



## Effect of starch substitution with pullulan on confectionery starch gel texture of lokum

### Şekerleme ürününe nişastanın pullulan ile ikame edilmesinin lokumda nişasta jel yapısı üzerine etkisi

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#### ABSTRACT

Production of many confectionery products such as sweetmeats and Turkish delights are based on mixture of starch, sugar and water, heated for pasting of the starch which is then poured in a mold to set as a gel. The main ingredients, sugar and starch are components which are determinants for the typical texture of these gels. Pullulan is a non-digestible fungal polysaccharide which can potentially be used as an ingredient in lokum production. The purpose of this study was partial substitution of starch used in the formulation of sugar-starch gels with pullulan and to evaluate the effects of cooking time and storage on gel texture. Starch fraction in a base formula was substituted with pullulan at three different levels. First two levels involved substitution of 10 and 20% of the starch with pullulan at a 1:1 ratio and the third level was performed by substituting 20% of starch at a starch/pullulan ratio of 2:3. Firmness and springiness values were determined to assess textural properties. Increased duration of cooking and storage increased mean firmness values however substitution at 20% pullulan did not result in significantly different mean values from the control formulation. Springiness was affected by cooking, storage and pullulan content and reduced loss in springiness was observed in stored samples with increasing pullulan content. Results obtained in this study show that pullulan may be added to lokum formulations for modification of retrogradation behavior however more research is needed on the subject with regard to optimization of product texture for satisfying consumer preference requirements.

#### MAKALE BİLGİSİ

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#### ÖZ

Lokum ve benzeri pek çok şekerleme ürününün üretimi hazırlanan bir şeker, nişasta ve su karışımının, ısıtılarak nişastanın pişirilmesi ve kalıplara dökülerek soğutulan karışımın jelleşmesi esasına dayanır. Ana bileşenler olan şeker ve nişasta bu tür jellere özgü tipik tekstür yapısının belirleyicileridir. Pullulan, lokum imalatında değerlendirilebilecek potansiyele sahip, sindirilemeyen bir fungal polisakarittir. Bu çalışmanın amacı şeker-nişasta jellerinin formülasyonunda nişastanın kısmen pullulan ile ikame edilmesinin, pişirme süresi ve depolama faktörlerinin de etkisiyle jel tekstürü üzerine etkisinin araştırılmasıdır. Formülasyonda kullanılan nişastanın bir bölümü 3 farklı seviyede pullulan ile ikame edilmiştir. İlk iki seviyede temel formülasyonda bulunan nişastanın %10 ve %20'lik bölümü 1:1 oranda pullulan ile ikame edilmiştir. Üçüncü seviyede ise nişastanın %20'si 2:3 oranında pullulan ile ikame edilmiştir. Örneklerin tekstürel analizi sertlik ve esneklik değerlerinin tespit edilmesiyle sağlanmıştır. Pişirme süresinin arttırılması ve depolama sertlik değerlerinde artışa neden olurken %20 pullulan ikamesi yapılmış ürünlerin ortalama sertlik değerleri ile kontrol formülasyon arasında anlamlı fark gözlemlenmemiştir. Nişastanın %20 seviyesinde 1:1 oranında ikame edildiği formülasyon ile kontrol formülasyon arasında sertlik değeri bakımından istatistiksel olarak önemli fark olmadığı tespit edilmiştir. Ortalama esneklik değerleri pişirme süresi, depolama ve formülasyon uygulamalarından önemli şekilde etkilenmiştir. Bileşimde yer alan pullulan miktarı arttıkça depolamada gerçekleşen esneklik kaybının azaldığı gözlemlenmiştir. Bu çalışma, lokum formülasyonlarında pullulan ilavesinin retrogradasyon özelliklerini modifiye etmek amacıyla kullanılabilirliğini, ancak tüketici tercihlerine en uygun tekstürel özelliklerin sağlanabilmesi açısından bu konuda kapsamlı bir optimizasyon çalışmasının gerekli olduğunu göstermiştir.

## 1. Introduction

Confectionery gels are often high sugar systems with one or more gelling components used to give the desired firmer or softer texture (Burey et al. 2009). Traditionally these products are produced by the simplest method of processing which involves cooking of the starch containing mixture in an open pan or kettle, depositing the final mixture into starch dusted molds and cutting of the gel slabs (Edwards 2007; Hartel et al. 2018). Turkish delight, 'lokum' as it is known in Turkish, can be described as a sugar-based jelly-like confection made using corn starch as a gel thickener (Göğüş et al. 2016). This confectionery gel has a soft, sticky consistency and is often packaged and eaten in the form of small cubes dusted with a mixture of icing sugar and starch to prevent sticking. Lokum recipes commonly contain various flavorings and nuts (Batu and Kirmaci 2009). Textural properties are the major criteria in evaluation of lokum quality (Demirbaker Kavak and Akpuna 2018).

Starch, the thickener traditionally used in lokum production is a natural polymer, the monomeric unit of which is glucose. Starch in its cooked form is readily digestible whereas pullulan has been described as a type of dietary fiber slowly digested in the human gut (Chaen 2010; Wolf et al. 2003) and hence it is used as a low-calorie food additive to provide bulk and texture. Pullulan is a non-ionic exopolysaccharide of fungal origin (Prajapati et al. 2013) that has received GRAS status (EFSA 2007). It is composed of maltotriose units linked through  $\alpha$ -1,6-glucosidic bonds that readily dissolve in water to increase viscosity without forming a gel (Singh et al. 2008). Composite starch-pullulan films have been a subject of interest recent studies with regard to utilization as a packaging material to extend product shelf life (Kim et al. 2014; Yan et al. 2012). A Chinese research group has investigated the effect of pullulan addition at levels of 0.01-0.5% on various properties of rice starch gels (Chen et al. 2017a; Chen et al. 2017b; Chen et al. 2014). Sheng et al. (2018) have more recently shown using tapioca starch that pullulan addition at levels of 5-10% has a significant effect on gelatinization and retrogradation properties of the starch-pullulan gels.

The main objective of this study was to investigate the effect of partial substitution of the starch in sugar confectionery gel product lokum and its effect on textural properties of the composite gel formed, also taking into account the effect of cooking time and storage. Pullulan addition was made by replacing 10-20% of the corn starch in a base confection formulation with 1:1 and 2:3 ratio of pullulan. Although the effect of starch substitution would not render the gels to be very low in calories or free of sugars, in doing so reduction in energy content and the added benefit of increased fiber content could be expected.

## 2. Materials and Methods

### 2.1. Materials

Pullulan used in this study was a product of Hayashibara Co. Ltd., Japan. The base ingredients in lokum production are starch, sugar, water and citric acid. Corn starch, beet sugar and citric acid were purchased from a local food raw material provider (Smart Kimya Ind. & Cons. Ltd. Co., İzmir, Turkey). Water used in the experiments was distilled water.

### 2.2. Preparation of the gels

The amount of sugar (120 g), water (150 g) and citric acid (0.35 g) used for preparing all samples were the same. The base formula (F1) contained 20 g of starch. In formulation 2 (F2) a 10% portion of the starch was substituted at a 1:1 ratio with pullulan (i.e. 18 g of starch and 2 g of pullulan were used). In formulation 3 (F3), 20% starch was substituted in the same way. In formulation 4 (F4), 20% of the starch was substituted with pullulan at a ratio of 2:3 in order to alleviate the weaker gelling properties of pullulan. The details of the formulations are summarized in Table 1.

**Table 1.** Starch and pullulan composition of gel samples prepared in the study.

| Ingredient | Base formula with starch (F1) | Substitution of 10% starch at 1:1 ratio (F2) | Substitution of 20% starch at 1:1 ratio (F3) | Substitution of 20% starch at 2:3 ratio (F4) |
|------------|-------------------------------|--|--|--|
| Starch     | 20 g (6.9% <sup>1</sup> )     | 18 g (6.2%)                                  | 16 g (5.5%)                                  | 16 g (5.5%)                                  |
| Pullulan   | 0                             | 2 g (0.7%)                                   | 4 g (1.4%)                                   | 6 g (2.1%)                                   |

<sup>1</sup>Percentage values represent relative quantity in whole formulation w/w.

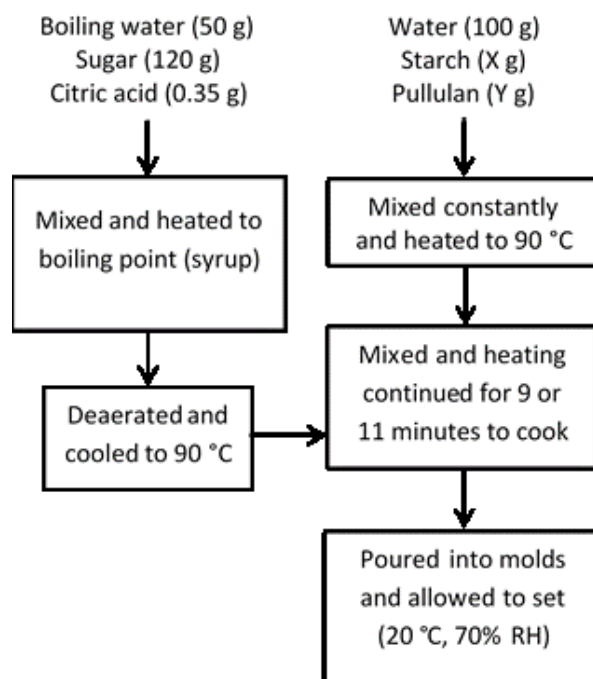
The added levels of pullulan were in agreement with the recommended levels of consumption of pullulan (JECFA 2011). One third of the water used in the formulation was reserved to suspend the starch (and pullulan) and the rest was used to fully dissolve the sugar and citric acid. These separately prepared mixtures were combined and cooked for a duration of either 9 or 11 minutes in a pan placed over a plate heater with constant stirring. The contents were poured into 5x5x2 cm molds, allowed to cool. The confectionery starch gels were left to set overnight. The production process of samples is summarized in Figure 1. Samples were stored in a humidity controlled incubator (GC400, Nüve, Turkey) at 20°C and 75% relative humidity (RH) for 7 days.

### 2.3. Texture analysis

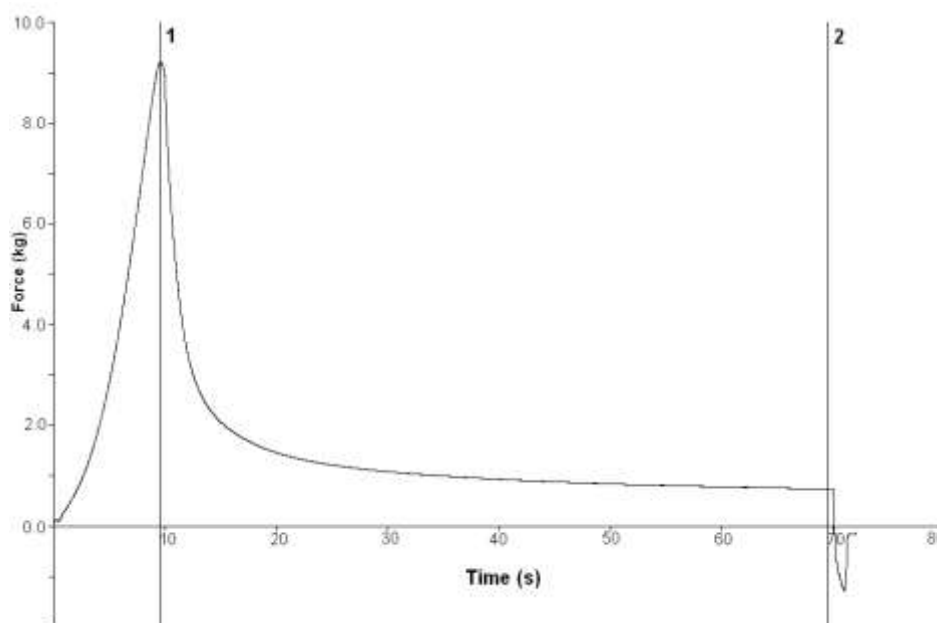
Textural analyses of the solidified starch confectionery gels were performed on a TA.XT Plus texture analyzer (Stable Micro Systems, London, UK) equipped with a 5 kg load cell and 20 mm Ø cylindrical probe according to the gummy confectionery application study SWT1/P35 (Stable Micro Systems 2000). Probe test speed was set to 1 mm s<sup>-1</sup> compression for 60 s. Springiness and firmness values were determined at 20°C and results were analyzed by ANOVA (SPSS v23.0). Analyses were performed in four replications on samples prepared in duplicate.

## 3. Results and Discussion

All samples produced in the study solidified in the form of a confectionery gel which could be removed from the mold and dusted with starch without deformation. No syneresis was observed in the products throughout the storage period of seven days. Textural analyses did not result in visible fracturing of the gels. The textural analysis result is presented as a graphical output of the force measured on the probe throughout the test duration (Figure 2). Once the trigger force of 5 g is attained, the probe proceeds to compress the sample to 20% of its original height. The probe is held at this distance for 60 seconds and then withdrawn from the sample to its starting position. The



**Figure 1.** Processes applied in the production of confectionery gel samples.

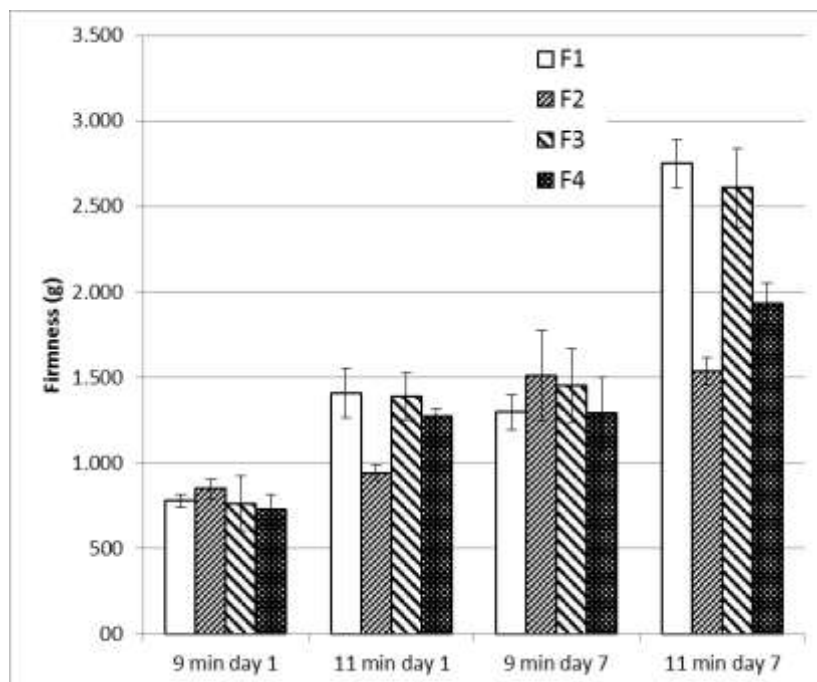


**Figure 2.** Texture graph obtained from standard formulation (F1) on day 7 of storage.

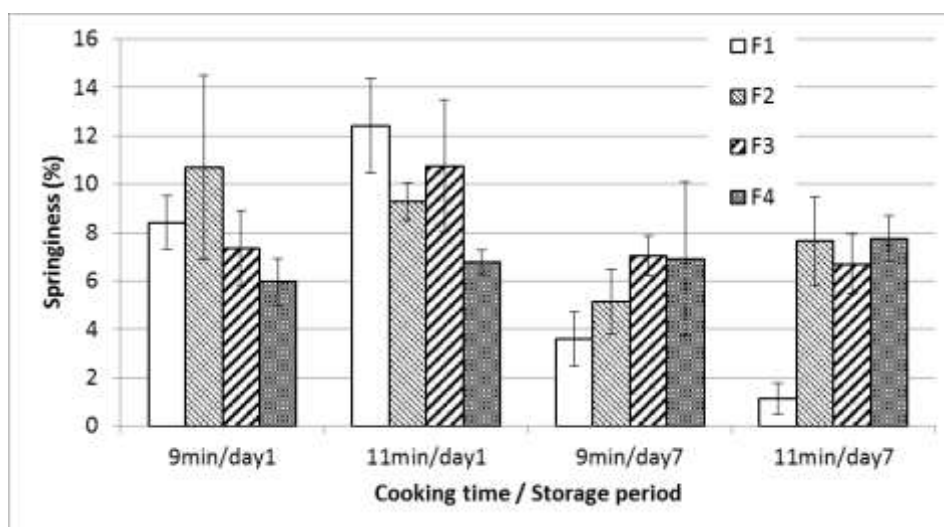
peak force is equivalent to firmness and the ratio of final force to peak force is expressed as a percentage is equivalent to the springiness value.

The mean firmness and springiness values obtained from the texture analyses are presented in Figure 3 and Figure 4, respectively. Based on the results of the statistical evaluation, increased cooking times and storage resulted in significantly higher mean firmness values. The basic formula (F1) resulted in a mean firmness value of 1.557 kg (N= 32), which was statistically the same as for the formulation where 20% of the starch was substituted at 1:1 ratio (F3). The other formulations F2 and F4 had significantly lower firmness mean values,

1.304 kg and 1.209 kg respectively (F1<sup>a</sup>, F4<sup>a</sup>, F2<sup>b</sup>, F3<sup>b</sup>; N= 32). The firmer gel structure with longer cooking time can be attributed to the pasting of the starch fraction whereas the increase in firmness upon storage is mostly related to the long term retrogradation of the polysaccharides (Fu et al. 2015). Previously performed studies on the interaction of non-ionic polysaccharide starch systems indicate that interaction between the different molecular structures have a significant effect on the gelation and retrogradation behavior. Synergistic effect of hydrocolloids has been reported to results in firmer gels with less syneresis (Funami et al. 2005). Chen et al. (2014) in their study investigating the pasting and rheological behavior of rice starch (5%, w/v) and pullulan (0.01-0.5%, w/v) system



**Figure 3.** Firmness values of sample gels (F1: base formula; F2: 10% of starch substitution; F3: 20% starch substitution; F4: 20% starch substitution, 2:3 ratio) (N= 8).



**Figure 4.** Springiness values of sample gels (F1: base formula; F2: 10% of starch substitution; F3: 20% starch substitution; F4: 20% starch substitution, 2:3 ratio) (N= 8).

have observed improved gelatinization at lower concentrations with a change to decreased gelatinization at higher concentrations, pointing out that the pasting and rheological characteristics of the starch are affected by pullulan attributable to interactions between starch granules, amylose molecules and pullulan. Pullulan in rice starch gels have also been indicated to result in retarding short and long-term retrogradation of amylopectin indicating that it could be used as an aging inhibitor to develop foods with longer shelf-life and improved mouthfeel (Chen et al. 2015).

Springiness is one of the determining textural characteristics of the traditional confectionery product lokum. It can be seen from Figure 4 that springiness values were also affected greatly by the formulation, heating period and storage. For the control

samples (F1) cooking the mixture for 11 min instead of 9 min resulted in increased springiness whereas storage for a period of 1 week resulted in significantly decreased springiness. Again, the pasting and retrogradation phenomena may be implicated in these observations. Statistical evaluation confirmed that there was significant interaction between all applications except for formulation vs. cooking time. Springiness value of F1 was highest and in the same Duncan grouping as that of F4 (F1<sup>a</sup>, F4<sup>ab</sup>, F2<sup>bc</sup>, F3<sup>c</sup>; N= 32). The loss of springiness during storage for the pullulan substituted formulations decreased with increasing pullulan content, suggesting a possible role of pullulan in delaying retrogradation. In fact, for the F4 samples, which contained the highest amount of pullulan, storage resulted in increased mean springiness values.

#### 4. Conclusion

Pullulan may be incorporated in solid or liquid food to replace starch; imparting the characteristics to food normally derived from starch as such as consistency, dispersibility, moisture retention. However, very few studies have been performed on the effects of partial replacement of starch in known food formulations with pullulan. This study provides preliminary insight to the effect substitution of starch would have on the textural properties of a model confectionery gel system designed to mimic lokum. The results obtained in this study show that incorporation of pullulan significantly influences textural properties of confectionery starch gels. Although equivalent firmness and springiness compared to the control formulation could be achieved with some applications, statistical evaluations confirm significant interaction of cooking procedures, storage and composition in rendering the texture of the product. Some of these interactions involve reducing of the retrogradation behavior in stored samples. This would imply that pullulan may be a valuable ingredient for gelled confectionery not only for the added nutritional benefits of reduction in calorific value and increased fiber but also as a hydrocolloid additive for reducing the effects of syneresis upon storage. Further research is necessary to fully describe and optimize the effect of pullulan substitution on the texture of sweet gels as well as other food matrices. Future studies should also take into consideration sensory profiling of these types of products as well as the effects of this non-digestible polysaccharide on digestibility of different food matrices.

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