plate, 50 mm in diameter) measuring bob using 3 mm gap size. 5 parallels were done in case of all measurements Results were recorded and analyzed using Rheoplus software ver 3.2 (Anton-Paar GmbH., Graz, Austria).

Measurement methods:

1. Amplitude sweep

Amplitude sweep methods are oscillatory tests performed at variable amplitudes, keeping the frequency at a constant value.

The amplitude sweep method was carried out at 20 °C, increasing strain value from 0.5 to 200%, at constant angular frequency (10 rad s^{-1}), using five replicates per sample.

Amplitude sweep rheograms (storage modulus (G', Pa) and loss modulus (G", Pa) in function of shear stress (τ, Pa)) of the samples were recorded. G' represents the elastic behaviour, G" represents the viscous behaviour of a test material. Based on the rheograms the following parameters were determined: G'_0, (Pa): initial storage modulus; G''_0 (Pa): initial loss modulus; DF: damping factor, the ratio of initial loss modulus to initial storage modulus; τ_{LVE} (Pa): shear stress at the end of linear viscoelastic range which is the strain at storage modulus decrease to 95% of its initial value; τ_{CO} (Pa): shear stress at crossover point of G' and G" curves which indicates the turning point between viscoelastic solid and liquid (Fig.1).

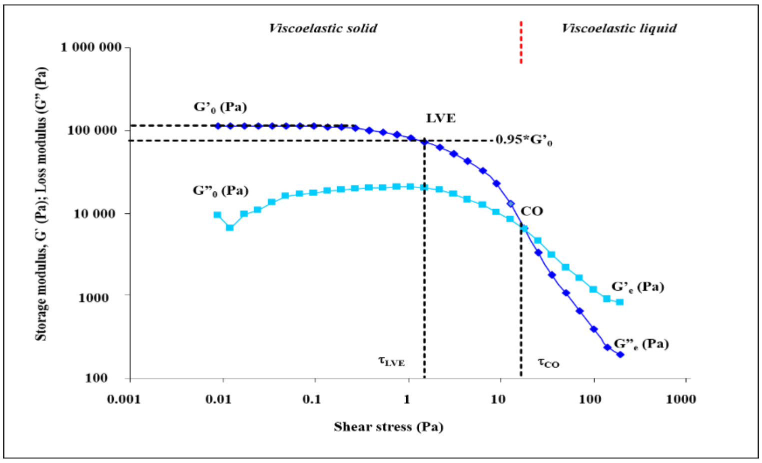

Figure 1. Amplitude sweep rheogram and parameters

Initial value of storage (G'$_0$) and loss (G"$_0$) modulus are determined at the initial measure point. At low amplitude values, in the linear viscoelastic (LVE) range, both the G' and G" curve show a plateau with constant values. The range of the tolerated deviation has to be defined previously by the user, e.g. as 5%. If 5% is the tolerance to be allowed all those G' values which are below 95% of the plateau value are considered to be outside of the LVE range.

At the beginning of measure dominance of the elastic behaviour (G'>G") was observed. After the end of LVE-range, G' and G" moduli values declined, and beyond the crossover-point of the curves the dominance of the viscous portion (G">G') occurred indicating that the sample was a viscoelastic liquid.

Loss factor (or damping factor, DF) can be calculated as the quotient of the lost and the stored deformation energy (DF=G"/G'). It shows the ratio of the viscous and the elastic portion of the viscoelastic deformation behaviour. In case of viscoelastic liquid, G"/G'>1, and in case of viscoelastic gel or solid G"/G'<1.

In my PhD dissertation reciprocal value of loss factor is named as "Strength Factor" (SF=G'/G") and is used to evaluate the strength of the heat stable fruit preparations. If SF value was higher than 1, the heat stable fruit preparation showed viscoelastic gel behaviour, and if SF value was smaller than 1, the sample showed viscoelastic liquid behaviour.

2. Frequency sweep

Frequency sweep methods are oscillatory tests performed at variable frequencies, keeping the amplitude at a constant value. Frequency sweep methods are used to investigate time-dependent shear behaviour since the frequency is the invert value of time. Short –term behaviour is simulated by rapid motion (at high frequency) and long-term behaviour by slow motion (at low frequency).

For each new sample before performing a frequency sweep, the limiting value of the LVE range has to be determined. First of all, an amplitude sweep had to be carried out, because the measurements has to be performed strictly within the LVE range.

The frequency sweep method was carried out at 20 °C, increasing frequency value from 10 to 100 Hz, at constant amplitude (0,5%), using five replicates per sample.

Frequency sweep rheograms (storage modulus (G', Pa) and loss modulus (G", Pa) in function of frequency) of the samples were recorded. Based on the rheograms the following parameters were determined: G'_0, (Pa): initial storage modulus; G''_0 (Pa): initial loss modulus; G'_e, (Pa): storage modulus at the end point; G''_e (Pa): loss modulus at the end point, DF_0; DF_e: damping factor, (the ratio of loss modulus to storage modulus in initial and end point).

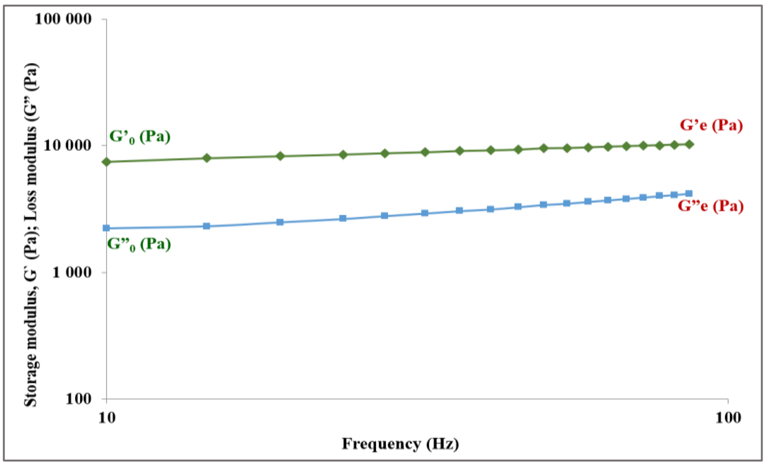

Figure 2. **Frequency sweep rheogram and parameters**

In my PhD dissertation DF was calculated at the initial ($DF_0=G''_0/G_0$) and end point ($DF_e=G''_e/G_e$) also. The ratio of DF_0 and DF_e was named as "Stability Factor" (St.F) which was used for evaluate the structure stability of the heat stable fruit preparations. If St.F value is higher and nearest to 1, it means de structure of the sample is more stable.

2. Temperature-dependent behaviour (dynamic-mechanical thermoanalysis)

Using this type of test, the only variable parameter is the temperature. Therefore, besides the constant dynamic-mechanical shear conditions, a profile of the measuring temperature is preset.

The temperature-dependent behaviour method was carried out at constant angular frequency (10 rad/s) at constant amplitude (2%), using five replicates per sample.

Two types of temperature-dependent behaviour method were performed:

- *Cooling down-heating up method in oscillatory mode:*

cooling down from +4°C to –18°C (cooling rate 4°C/min), keeping at –18°C for 15 min, heating up from –18°C to +4°C (heating rate 4°C/min)

Temperature-dependent behaviour rheograms (storage modulus (G', Pa) and loss modulus (G", Pa) in function of temperature) of the samples were recorded (Figure 3).

Based on the rheograms the following parameters were determined: G'_0, (Pa): initial storage modulus; G''_0 (Pa): initial loss modulus, G'_0, (Pa): initial storage modulus; G''_0 (Pa): initial loss modulus, G'e, (Pa): storage modulus at the end point; G''_e (Pa): loss modulus at the end point, and ratio of these values (G'_e/G'_0 and G''_e/G''_0). If the ratio of G'_e/G'_0 and G''_e/G''_0 is close to 1, it indicates that the structure of the sample has not changed during cooling down-heating up.

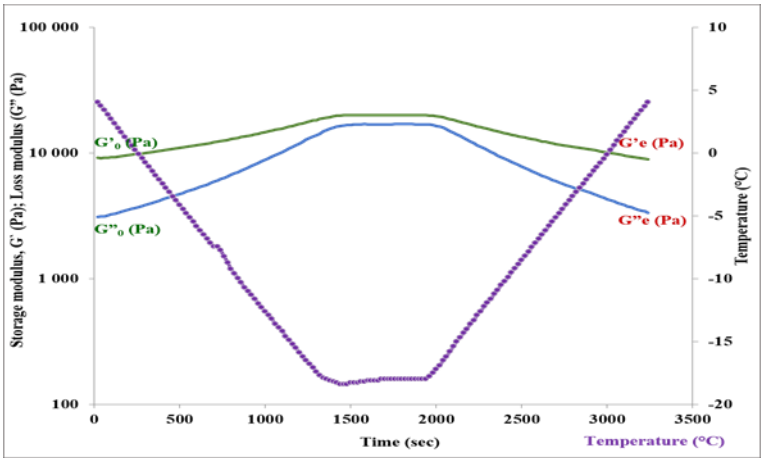

Figure. 3. Cooling temperature-dependant rheogram and parameters

- *Heating up-cooling down method in rotational mode:*

Heating up from +20°C to +100°C (heating rate 4°C/min), keeping at +100°C for 15 min, cooling down from +100° to +20°C (heating rate 4°C/min) (Fig.4).

Heating up temperature-dependent behaviour rheograms (viscosity (η) in function of temperature) of the samples were recorded.

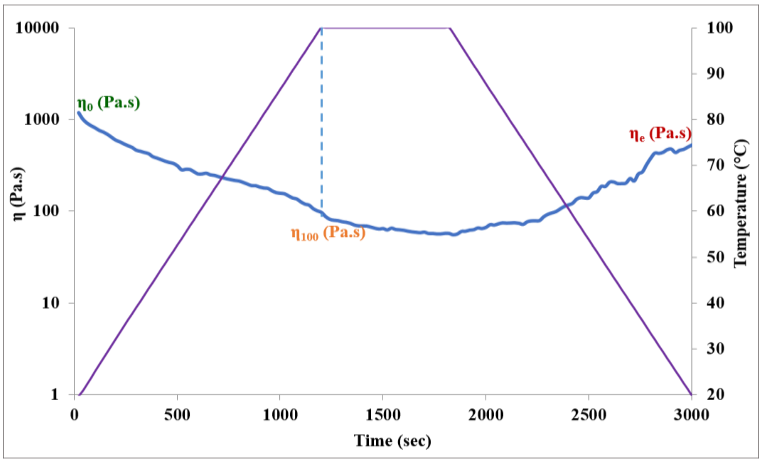

Figure 4. Heating temperature-dependent rheogram and parameters

Based on the rheograms the following parameters were determined: η_0, (Pa.s): initial viscosity at 20°C; η_v, (Pa.s): at the end point; η_{100}, (Pa.s): viscosity of 100°C. Because of the boiling of water in fruit preparations, initial viscosity at 20°C and viscosity at 100°C were compared and evaluated.

2.3.3. Texture profile analysis

Analysis of texture characteristics was performed by Brookfield LFRA Texture Analyser using five replicates per sample. Texture ProLite software was used for data analysis.

Performed measurement method was the following:

- texture profile with two bite cycle,
- target speed: 2 mm/s,
- target value: 20 mm,
- probe : TA17-25 mm, D, 30° Clear Perspex

Texture profile (load (g) in function of time (sec)) of the samples were recorded (Figure 5).

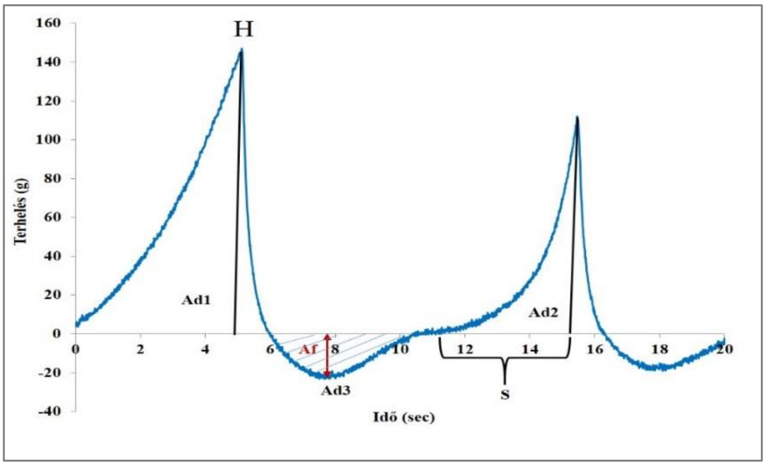

Figure 5. Texture profile of fruit preparations and its parameters

H:	hardness (g)	S:	springiness (m)
Ad_1, Ad_2	area of 1st and 2nd peak	C:	cohesiveness (-)
Ad_3	adhesiveness (gs)	CH:	chewiness
G:	gumminess		

2.3.4. Determination of baking stability

For determination of baking stability of fruit preparations baking test was performed in every month of storage. The fruit preparations were almost directly in contact with the baking tray and is exposed more strongly to the heat from the bottom. Baking time was 20 min, and baking temperature was 200°C. During and after the baking the changes in shape and size were observed and evaluated.

2.3.5. Sensory analysis

Scoring method was used for the sensorial evaluation of heat stable fruit preparation to determine the highest amount of dried, grinded apple pomace concentration which could be tolerated by consumers. In every measurement date 15 expert judges tasted the baking stable fruit preparation samples. The evaluation criteria were the following: odour (max. 10 score), taste (max. 10 score), granularity (max. 10 score) and texture (max. 20 score).

2.3.6. Statistical evaluation

Statistical evaluation of measured data was performed using SPSS Statistics v20 program.
Parameters were analysed by analysis of variance (ANOVA) at 95% significance level. Differences between the rheological parameters of the different composition samples and the consecutive samplings were analysed by Tuckey-test at 95% significance level. Relations of different attributes of different samples was investigated by Pearson correlation.

3. RESULTS

Aim of my PhD thesis was to investigate whether dried apple pomace as texture modifier is suitable for replacing pectin in baking stable fruit preparations. Rheological measurements were performed to evaluate effect of apple pomace variety and concentration on the texture and stability of baking stable fruit preparations, and to follow the changes of structural attributes. Rheological measurements were performed using oscillatory rheometer operated in three measurement modes. Texture profile analyses was performed by LFRA texture analyser. Sensory test was also carried out.

Results of amplitude sweep measurements showed that replacing pectin in part by apple pomace had a significant effect on rheological properties of baking stable fruit preparations. Using pectin (60%) and apple pomace (40%) in combination resulted a stronger and better gel structure than either exture modifier alone. Solid character of baking stable fruit preparations remained and even increased during storage as indicated by increase of initial G'_0, τ_{LVE}, τ_{CO} and "Strength Factor" (SF).

The frequency sweep method refers to the stability and the time-dependent behavior of baking stable fruit preparations. It was proved that baking stable fruit preparations produced by all the three varieties of apple pomace were suitable for long term storage. Increasing apple pomace concentration in the baking stable fruit preparations increased the stability more intensively than the control including pectin. "Stability factor" ($St.F=DF_v/DF_0$) as qualifier parameter proved to be suitable for predict the storage attributes of baking stable fruit preparations.

Baking stable fruit preparations are frozen and then baked together with dough. During the process it should keep its original texture and sensorial quality. Effect of this procedure was evaluated by using temperature sweep test methods. Texture of baking stable fruit preparations proved to be stable without structural changes during freezing and thawing.

Based on results of bakery test it was observed that baking stable fruit preparations with 40% apple pomace and 60% pectin showed the highest viscosity values in case of all the three apple varieties tested. Viscosity of baking stable fruit preparations at 100°C did not decrease during storage indicating that fruit preparations remain resistant against baking during shelf-life.

Texture profile analysis an objective tool for evaluate sensorial quality of food products was also used for characterization of texture of baking stable fruit preparations. Increasing hardness of fruit preparations during storage was a result of syneresis. The only exception was the sample with 100%. Artemisz apple pomace which could not bind water properly.

Resistance against baking was evaluated by extension test in order to test whether samples could keep their shape and texture during baking procedure. Extension values increased by increasing apple pomace concentration indicated decreasing resistance against baking and increasing flow ability of jams. Best baking resistance was shown by samples with 40% pomace concentration. However, baking resistance increased during storage as indicated by decreasing extension values.

Results of sensory analysis of baking stable fruit preparations showed that increasing pomace concentration resulted more fresh and more fruity odour. However, taste of baking stable fruit preparations was not influenced by apple pomace addition. Above 50% apple pomace particles were perceived by consumers and influenced adversely overall impression of the samples. Acceptance of baking stable fruit preparations decreased after 8 months storage suggesting that shelf-life of these products should be no longer than 8 months.

Based on the correlation analyses it was proved that apple pomace concentration had stronger influence on baking stable fruit preparation quality than the apple variety used.

4. NEW SCIENTIFIC RESULTS

1. I have proved that apple pomace as natural texture modifier is suitable for replacing pectin in baking stable fruit preparation. Considering results of both the instrumental and sensorial tests it was concluded that pectin could be replaced by mixture of 40% apple pomace and 60% pectin in baking stable fruit preparation without adverse effects. It was found that baking stable fruit preparation contains apple pomace have better storage attributes than that contains solely pectin. Shelf-life of the products proved to be 8 months. I have proved that baking stable fruit preparation contains pectin and apple pomace proved to be stable without structural changes during freezing and thawing.

2. Based on my results it was proved that amplitude sweep oscillation measuring method is suitable for examination of structure stability of baking stable fruit preparations, and for evaluate the structural changes during storage. Investigated parameters: G'_0, G''_0, $\tau_{LVE,}$ and τ_{CO}, additionally "Strenght factor" (SF= G'/G") are suitable for objective feature the structural attributes of baking stable fruit preparations.

3. I have proved that frequency sweep method confirm the results of amplitude sweep and sensory analysis, and that based on frequency sweep rheograms, storage attributes are predictable. "Stability factor" ($St.F=DF_v/DF_0$) as qualifier parameter is suitable for feature the storage attributes baking stable fruit preparation.

4. I have confirmed that baking stability is reproducible determinable by rotational rheology method. Viscosity at 100°C (η_{100}) parameter showed good correlation with the results of baking stability tests, so it is suitable for pre-indicate the results of baking stability tests.

5. Based on the rheology and sensory results I have proved that apple pomace concentration has stronger influence on baking stable fruit preparation quality than the apple variety used.

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