Çukurova Üniversitesi Mühendislik Fakültesi Dergisi, 39(2), ss. 407-414, Haziran 2024
Cukurova University Journal of the Faculty of Engineering, 39(2), pp. 407-414, June 2024

Effects of Adding Pectin to Milk in Varying Amounts on the Rheological Properties of Milk

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Geliş tarihi: 09.01.2024 Kabul tarihi: 27.06.2024

Atıf şekli/ How to cite: ÖZBOLAT, V., (2024). Effects of Adding Pectin to Milk in Varying Amounts on the Rheological Properties of Milk. Cukurova University, Journal of the Faculty of Engineering, 39(2), 407-414.

Abstract

Pectin, which is used as an additive in the food, cosmetics, pharmaceutical, and health sectors due to its safety, non-toxicity, low production cost, and high availability, is used as a thickener, gelling agent, brightener, stabilizer, emulsifier, and fat and sugar replacer in low-calorie foods. It is also used in milk and dairy products as a stabilizer to prevent proteins from clumping. In this study, the rheological properties of pectin and milk mixtures with pectin/milk powder (w/w) ratios of 0.1, 0.25, 0.5, 0.75, 1 and 1.5 were examined. First, a flow curve test was applied in the range of 0,01-1000 s^{-1} to obtain the viscosity curves and yield stress values of the samples. Then, an amplitude sweep test was performed at a fixed frequency of 10 rad/s and in the strain range of 0.01-100% to determine the linear viscoelastic range (LVR) of the samples and the solid and liquid structure of the samples. To determine the time-dependent behavior of the samples in non-destructive deformation, frequency sweep tests were performed at constant strain (0.01%) in the LVR range obtained from the amplitude sweep test and in the range of 0.1-100 rad/s. Finally, three interval thixotropy tests (3ITT) were performed to observe the structural recovery of the samples. As a result of rheological tests, it was determined that pectin-free milk showed Newtonian properties, other samples showed shear thinning properties, and viscosity values increased as the pectin rate increased. While all samples are solid at low strains, the liquid feature becomes dominant at high strains. It has been observed that as the pectin ratio in milk increases, the strain values at the yield point, where the liquid feature becomes dominant, also increase. Except for the sample with the highest pectin content, it was observed that the dominance of the storage modulus over the loss modulus was greater at low frequencies than at high frequencies. As a result of 3ITT, it was determined that the percentage of recovery at the 600th second increased as the pectin rate increased.

Keywords: Pectin, Milk, Rheology, Food

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Değişen Miktarlarda Pektinin Süte Eklenmesinin Sütün Reolojik Özelliklerine Etkisi

Öz

Güvenli olması, toksik olmaması, düşük üretim maliyeti ve yüksek bulunabilirliği ile gıda, kozmetik, ilaç ve sağlık sektörlerinde katkı maddesi olarak kullanılan pektin; bu alanlarda kıvamlaştırıcı, jelleştirici, parlatıcı, stabilizatör, emülgatör olarak ve düşük kalorili gıdalarda yağ ve şeker ikamesi olarak kullanılmaktadır. Süt ve süt ürünlerinde kıvam arttırcı olarak kullanılmasının yanında proteinlerin topaklanmasını önlemek amacıyla stabilizatör olarak da kullanımı mevcuttur. Bu çalışmada, pektin/süt tozu (a/a) oranı 0,1, 0,25, 0,5, 0,75, 1 ve 1,5 olan pektin ve süt karışımların reolojik özellikleri incelenmiştir. İlk olarak, numunelerin viskozite eğrilerini ve akma gerilmesi değerlerini elde etmek için 0,01-1000 s^{-1} aralığında akış eğrisi testi uygulanmıştır. Daha sonra, numunelerin doğrusal viskoelastik aralığını (LVR) ve numunelerin katı ve sıvı yapısınını belirlemek için 10 rad/s sabit frekansta ve %0.01-100 gerinim aralığında genlik tarama testi yapılmıştır. Numunelerin tahribatsız deformasyonda zamana bağlı davranışını belirlemek için genlik tarama testinden elde edilen LVR aralığındaki sabit gerinimde (%0.01) ve 0.1-100 rad/s aralığında frekans tarama testleri yapılmıştır. Son olarak, numunelerin yapısal yenilenmesini gözlemlemek amacıyla üç aralıklı tiksotropi testi (3ITT) yapılmıştır. Reolojik testler sonucunda pektin içermeyen sütün Newtonian özellik gösterdiği, diğer örneklerin kesme incelmesi özelliği gösterdiği ve pektin oranı arttıkça viskozite değerlerinin artığı belirlenmiştir. Tüm örnekler düşük gerinimlerde katı özellikte iken, yüksek gerinimlerde sıvı özellik baskın hale gelmektedir. Sütteki pektin oranı artıkça sıvı özelliğin baskın hale geçtiği akma noktasındaki gerinim değerlerinin de yükseldiği görülmüştür. Pektin oranı en yüksek örnek hariç diğer örneklerde depolama modülünün kayıp modülene baskınlığının düşük frekanslarda yüksek frekanslara göre daha fazla olduğu gözlemlenmiştir. 3ITT sonucunda, 600. saniyedeki yapısal yenilenmenin pektin oranı artıkça artığı belirlenmiştir.

Anahtar Kelimeler: Pektin, Süt, Reoloji, Gıda

1. INTRODUCTION

Pectin, the structural component of plant cell walls, is an excellent carbohydrate polymer produced from natural sources [1]. Today, the main source of pectin, which is used commercially as a thickener, gelling agent, brightener, stabilizer, and emulsifier, is citrus peel (85.5%), although apple pulp (14%) and sugar beet pulp (0.5%) are also used as sources [2]. Extracted pectin is included as a functional food ingredient in numerous food products because it is a safe, non-toxic substance with low production costs and high availability [3,4]. Pectin has many health and nutritional benefits. As a soluble dietary fiber, it has various beneficial gastrointestinal and physiological effects. With a diet rich in pectin, it is possible to reduce total cholesterol and low-density lipoprotein (LDL) level in the blood without affecting high-density lipoprotein (HDL) levels [5]. Pectin has shown chemoprotective properties against metastasis [6] of cancer and the growth of primary tumors [7] in many types of cancer, such as colon cancer [8], prostate cancer [9], pancreatic cancer [10], and breast cancer [11].

Rheology studies the flow and deformation of matter under the influence of force. When an external force is applied, the ideal solids deform while the ideal liquids flow. Materials between these two exhibit viscoelastic properties. For the materials to have the desired flow properties, materials called rheology modifiers are added to the fluid [12]. Rheology modifiers are added to many products used in sectors such as food, pharmacy, and cosmetics, according to the requirements of the application, such as food packaging and storage conditions, aroma release, and 3D food printing [13]. In the present study, the effect of adding pectin to milk at different rates on rheological properties, which is essential in the food industry, was examined.

2. MATERIALS AND METHODS

2.1. Materials

Lean milk powder was purchased from Bagdat Baharat (Ankara, Türkiye), and apple pectin (E440) originating from France was purchased from Alfasol (İstanbul, Türkiye). Medium-gelling apple pectin was used in this study. The nutritional values of lean milk powder used in the experiments are given in the table below.

Table 1. Nutrition facts of lean milk powder.

Nutrition facts per 100 g	
Energy	383kcal/1603kJ
Total fat	1.61g
Saturated fat	1.08g
Total carbohydrate	52.10g
Total sugars	48.63g
Fiber	0g
Protein	38.6g
Salt	0.58g

2.2. Sample Preparation

Milk was obtained by adding milk powder to distilled water in a milk powder-to-water ratio of 1:9 (w/v) and mixing at 300 rpm for 40 min. Then, various weights of pectin were added to the resulting milk and mixed at 1000 rpm for 20 min to obtain pectin milk mixtures. The amounts of materials used in the preparation of samples are given in Table 2 and samples are henceforth referred to as MP1, MP2, MP3, MP4, MP5, and MP6.

Table 2. Water, milk powder, and pectin amounts in the samples.

Sample	Distilled water (ml)	Milk power (g)	Pectin (g)
MP1	18	2	0.2
MP2	18	2	0.5
MP3	18	2	1
MP4	18	2	1.5
MP5	18	2	2
MP6	18	2	3

2.3. Rheological Measurements

Rheological measurements were performed using an MCR 302e rheometer (Anton Paar, Austria) with a 50-mm diameter parallel-plate tool. On the other hand, a 26-mm cup and bob double gap measuring system was used to measure the rheological properties of milk. The flow and viscosity curves were obtained from the rotational test, which was performed at shear rates ranging from 0.01 to 1000 s^{-1} for pectin and milk mixtures and from 1 to 1000 s^{-1} for milk. The duration of a data point decreased logarithmically from 30 s to 1 s for mixtures and linearly from 10 s to 1 s for milk. The rheological tests were preceded by a pre-shear of 20 s at 1 s^{-1}. The amplitude sweep test was carried out at a constant angular frequency of 10 rad/s in a strain range of 0.01 to 100% to record the storage module (G') and loss module (G''). The frequency sweep was performed to obtain G', G'' and complex viscosity (|η*|) in the frequency range of 100 rad/s to 0.1 rad/s and at a constant strain of 0.01%, which was within the linear viscoelastic range determined in the amplitude sweep test. A three interval thixotropy test (3ITT) was conducted to observe the structural breakdown and recovery of samples. In this test, a constant frequency of 10 rad/s and a constant strain of 0.5% (within the linear viscoelastic range) were chosen at intervals of 1 and 3. In interval 2, the sample was sheared for 120 s at a shear rate of 100% and a constant frequency of 10 rad/s. A constant temperature of 25˚C was chosen for all experiments. A peltier-controlled temperature system with an active hood was used to control the temperature very precisely and to ensure that the temperature gradient in the samples was <0.1˚C. RheoCompass (Anton Paar, Austria) software was used to process the results and draw the graphics.

3. RESULTS AND DISCUSSIONS

3.1. Viscosity Measurements

The viscosity curves of the samples obtained from the rotational tests are shown in Figure 1. Samples MP1, MP2, MP3, MP4, MP5 and MP6 showed shear thinning behavior of viscoelastic solids. That is, as the shear rate increased, the viscosity of the samples decreased. This behavior is an important feature desired in the 3D printing of foods. However, milk that does not contain any pectin showed Newtonian behavior. The viscosity of milk at 25 °C was found to be around 1.9 mPa.s. Compared to the viscosity of water, there was no significant increase in the viscosity of milk obtained by adding milk powder to water with a milk powder/water (w/v) ratio of 1/9. On the other hand, adding pectin to milk, even in low amounts, appears to significantly increase viscosity, and viscosity values increased by increasing the amount of added pectin.

3.2. Amplitude Sweep Tests

Amplitude sweep tests were also applied to obtain the storage modulus (G') and loss modulus (G") of samples as a function of shear strain (%). G' represents the solid component and G" represents the liquid component of the sample. As can be seen from Figure 2, G' is more dominant than G" in all samples, which shows that the samples have viscoelastic solid properties. The solid feature is most dominant in MP6 and the magnitude of this dominance decreases as the amount of pectin in the samples decreases. Using this test, the linear viscoelastic regions (LVER) of the samples were also determined. The region in the graph where G' exhibits a plateau is referred to as the LVER. In the LVER, the applied stress is not large enough to cause structural distortion of the structure. Beyond the LVER boundary, the sample begins to deform permanently, and the sample stability is not at a level that prevents precipitation within the sample. Therefore, it is of great importance to know the LVER limit of the samples. As the pectin amounts increased, the linear viscoelastic regions of the samples lengthened. While the LVER limit for MP6 was 7.02%, it was 5.37%, 2.91%, 2.07%, and 1.07 for MP5, MP4, MP3, and MP2, respectively. This limit was below 1% for MP1.

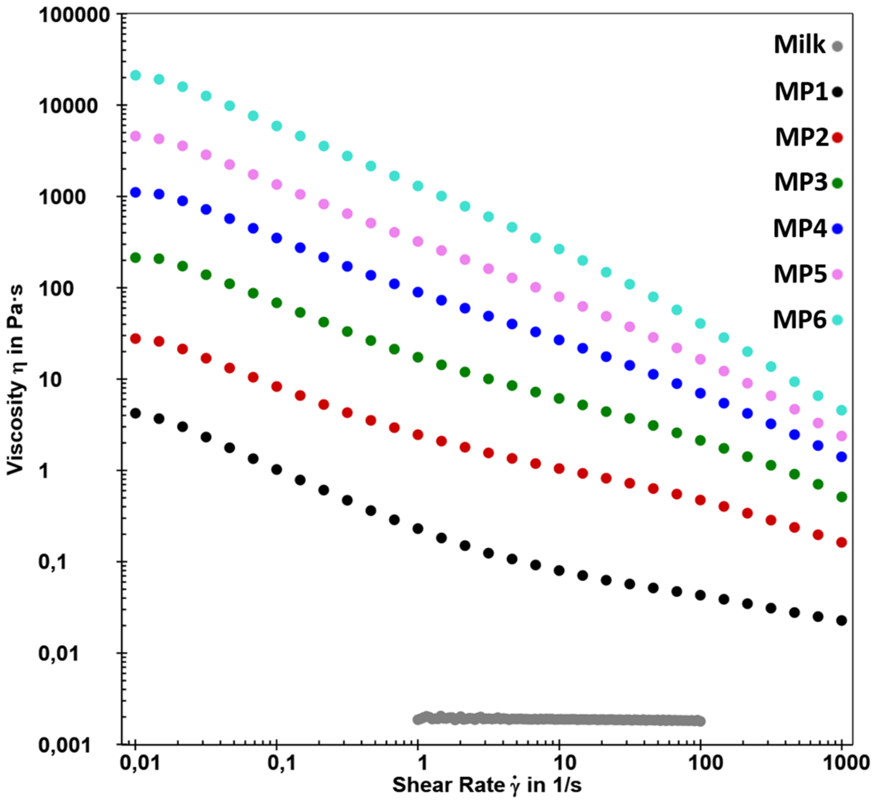

Figure 1. Viscosity vs shear rate graph of the samples

Yield stress is the minimum stress required to initiate flow [14]. Yield stress is essential in the design of food packaging and applications such as 3D food printing. For food to come out of its package, it is necessary to apply more stress than shear stress. In extrusion-based 3D printing, the applied stress must exceed the shear stress. While the yield stress of MP6 was found to be 426 Pa, this value was determined to be 93.2 Pa for MP5, 16.89 Pa for MP4, 3.778 Pa for MP3, 0.5543 for MP2, and 0.05347 Pa for MP2. As can be seen, as the pectin ratio in the samples increases, the yield stress increases. A larger yield stress indicates that the structure is more stable, the layer thickness is higher, and the character is more gel-like. When stress is applied to materials below the yield stress, no significant change is observed in their internal structure. At stresses below the yield stress value, the material exhibits reversible viscoelastic behavior. However, as the shear rate increases, non-covalent interactions in the gel under shear stress are broken, causing the material to exhibit viscous flow.

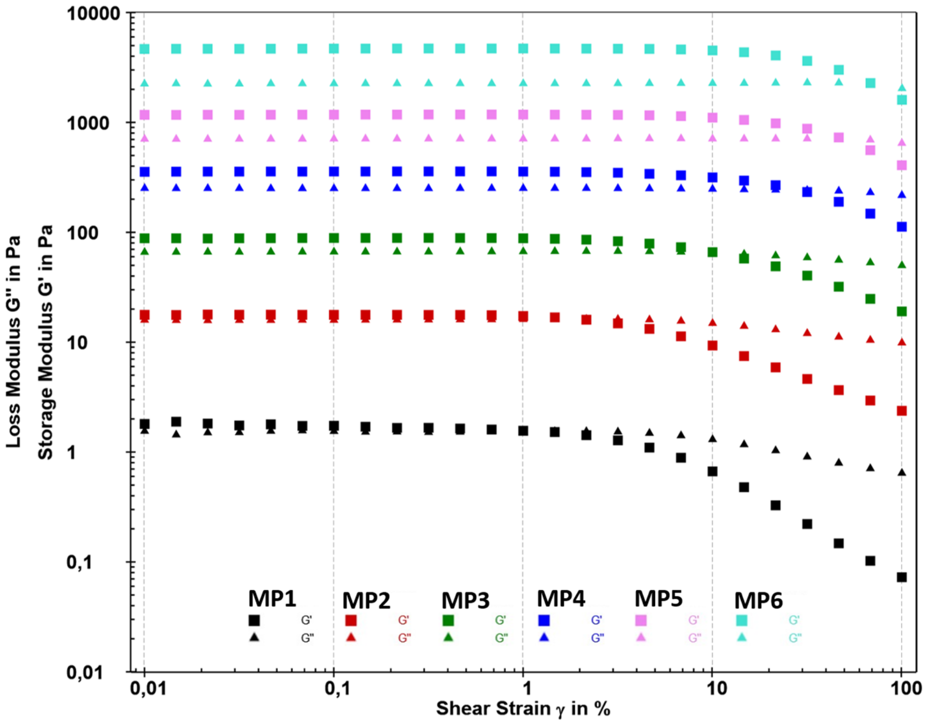

Figure 2. Amplitude sweep test results of the samples

The point where G' curve intersects with G" curve is called the flow point. Beyond this point, the G" value exceeds the G' value and it flows like a liquid. Table 3. shows the shear strain, shear stress, and storage modulus values of the samples at their flow points. While a shear stress of 2229.1 Pa is required for MP6 to flow like a liquid, this value decreases as the pectin rate in the samples decreases. In particular, for MP2 and MP1, the required shear stress reaches values very close to 0.

3.3. Frequency Sweep Tests

Frequency sweep tests were also performed to determine the time-dependent changes in the storage and loss modulus of samples at constant shear strains. The tests were performed between 0.1 and 100 rad/s, and the constant shear strains were within the linear viscoelastic region determined as a result of the amplitude sweep tests. As seen in Figure 3A, because G' values of MP6, MP5, MP4, and MP3 were higher than their G" values, the samples exhibited typical gel-like behavior.

Table 3. Shear strain, shear stress, and storage modulus values of the samples at flow points.

Sample	Shear strain (%)	Shear stress (Pa)	Storage modulus (Pa)
MP1	1.38	0.030031	1.5342
MP2	2.08	0.4752	16.151
MP3	10.8	9.8738	64.484
MP4	29.3	99.599	240.48
MP5	49.4	491.67	704.82
MP6	71.9	2229.1	2195.7

The dominance of G' over G" is higher at low frequencies, except for MP6, and is lower at high frequencies. For MP2, G" became dominant over G' after a crossover point (ω=12.6 rad/s and G'=G"=12.99 Pa), indicating that the sample behaved as a viscoelastic liquid after this point. As the frequency increased, this feature became more evident. Figure B shows the shear-thinning behavior of the samples. As can be seen from Figure 3C, samples with low pectin amounts have more liquid character, while MP6 has the least liquid feature because the more the elastic modulus depends on frequency, the more liquid-like the material is.

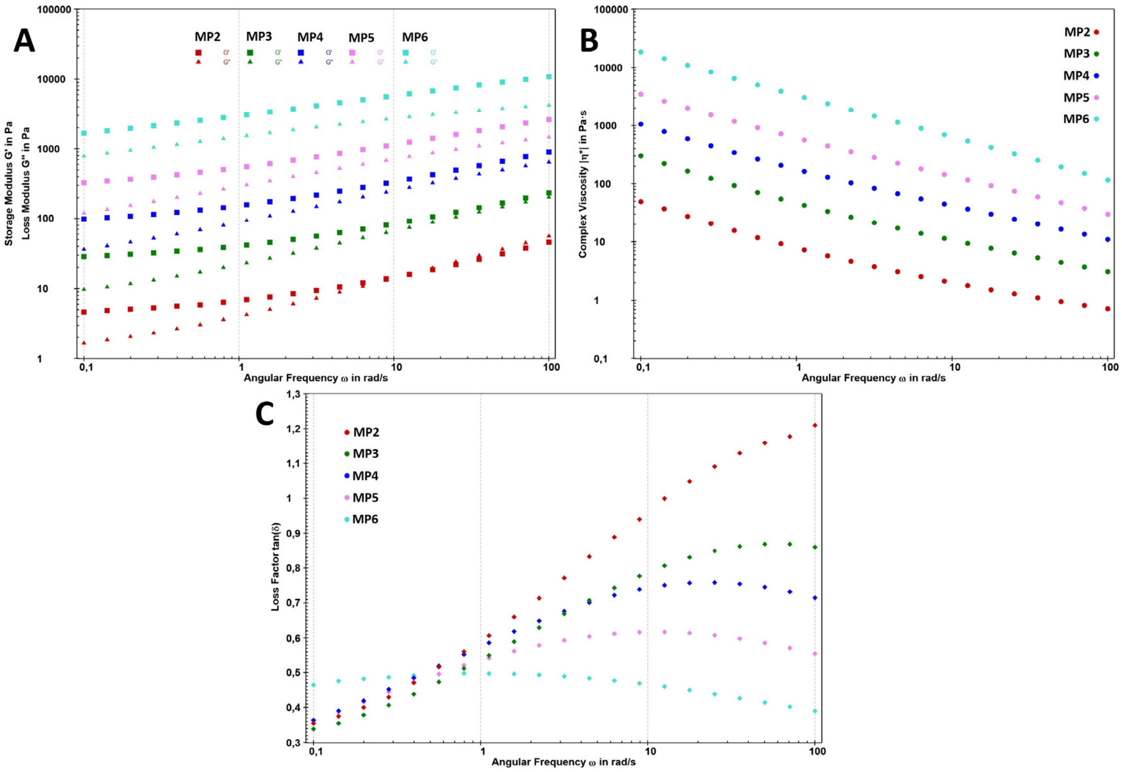

Figure 3. Frequency sweep test results: A) storage and loss modules vs. angular frequency, B) complex viscosity vs. angular frequency and, C) loss factor vs. angular frequency.

3.4. Thixotropy Tests

Under high force, the structural strength of the materials decreases and recovers over a certain period when the force is reduced or removed. In this study, low shear strain (0.5%) was first applied for 120 s, then high shear stain (100%) was applied for 120 s to ensure that the material undergoes structural deformation, and finally, its regeneration was investigated by applying 0.5% shear strain for 600 seconds. While all samples showed solid properties in the first interval, i.e., at low shear strain, they exhibited liquid properties when high shear strain was applied in the second interval (Figure 4). As the shear strain is reduced again in the third interval, the G' values of the samples increase more than G'. While MP1 and MP2 still showed liquid properties in the third region at 600 s, MP3 started to exhibit solid properties again after 435 s. When the shear strain applied in MP4, MP5, and MP6 is reduced to 0.5%, the G' value immediately exceeds G'. This indicates that these samples exhibit solid properties in the third interval.

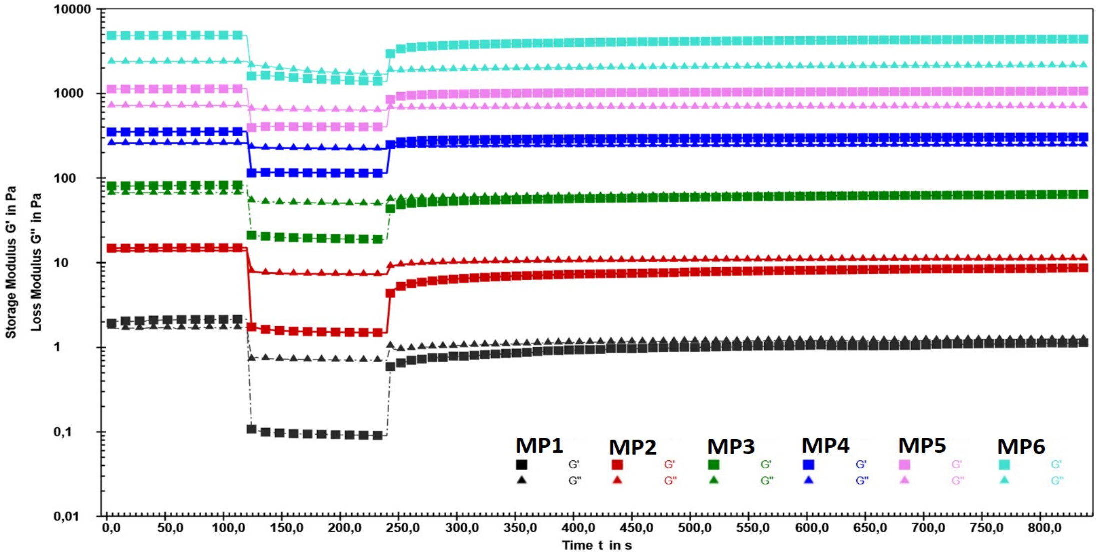

Figure 4. Three interval thixotropy test (3ITT) results of the samples

Recovery values calculated as the percentage of the G' value at the 600th second in the third region corresponding to the G' value at the 120th second, the last data point of the first interval, are given in Table 4. While MP1 had 52.56% recovery at the 600th second, this value increased as the pectin rate increased in the samples, and the recovery value became 89.70% in MP6. Recovery values at 600 s were calculated as 57.75%, 77.38%, 86.37%, and 88.36% for MP2, MP3, MP4, and MP5, respectively.

Table 4. Recovery values of the samples at 600 s.

Sample	Recovery (%) at 600 s
MP1	52.56
MP2	57.75
MP3	77.38
MP4	86.37
MP5	88.36
MP6	89.70

4. CONCLUSION

In this study, flow curve, amplitude and frequency sweep, and thixotropy tests were applied to examine the rheological properties of samples obtained by mixing milk and pectin in different ratios. From the flow curve test, it was observed that the milk had Newtonian properties and, with the addition of pectin, it exhibited shear thinning, which is a desired feature in applications such as 3D printing. It was observed that viscosity values increased significantly as the amount of pectin added increased. Yield stress, which is important for applications such as food packaging design and 3D printing, was calculated to be highest in MP6 with 426 Pa. As the amount of pectin mixed into the same amount of milk increased, the flow point, which is the point where the material turns into liquid, was observed at higher shear strain values. Shear strain and storage modulus values also increase with the amount of pectin. This means that samples with high pectin content must be exposed to more stress to show liquid properties. While samples containing low pectin appear to have liquid character at high frequencies, all samples are solid-like at low frequencies. This shows that it will exhibit solid properties during shelf waiting time, which is especially important for food products. While the recovery percentages at 600 s increased as the pectin amounts in the samples increased and reached 86.37% in MP4, the addition of more pectin increased the recovery value slightly and reached 89.70% in MP6.

5. ACKNOWLEDGEMENTS

This research was supported by the Çukurova University Scientific Research Projects Coordination Unit (Project Numbers: FAY-2022-14493 and FBA-2019-12182).

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