TECHNO-FUNCTIONAL PROPERTIES OF BAKERY PRODUCTS CONTAINING LEGUME AND NUT FLOURS

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Ilgın DOĞRUER

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We approve the thesis of **Ilgın DOĞRUER**

Examining Committee Members:

Prof. Dr. Fatma Banu ÖZEN
Department of Food Engineering, İzmir Institute of Technology

Assoc. Dr. Şükrü GÜLEÇ
Department of Food Engineering, İzmir Institute of Technology

Prof. Dr. S. Nur DİRİM
Department of Food Engineering, Ege University

17 July 2023

Prof. Dr. Fatma Banu ÖZEN
Supervisor, Department of Food Engineering,
İzmir Institute of Technology

Assoc. Dr. Ayşe Handan BAYSAL
Head of the Department of Food Engineering

Prof. Dr. Mehtap EANES
Dean of the Graduate School of
Engineering and Sciences

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ABSTRACT

TECHNO-FUNCTIONAL PROPERTIES OF BAKERY PRODUCTS CONTAINING LEGUME AND NUT FLOURS

The purpose of this study is to develop nut and legume flour-based cookie formulations with improved functional properties and to investigate the rheological, spectroscopic, and technological characteristics of these products. In addition to sensory testing, the rheological, spectroscopic, and technological properties of cookies made with different ratios of double (combinations of chickpea-hazelnut and chickpea-carob flours) and triple composite flours (chickpea-hazelnut-carob flours) were assessed. The findings of the flour analyses show that the protein contents of raw and cooked chickpea flours are higher than wheat flour. Hazelnut flour stands out for having a high-fat content; 35 times higher compared to wheat flour, and 6 times as chickpea flour. Pre-cooked chickpea flour has a strong capacity to retain water when compared to the other flours used in the formulation of gluten-free cookies. Its capacity to hold water is about 3.5 times greater than that of wheat flour. The sample with 90% chickpea flour has the highest firmness (N) value and the greatest difference from the other formulations, according to the rheological properties. However, among all the samples, the dough with the highest hazelnut content (60%) gets the lowest firmness grade. In accordance with principal component analysis, all cookie dough samples that contain double and triple composite flours are grouped based on their formulations, and cookies that just contain chickpea flour are separated from the others. Moreover, it may be concluded from the sensory evaluation of the cookies that the inclusion of hazelnut and carob flour influences customer preferences favorably.

ÖZET

BAKLAGİL VE KABUKLU YEMİŞ UNU İÇEREN UNLU MAMULLERİN TEKNO-FONKSİYONEL ÖZELLİKLERİ

Bu çalışmanın amacı, fonksiyonel özellikleri iyileştirilmiş yemiş ve baklagil unu bazlı kurabiye formülasyonları geliştirmek ve bu formülasyonların reolojik, spektroskopik ve teknolojik özelliklerini analiz etmektir. Kurabiye formülasyonlarının temel bileşenleri olan nohut unu, keçiboynuzu unu ve fındık unu bu çalışmada fiziksel, besinsel ve spektroskopik özellikleri açısından incelenmiştir. Duyusal testlerinin yanı sıra ikili (nohut-fındık ve nohut-keçiboynuzu unları kombinasyonları) ve üçlü karışım unlar (nohut-fındık-keçiboynuzu unları) ile farklı oranlarda yapılan kurabiyelerin reolojik, spektroskopik ve teknolojik özellikleri değerlendirildi. Un deneylerinin bulguları, çiğ ve önceden pişirilmiş nohut unlarının protein içeriğinin buğday unundan çok daha yüksek olduğunu (neredeyse iki kat daha yüksek) göstermektedir. Fındık unu, yüksek yağ içeriğine sahip olmasıyla öne çıkmaktadır ve buğday ununa kıyasla yaklaşık 35 kat, nohut ununa kıyasla ise altı kat fazla yağa sahiptir. Ön pişirilmiş nohut unu, glütensiz kurabiye formülasyonunda kullanılan diğer unlara kıyasla güçlü su tutma kapasitesiyle öne çıkıyor. Nohut ununun su tutma kapasitesi buğday unundan yaklaşık 3,5 kat daha fazladır. Kurabiye hamurunun reolojik özelliklerine göre %90 nohut unu içeren örnek en yüksek sertlik değerine ve diğer formülasyonlara göre oldukça büyük bir degree sahiptir. Ancak tüm örnekler içerisinde en yüksek fındık içeriğine (%60) sahip hamur en düşük sertlik derecesini almıştır. PCA'ya göre ikili ve üçlü karışım un içeren tüm kurabiye hamuru örnekleri formülasyonlarına göre ayrılmıştır ve sadece nohut unu içeren kurabiye örnekleri diğerlerinden belirgin bir şekilde ayrışmaktadır. Ayrıca glutensiz kurabiyelerin duyusal değerlendirmesinden fındık ve keçiboynuzu unu ilavesinin tüketici tercihlerini olumlu yönde etkilediği sonucu çıkarılmıştır.

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LIST OF ABBREVIATIONS

CD	Celiac Disease
CF	Carob Flour
CPF	Chickpea Flour
COS	Corn Starch
GF	Gluten Free
EC	Emulsion Capacity
ES	Emulsion Stability
FC	Foaming Capacity
FS	Foaming Stability
GI	Glycemic Index
HF	Hazelnut Flour
OAC	Oil Absorption Capacity
RDS	Rapid Digestible Starch
SDS	Slowly Digestible Starch
SEM	Scanning Electron Microscope
WF	Wheat Flour
WRC	Water Retantion Capacity

CHAPTER 1

INTRODUCTION

In recent years, the consumption of gluten-free products has increased significantly. According to studies by Golley et al., (2014) and Reilly (2016), the rise in the number of people who follow a gluten-free diet can be attributed to better diagnosis, increased awareness of gluten allergy, intolerance, and sensitivity, or more pervasive perception that gluten-free products are healthier. The three main gluten-related illnesses that impact a wide portion of the population are celiac disease (CD), wheat allergy, and non-celiac gluten sensitivity (NCGS) (Catassi et al., 2013). Gluten-containing foods harm the small intestine and decrease the nutritional absorption in CD patients who consume them. The elimination of gluten from the diet is the only treatment for celiac disease and other gluten-related illnesses. Most importantly for people with celiac disease, increasing the variety of gluten-free products is vital. Even while the market for gluten-free products is constantly expanding, gluten-free products available in the current market are either very inadequate in terms of nutritional values or are not very successful in taste compared to gluten-containing alternatives. Generally, these gluten-free products are produced using mostly wheat and corn starch instead of legume flours with high nutritional value, and this situation causes nutritional deficiency in food products, particularly in terms of protein. Legume flours and other good-tasting raw materials can be added to the formulations to solve this issue. In the current study, it was aimed to produce a gluten-free product with high nutritional value by using chickpea flour, which is a legume flour with high protein content. In addition, with the addition of carob and hazelnut flours to this product, it was intended to develop a tasty alternative to gluten-free products on the market which do not have the best nutritional properties by breaking the prejudices in the eyes of the consumers.

Leguminosae, a family of plants with around 17,600 species and about 690 genera include dicotyledonous seeds called legumes. Legumes are food sources with a number of health advantages. They include considerable levels of vitamins, minerals, and complex carbohydrates as well as proteins, dietary fibers, and other nutrients (Du et al., 2014). Legumes are the second-largest source of human food in developing nations, behind cereals, especially in those with poor incomes. They are utilized to increase the variety of human diets and offer developing countries an affordable supply of protein (Maninder et al., 2007). The fifth most important crop in the world is the chickpea. The top exporters of high-quality grain are India, Turkey, Pakistan, and Mexico (Kaur & Singh, 2005). The chickpea seed has a high protein digestibility, high levels of complex carbohydrates (low glycemic index), and is a great source of vitamins and minerals (Mittal et al., 2012). Despite this advanced nutritional content of chickpeas, its unique taste and smell when used in bakery products may be the reason why consumers do not prefer this product because they are not used to it. In this study, it was tried to suppress the unwanted taste and flavor from chickpea flour by adding carob and hazelnut flour in various proportions to the cookies. The addition of hazelnut and carob flours can increase the consumer's acceptance rate of cookies, while at the same time increasing the functional properties of the product. Carob flour stands out with its high phenolic content and fiber source (Tsatsaragkou et al., 2014). In addition, with its cocoa-like taste and smell, it is an attractive option for consumers and a successful alternative to the baked goods containing cocoa. Due to its unique nutritional combination of proteins (15–19%), carbohydrates (15–17%), fat (60–70%), and vitamins, the hazelnut is one of the most significant of the nut species (Yagcı & Gogus, 2009). When hazelnut flour is added to the bakery products, thanks to its high-fat content, it carries the taste, smell and textural properties of these products to higher levels. This situation also increases the consumer's preference for the products containing hazelnut flour.

The aim of this study is to obtain cookie formulations with increased functional properties, which contain legumes and nut flours, and to investigate rheological, spectroscopic and technological properties of these formulations. In this study, the physical, nutritional and spectroscopic properties of chickpea flour, carob flour and hazelnut flour which are the main ingredients of cookie formulations were investigated (Chapter 3). Rheological, spectroscopic, technological and *in vitro* digestion properties of the cookies formulated using various proportions of double (chickpea-hazelnut and chickpea-carob flour combinations) and triple composite flours (chickpea-hazelnut-carob flours) were evaluated and sensory analysis of the selected cookies were also done (Chapter 4).

CHAPTER 2

LITERATURE REVIEW

Gluten consumption can cause celiac disease (CD), an autoimmune disorder that manifests itself as a particular serological and histological profile in those with a family history. The generic word for the proteins that are alcohol-soluble and found in a variety of cereals, including wheat, rye, barley, spelt, and kamut, is gluten. Celiac disease patients need to adhere to a strict, lifelong gluten-free diet. One of the most prevalent autoimmune diseases, CD is estimated to affect 0.5–1% of the general population (Caio et al., 2019). The CD was believed to be associated with kids until 20 years ago. However, in recent years, a rise in the number of adult-diagnosed cases has been observed. Because CD causes moderate and infrequent symptoms in adults, it is normal for many people to go years without receiving a diagnosis. According to estimates, between 2 and 7 instances of CD might go untreated for every new patient who receives the diagnosis (García-Manzanares & Lucendo, 2011).

In the past, individuals who had celiac disease were not allowed to consume conventional wheat-based foods such as bread and spaghetti, and all varieties of bakery goods, but during the past 20 years, an increasing number of gluten-free (GF) alternatives to these items have reached to the market. Initially, GF items were only available at specialty diet food stores. Then, they made their way into typical supermarkets, where they may now be found on the same shelf as their gluten-containing versions or in dedicated areas with a variety of GF items. The classification and labeling of gluten-free products as well as their sale are governed by special laws (Gorgitano & Sodano, 2019). After consuming even little amounts of gluten, persons with celiac disease or gluten-related illnesses including wheat allergy and non-celiac gluten sensitivity have serious health issues. Consuming foods made from wheat, barley, rye, or oats that contain gluten is closely linked to these disorders. Together with those who are to consume GF goods, those seeking to maintain a healthy diet have boosted demand for these goods (Rocchetti et al., 2019). In this regard, the food industry has to diversify its functional food production by conducting research on advanced ingredients and formulations. Hence, because of customers' increasing knowledge over the past several years, both the food industry and academics intensified their interest in the quest for GF flour (Culetu et al., 2021).

It's challenging to substitute gluten in food products because of several problems, including dietary deficiencies and textural properties. For instance, since the dough for GF products lacks cohesion, flexibility and baking quality, it is more challenging to work with them (Cappelli et al., 2020). GF goods typically have high starch levels, low fiber levels, short shelf life or texture problems, such as harder breadcrumbs (Demirkesen & Ozkaya, 2020). In order to achieve the goal to formulate goods that are comparable to those made with wheat, additional research is being done to investigate the combinations of various GF flours and other components (Saturni et al., 2010). Due to their nutritious properties, legumes are commonly utilized as flours in GF food products. Proteins, complex carbohydrates, fiber, micronutrients, and antioxidant compounds are all significant sources of these nutrients. Chickpeas are protein-rich legumes with strong emulsifying qualities and the capability of increasing the volume of GF bread (Aguilar et al., 2015).

2.1. Chickpea and Chickpea Flour

Specifically, four major legume crops are grown in the Mediterranean area which are peas, chickpeas, lentils, and fava beans due to its temperate weather (Hernández-López et al., 2022). Chickpea (Cicer arientum L.) is considered as one of the most valuable legumes in terms of their nutritional content. It is grown in most of the world but India, Turkey, and Australia produce significant proportion of chickpeas (Jukanti, Gaur, Gowda, & Chibbar, 2012). In 2020, the production volume of chickpeas in India amounted to more than 11 million metric tons. Turkey came in second at an estimated 630,000 metric tons of chickpeas. In the same year, around 15 million metric tons of chickpeas were produced worldwide. In 2021, 4,750,00 tons of chickpeas were produced in Turkey, and 481,667 ha area was used for cultivation of this product (FAOSTAT, 2022).

Legumes have an important role in the human diet due to their nutritional value. They have high protein, dietary fiber, and complex carbohydrate content (Wang et al., 2010). Chickpea (Cicer arietinum L.) is one of the most important legumes on the basis of whole grain products (Ravi and Suvendu, 2004). Depending on the variety, the protein content of chickpeas changes between 20.9 to 25.27%, and albumin, globulin and prolamine contents range between 8.39–12.31%, 53.44–60.29%, 3.12–6.89%, and 19.38–24.40%, respectively (Dhawan et al., 1991). The proteins contained in legumes are rich in lysine, leucine, aspartic acid, glutamic acid, and arginine which are branched-chain amino acids (Oomah, 2001). The carbohydrate content of chickpea mostly consists of monosaccharides which are ribose, fructose and glucose. Oligosaccharides, mainly raffinose, ciceritol, and stachyose, are also found in chickpea grains (Berrios et al., 2010, Alajaji and El-Adawy, 2006). Total lipid content of chickpea varies between 4.5 to 6 g oil/100 g and the major part of it is consisted of lecithin. Unsaturated fatty acids which are mostly linoleic, oleic and linolenic acids form a large portion of the fatty acid content of the chickpea grains (Danuta et al., 2015). Moreover, the mineral contents of grains are also important for human health. For chickpeas, Ca, P, Mg, Fe and K are the minerals that dominate the mineral content. However, thermal processes can easily cause a decrease in their mineral content (Wang et al., 2010). The phenolic content of food products is also an important parameter due to their antioxidant, antifungal and antibacterial effects, and chickpeas are a good source of polyphenols and flavonoids. The content of phenols is directly related to the color of the bean, and darker colored beans have higher phenolic content and also higher antioxidant properties (Segev et al., 2010). Besides their antioxidant properties, phenols have an important role in reducing oxidative stress in living organisms (Tiwari et al., 2009).

Chickpeas also have some anti-nutritional matter besides their great nutritional properties. Pythic acid which can be bound to important cations making them insoluble and un-absorbable, and protease inhibitors that directly affect the important enzymatic modifications needed for different properties of foods like water absorption and foaming are among these anti-nutritional factors (Jukanti, Gaur, Gowda, & Chibbar, 2012). Some processes effective for reducing these anti-nutritional effects of chickpeas are pounding, soaking, germination, and fermentation (Hotz & Gibson, 2007). Thermal processes that are applied to chickpeas have benefits of increasing protein digestibility while reducing the anti-nutritional factors, especially phytic acid and tannins (Wang et al., 2010).

Depending on cultural and personal preferences, chickpea seed is prepared and cooked in a variety of ways. To achieve a suitable texture for the consumer, an improvement in the nutritional elements, and an increase in protein digestibility, several domestic processing techniques (decortications, soaking, sprouting, fermenting, boiling, roasting, parching, frying, and steaming) can be applied. As a result of these techniques, different types of chickpea flour can be obtained (Mittal et al., 2012). Raw, pre-cooked, toasted, and germinated flours are examples of different types (Ouazib, Garzon, Zaidi, & Rosell, 2016; Sofi, Singh, Muzaffar, Mir, & Dar, 2020). Chickpeas gained popularity due to their nutritional advantages throughout the world, and in order to increase the consumption of these grain legumes, their flours have been added to food products like bread, spaghetti, cakes, and even biscuits. As an example, chickpea flour was used in GF bread formulation and provided good sensory reception and an acceptable loaf volume (Rachwa-Rosiak, Nebesny, & Budryn, 2015).

The term "ash content" describes how much ash would remain after burning 100 g of flour. More germ, bran, and outer endosperm present in the flour indicate a higher ash level. Reduced ash concentration shows that the flour has been processed more thoroughly (i.e., a lower extraction rate) (Committee, 2015). Chickpea flour has 3.5 times greater ash concentration than wheat flour. This is comparable to Hefnawy et al. (2012) who reported that the ash level of chickpea flour was 3.4%, although lower values (2.7 %) were discovered for chickpea flour in another study (Osorio-Diaz et al., 2008).

The nutritional value of chickpea flour has been thoroughly investigated. According to the reports in literature, it is a good source of protein corresponding to 24.4–25.4% of the total which is about two times as much as wheat flour (9.3–14.3%). Lysine which is an essential amino acid is known to be abundant in chickpea flour, while methionine, tryptophan, and cysteine which are the amino acids with sulfur are limited (Dandachy, Mawlawi, & Obeid, 2019). Linoleic acid is an important polyunsaturated fatty acid (PUFA), and chickpea flour is regarded as an excellent source of this particular fatty acid (3.7–5.1%). Compared to wheat flour (0.9–1.8%), chickpea flour has a higher fiber content (3.9–11.2%) (Zia-Ul-Haq et al., 2007).

Generally, GF products do not have the same nutritional and functional properties as gluten-containing alternatives because GF products are commonly made of non-enhanced or fortified starch. Celiac patients generally consume GF products having higher glycemic indexes due to the high pre-gelatinized starch content in these items (Lamacchia, Camarca, Picascia, Di Luccia, & Gianfrani, 2014). Numerous researchers have suggested the feasibility of mixing legume flour with wheat flour in different product formulations such as adding it into durum wheat flour in pasta formulations, even though the conclusions about the impact of such additions on the organoleptic characteristics of pasta are still debatable (Padalino et al., 2014).

Since plant crops are the primary sources of calories for a significant segment of the global population, particularly in developing nations, these crops have held a significant role in the human diet. Due to the economic and the social reasons, several millions of people in Asia and Africa are consuming legumes to obtain almost 80% of their protein needs according to FAO. The types of legumes used to meet the protein need are generally chickpea cultivars (Man et al., 2015). It has been noted that wheat flour can be completely or partially replaced with chickpea flour while making various types of cakes. Nevertheless, it was stated that as the percentage of chickpea flour substituted for wheat flour increased, the texture of the cake got stiffer, gummier, and less cohesive (Gómez, Oliete, Rosell, Pando, & Fernández, 2008). However, muffins made from chickpea flour have better viscoelastic batter and sensorial properties than wheat gluten batter according to Herranz et al. (2016). Also, chickpea flour enriched with plantain flour in wheat flour was used in biscuits production. As a result, the fracturabilities of biscuits were decreased and nutritional values were increased (Yadav, Yadav, & Dhull, 2012).

As previously stated, chickpea flour differs chemically from wheat flour, which has a significant impact on the appearance, taste, and behavior of dough during and after baking. Water and oil absorption capacities and emulsion and foaming capacities are important parameters to understand the behavior of the dough and the baked products.

Water absorption capacity (WAC) is the ability to retain water against gravity as a result of physicochemical interactions and it is also the ability to bind water molecules being dependent on protein structure and conformation (Zayas, 1997). WAC can influence potential food applications by determining the structure and organoleptic properties of food products (Singhal et al., 2016). High WAC results in brittle and dry food products, particularly during storage, whereas low WAC in food products is related to the inefficiency in storing water (Boye, Zare, et al., 2010). It is also one of the most important quality traits since it helps to determine absorption during baking and is closely related to the yield and quality of bakery goods (Sapirstein, Wu, Koksel, & Graf, 2018). Flours from different chickpea varieties can have different water absorption capacities. Hodge and Osman (1976) claimed that flours with high water absorption contain more hydrophilic constituents such as polysaccharides. When various legume flours are considered, WAC of the legume flours ranged from 1.12 g/g to 1.89 g/g and the protein contents of legume flours have an impact on their WAC as well (Du, Jiang, Yu, & Jane, 2014).

Oil absorption capacity (OAC) of flour is also an important parameter because it improves the mouthfeel and flavor of the product (Kinsella, 1976). Chickpea flour has a lower oil absorption capacity than wheat flour and this property depends on the variety of chickpeas (Sanjeewa et al., 2010). The capillary interactions used in the oil-absorbing process allow the absorbed oil to be maintained in the structure. Hydrophobic proteins are primarily responsible for oil absorption. Particle sizes, starch and protein concentrations, protein types (Sathe et al., 1982), and non-polar amino acid side chain ratios on the protein molecule surface all have an impact on the OACs of various legume flours (Chau et al., 1997). Binding quality of hydrophobic proteins to lipids is better and especially non-polar amino acid side chains bind to the paraffin chains of fats.

The ability and capacity of a protein to assist in the development of an emulsion are reflected by its emulsion activity, and it is connected to the capability of proteins to absorb the interfacial region of oil and water in an emulsion. The emulsion activity of the different legume flours varies differently, and chickpea flour had the lowest value (61.14%) while tiny red bean flour had the highest (92.20%) according to a study comparing the properties of various legume flours (Du, Jiang, Yu, & Jane, 2014).

The carbohydrate, lipid, and sterol contents as well as their protein levels found in the legume flours are the cause of the variations in their emulsion activity and stabilities. Protein-polysaccharide complexes may sterically restrict the protein's surface hydrophobic regions at high polysaccharide concentrations, reducing the rate at which those regions diffuse (Ganzevles, Cohen Stuart, Vliet, & de Jongh, 2006). According to Mokni Ghribi et al. (2015), it can be assumed that various interactions between the proteins and polysaccharides could have a significant impact on the properties of emulsions. Moreover, most proteins have several polar side chains with peptides on the parent chains, making them hydrophobic and altering their solubility and emulsification properties. Since chickpea flour has a lower protein level than the other varieties of bean flours, it has poorer emulsion activity (Du, Jiang, Yu, & Jane, 2014).

Continuity of the interfacial area over a specific time period is related to the emulsion stability since it typically represents the proteins' capacity to give an emulsion strength for resistance to stress and changes (Singh et al., 2010). Emulsion stabilities of different chickpea flours ranged from 76.6-82.1%, The interfacial film generated by proteins, which keeps the air bubbles in suspension and reduces the rate of coalescence, is generally what determines the foaming capacity and stability. The presence of proteins and other ingredients in flour, such as carbohydrates, affects the ability of flours to form a foam (Sreerama, Sashikala, Pratape, & Singh, 2012). Also, there were considerable variations in the foaming capacities (FC) and foam stabilities (FS) of the flours made from various chickpea cultivars. Proteins are surface active components that make them foam when stirred. According to a study in literature, flours from various chickpea cultivars produced reasonably thick foams with modest foam volumes but excellent foam stabilities (Kaur & Singh, 2005). It was reported that increased concentration promotes increased protein-protein interactions, which raise viscosity and make it easier for a multilayer cohesive protein film to develop at the interface (Adebowale & Lawal, 2004). Hence, this film creation provides resistance to the coalescence of bubbles. Additionally, after 120 minutes of storage, all of the chickpea flours displayed extremely high foam stabilities (>90%) (Kaur & Singh, 2005). It was concluded that capacity of the film created around the trapped air bubbles to remain intact without draining determines foam stability, and only very surface-active solutes can produce stable foams (Cherry & McWatters, 1981). Since the chickpea flours have strong foam stability, it is likely that the native proteins found in them are highly surface-active and soluble in the continuous phase which is water.

The bulk densities of the flours from different legumes have significant variations. The bulk density for legume flours ranged from 0.543 g/mL to 0.816 g/mL, with lentil flour and black bean flour having the highest and lowest values, respectively. The bulk densities of several chickpea cultivars have a variation from 0.536 g/mL to 0.571 g/mL according to Kaur and Singh (2005). Investigation of the effect of chickpea variety on the bulk density of chickpea flours in another research indicated values on average 0.573 g/mL (Du, Jiang, Yu, & Jane, 2014).

Recent studies either used low percentages of chickpea flour (20%) or had negative outcomes for high percentages of legume flour (more than 40%) in terms of consumer acceptance. According to the literature, chickpeas are one of the easiest beans to use in baked goods. Because of the decreases in acrylamide concentration in cookies and snacks, its use has been shown to be effective as a substitute for other flours (Torra et al., 2021). Belorio et al. (2016) claim that while developing a cookie formulation, it is crucial to pay attention to the rheology of the dough. Cookie dough that is too soft or too firm is difficult to work with; as a result, the dough must be sufficiently cohesive to hold together during the process and allow for simple lamination without becoming overly sticky to the point where it sticks to the rolling mill. It is required for cookie dough to have a minimal proportion of small-sized particles, which chickpea flour naturally has, in order for it to be cohesive and laminable. According to Luzfernandez and Berry (1989), adding chickpea flour had a negative impact on the rheological and baking qualities of wheat flour. However, it was noted that if the negative effects of its supplementing on the quality of baked goods could be avoided, chickpeas may be employed for enrichment with beneficial effect in a nutritional way.

The fracture strength of biscuits dramatically enhanced with the addition of chickpea flours, reaching its peak at a 40% concentration, according to Yadav et al. (2011). As the percentage of chickpea flour in the blends grew, the protein and crude fiber content of biscuits dramatically increased, rising from 7.1 to 9.2%. The sensory qualities of biscuits made by substituting chickpea flour for refined wheat flour up to 20% at a time were more or less comparable to those of control biscuits.

Extensograph findings showed that while dough extensibility remained unchanged, dough resistance to extension, dough energy, and proportional number all decreased when more lupin flour was added to the recipe with wheat flour. In addition, adding chickpeas to wheat flour decreased the dough's resistance to extension and proportional number while increasing the dough's extensibility and energy. By employing organoleptic assessment, it was observed that adding either 10% chickpeas, or 15% lupin flour may substitute wheat flour in cookie recipes without having a negative impact on baking performance or changing the final product's physical qualities (Malunga et al., 2014).

Cakes and cookies are easier to make using pulse flour than the loaves of bread. Gluten network is not necessary to produce products like cakes and cookies with high qualities, and pulse flours do not generate a gluten network when combined with wheat flour, making it possible to totally replace wheat flour with pulse flour. Several factors affect the creation of the gluten network including the inclusion of additional components such as sugar or fat, the lower proportion of wheat flour in the overall recipe, and the reduced mechanical energy used during the mixing process (Belorio & Gómez, 2020). The combined use of other ingredients like sugar and aromatics, also fat or oil helps mask the off odors of pulse flours and minimizes challenges with the acceptability of baked goods made with these flours. The nutritional advantages of using legume flour must be balanced against the fact that the inclusion of these components reduces the organoleptic quality of the final product (Bravo-Núñez & Gómez, 2021). Table 2.1. provides a summary of some other studies performed using chickpea flour in literature.

Table 2.1. Literature findings about food products made with chickpea flour

Type of Flour	Findings	Reference
pinto bean, lima bean, red kidney bean, lentil, chickpea	• Compared to other legume flours, black bean flour has a much higher OAC. • Since chickpea flour has a lower protein level than the other varieties of bean flour, it has rather limited emulsion activity. • Lentil flour had the highest protein content.	Du, S. K., Jiang, H., Yu, X., & Jane, J. L. (2014). Physicochemical and functional properties of whole legume flour. *LWT - Food Science and Technology*, *55*(1), 308–313. https://doi.org/10.1016/j.lwt.2013.06.001
chickpea flour	• Different treatments gave flours a high ability to bind water, and their rheological profiles were mostly influenced by starch characteristics. • The bread baked with roasted chickpea flour has the largest specific volume. • Bread produced with cooked chickpea flour had the softest texture. • In terms of sensory qualities, bread produced with germinated chickpeas received the lowest overall acceptance rating.	Ouazib, M., Garzon, R., Zaidi, F., & Rosell, C. M. (2016). Germinated, toasted and cooked chickpea as ingredients for breadmaking. *Journal of Food Science and Technology*, *53*(6), 2664–2672. https://doi.org/10.1007/s13197-016-2238-4
Chickpea flour, wheat flour	• The addition of chickpea flour raised the mineral and fat content of pasta, raising the food's nutritious value. • The levels of resistant starch and dietary fiber in the two varieties of pasta were comparable. However, pasta with chickpeas had a much larger indigestible percentage. • The peak and overall phases of hyperglycemia were both decreased by chickpea flour.	Goñi, I., & Valentín-Gamazo, C. (2003). Chickpea flour ingredient slows glycemic response to pasta in healthy volunteers. *Food Chemistry*, *81*(4), 511-515.

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Table 2.1 (cont.).

Chickpea flour, Wheat flour, Plantain flour	• Plantain and chickpea flour can each be added up to 20% of refined wheat flour to create biscuits with acceptable sensory characteristics and increased protein and fiber content. • As the mixes' percentage of plantain and chickpea flour expanded, the weight of the biscuits dropped. • Due to plantain and chickpea flours' lower oil absorption capabilities compared to wheat flour, the fat level decreased as chickpea flour replacement increased.	Yadav, R. B., Yadav, B. S., & Dhull, N. (2011). Effect of incorporation of plantain and chickpea flours on the quality characteristics of biscuits. *Journal of Food Science and Technology*, *49*(2), 207–213. https://doi.org/10.1007/s13197-011-0271-x
Chickpea flour, wheat flour	• Protein content of chickpea flours ranged from 22.48 to 25.18 g/100 g. • Compared to white chickpea flour, whole chickpeas have greater fiber. • Because of its higher moisture and protein content as well as its reduced fat level, Pedro-Sillano was the kind that was the most unique.	Gómez, M., Oliete, B., Rosell, C. M., Pando, V., & Fernández, E. (2008). Studies on cake quality made of wheat–chickpea flour blends. *LWT - Food Science and Technology*, *41*(9), 1701–1709. https://doi.org/10.1016/j.lwt.2007.11.024
Chickpea flour, rice flour	• To produce bakery goods like cookies, a novel foundation material called rice-chickpea composite flour may be employed. • Its proximate composition and pasting abilities changed significantly when rice flour was replaced with chickpea flour to the tune of 20% (w/w). • The pasting and viscoelasticity of the doughs were further enhanced by the addition of exudate gums.	Hamdani, A. M., Wani, I. A., & Bhat, N. A. (2020). Gluten free cookies from rice-chickpea composite flour using exudate gums from acacia, apricot and karaya. *Food Bioscience*, *35*, 100541. https://doi.org/10.1016/j.fbio.2020.100541

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Table 2.1 (cont.).

Chickpea flour	• The physical characteristics of the snack made with chickpea flour were impacted by changes in extrusion settings, feed moisture level, screw speed, and barrel temperature. • Products having a high expansion ratio, a low bulk density, and low hardness, all of which are excellent extruded snack characteristics.	Meng, X., Threinen, D., Hansen, M., & Driedger, D. (2010). Effects of extrusion conditions on system parameters and physical properties of a chickpea flour-based snack. *Food Research International*, *43*(2), 650–658. https://doi.org/10.1016/j.foodres.2009.07.016 (cont. on next page)
Different types of chickpea flours	• The incorporation of chickpea flours at a 20% ratio often showed higher ash, lipid, and protein levels in bread when compared to the control (100 % wheat bread). • In comparison to bread made with mature and black chickpea flours, bread made with immature, germinated, and fermented chickpea flours had a reduced phytic acid content. • The highest overall phenolic content in bread was produced by using chickpea flour that had not completely matured and had germinated.	Yaver, E. (2022). Nutritional and textural properties and antioxidant activity of breads prepared from immature, mature, germinated, fermented and black chickpea flours. *Journal of the Science of Food and Agriculture*, *102*(15), 7164–7171. https://doi.org/10.1002/jsfa.12082

2.2. Carob and Carob Flour

Since the ancient times, the carob tree (Ceratonia siliqua L., Fabaceae) has been cultivated in most of the Mediterranean Basin, which has generally moderate climates and wet, rain-fed orchards. The ancient Greeks carried it from its native Middle East to Greece and Italy because they understood its value. Around the world, carob is mostly farmed in regions with Mediterranean climates. The carob tree begins to produce significant amounts of pods around the age of 15 years, yet it may not reach full maturity until it is 50 years old (Barak & Mudgil, 2014). The FAO has determined that an 81832 hectare area is specifically used for cultivating carob, which yields a total output of 163000 metric tons of carob pods (Food and Agricultural Organization of the United Nations). Spain (40000 tons yearly), Italy (31000 tons), Portugal (23000 tons), Greece (22000 tons), and Morocco (20500 tons) are the top 5 carob-producing countries. These countries account for 25%, 19%, 14%, 13%, and 12% of global output, respectively. Turkey, Cyprus, and Algeria are also countries that produce carob, with a yearly output of 14000, 5000, and 3000 tons, respectively (FAOSTAT 2012). Turkey's Mediterranean and Aegean areas have been producing cultivated and wild carob varieties. In Turkey, carob trees are mostly found on the southern slopes of rocky terrain and calcareous soil and all carob trees are prized as forest trees (Baktir, 1988). From Urla (Izmir) to Samandag (Hatay), production in Turkey is centered along the coast in the Aegean (4%) and Mediterranean (96%) areas. Provinces like Mersin, Antalya, Mugla, Adana, Burdur, and Aydin are the biggest producers (Tous et al., 2014). Various usages of carob can be seen in Figure 2.1.

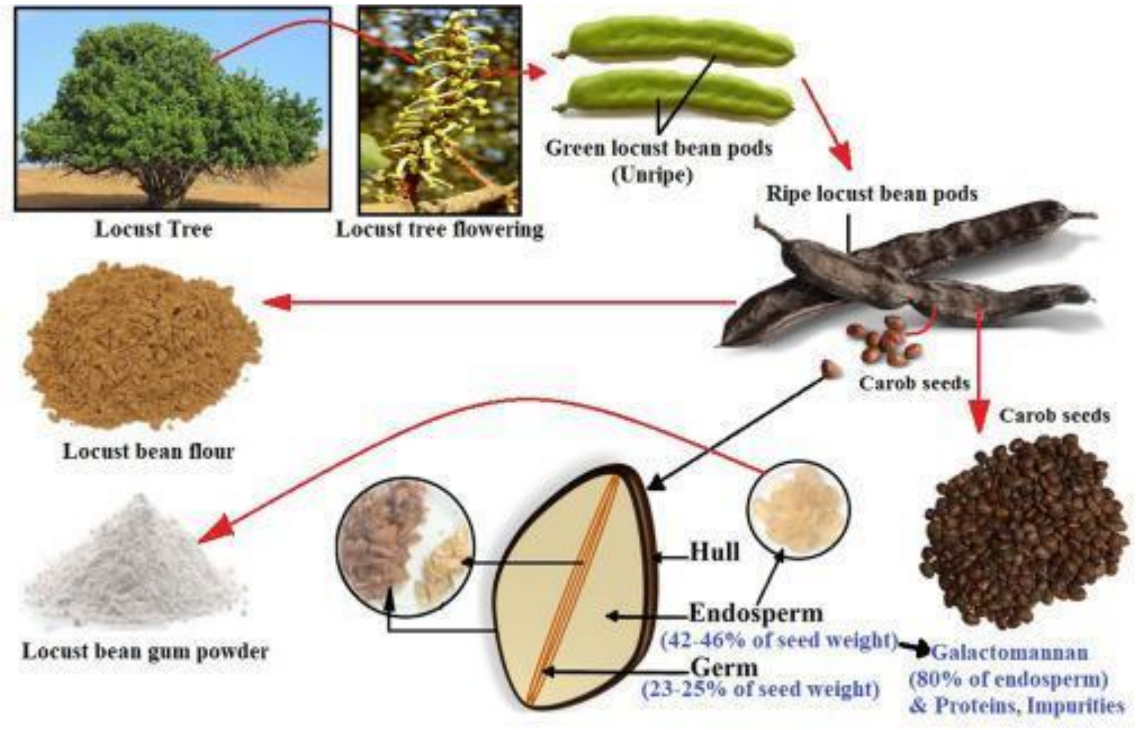

Figure 2.1. Different uses of carob (Source: Prajapati et al., 2021)

Bean gum, a polysaccharide (galactomannan) found in the endosperm of the carob seeds, is the fruit's primary usage in the food industry. Carob kibbles (deseeded chopped pods), which are high in sugars (48–56%) but may also include a sizable quantity of polyphenols, can be considered an agri–food waste item (Cavdarova & Makris, 2014). The carob pods are kibbled to separate the seeds from the pulp after being dried following the harvesting to reduce the moisture to around 8%.

The locust bean gum (LBG), a material used as a natural food ingredient and in the pharmaceutical sector, is produced from the carob seed. The husk, endosperm, and germ make up the three components of a carob seed (Prajapati, Jani, Moradiya, Randeria, & Nagar, 2013). Different parts can be used in the production of various products (Figure 2.1). The seeds are initially de-husked using either diluted sulfuric acid treatment or a thermo-mechanical procedure known as acid peeling or thermal peeling. After being separated, the endosperm is ground and sieved to create a fine powder that may be used to make native locust bean gum. Whereas the carob bean gum obtained by thermo-mechanical peeling is considerably darker in color because of the heating or roasting process, the carob bean gum obtained through acid peeling is pale in color and has a high viscosity. By dissolving LBG in heated water, it may be further clarified. To get cleared or pure LBG, the solution is dried and milled after being filtered to eliminate any insoluble materials (Barak & Mudgil, 2014).

The carob tree produces fruits in the shape of pods. When completely developed, the pod is elongated, flattened, straight or slightly curved, light to dark brown in color, and has a leathery surface that is wrinkled. The pulp and the seeds make up the carob pod's two primary components (Nasar-Abbas et al., 2015). The pulp is processed in the food industry to produce carob syrup and carob powder. The crushed carob pulp is soaked in water to make carob syrup. After draining, the mixture is heated till the syrup is formed (Özcan, Arslan, & Gökçalik, 2007). The pulp is first dehulled, then crushed to various sizes, roasted, and then processed into a fine powder, known as carob flour or powder, to make carob powder (Ortega et al., 2009).

Carob is also used as a good alternative to cocoa since it has high amounts of phytochemicals including proteins and amino acids, fatty acids, carbohydrates, and polyphenolic compounds. Polyphenolic compounds have numerous positive impacts on health (Loullis & Pinakoulaki, 2017) and both cocoa and carob have high nutritional values. Carob kibble's chemical content changes according to genetic, environmental, and climatic conditions, as well as harvesting season. The phenolic profile and biological activity of carob kibble are greatly influenced by the plant type (male, female, or hermaphrodite) and cultivar (Sánchez et al., 2010). The principal sugars in carob kibble are sucrose (65% to 75%), fructose and glucose (15% to 25% of the total sugars), which together account for a high sugar content of 30% to 60% (Biner, Gubbuk, Karhan, Aksu, & Pekmezci, 2007). A minor concentration of additional sugars, including maltose, raffinose, stachyose, verbascose, xylose, inositols, and others, are present in carob kibble in addition to the three primary sugars (sucrose, glucose, and fructose) (Nasar-Abbas et al., 2015). Depending on the type, region of origin, stage of development, and farming techniques, carob may have a different concentration of amino acids. Leucine, valine, aspartic (aspartic acid + asparagine) acid, alanine, and glutamic (glutamic acid + glutamine) acid, make up 57% of the pulp's total amino acid content in carob, whereas cysteine is present in the least amount. Carob is a good source of amino acids since it includes all seven essential amino acids: valine, isoleucine, leucine, phenylalanine, and lysine (Ayaz et al., 2007).

A significant quantity of protein (2% to 7%), fiber (up to 40%), and minerals including potassium (993 to 1089 mg/100 g), calcium (266 to 319 mg/100 g), phosphorus (76 to 79 mg/100 g), and magnesium (55 to 56 mg/100 g) are also present in carob fruit along with low amounts of fat (0.9% to 1.3%) (Nasar-Abbas et al., 2015). Oleic acid (C18:1n9), linoleic acid (C18:2n6), and linolenic acid (C18:3n3) as unsaturated fatty acids, as well as palmitic (C16:0) and stearic (C18:0) as saturated fatty acids are the major fatty acids in carob composition (Sigge, Lipumbu, & Britz, 2011). Carob may be considered a healthy food source and a perfect ingredient for the formulation of low-fat goods due to its extremely low-fat level (Gubbuk, Kafkas, Guven, & Gunes, 2010).

Dietary fiber from carob is distinctive in its composition. It is mostly insoluble and contains cellulose, hemicellulose, lignin, and galactomannan in amounts between 30-40% of carob pulp (Würsch et al., 1984). The distinctive characteristic of carob dietary fiber, which distinguishes it from the other dietary fibers, is due to the presence of high concentrations of polyphenols as well as proteins and minerals (Owen et al., 2003). Carob fiber's distinctive structure and high polyphenolic concentration make it a valuable addition for baked products (Loullis & Pinakoulaki, 2017). Although soluble polyphenols as gallic acid, hydrolyzable tannins (gallotannins), and flavonol glycosides are found in significant concentrations, carob fiber is primarily insoluble (Haber, 2002). Secondary plant metabolites known as polyphenols have a role in the pigmentation, growth, and reproduction of plants in addition to protecting them from herbivores, diseases, or rival plants as well as from UV radiation and oxidants (Cavdarova & Makris, 2014). Important phytochemicals known as polyphenols have been linked to the prevention of a number of illnesses, including cancer. Since carob pulp constitutes around 90% of the carob pod, carob polyphenols are mostly found in carob pulp. While the method employed for polyphenol extraction has a major impact on both their content and profile, the concentrations of polyphenols in carob are greatly influenced by genetic, environmental, and agricultural variables (Papagiannopoulos, Wollseifen, Mellenthin, Haber, & Galensa, 2004). In terms of their profile, carob polyphenols may be found in free, bound, and soluble conjugated forms. They mostly belong to the phenolic acid, flavonoid, and tannin families. The phenolic acids, which are further classified into hydroxybenzoic and hydroxycinnamic acids, are the most prevalent polyphenols in carob pods. Gallic acid is the main free acid among the hydroxybenzoic acids (Owen et al., 2003). In addition to enhancing the cocoa-like flavor and aroma of carob pulp during processing, roasting has an impact on the number of polyphenols present in carob products (Loullis & Pinakoulaki, 2017). While certain phenolic compounds may break down when being roasted, other polymer components may release polyphenols, enhancing the carob's overall phenolic concentration and antioxidant action (Özcan, Arslan, & Gökçalik, 2007).

Many epidemiological studies back up the idea that frequent consumption of foods and drinks high in polyphenols significantly lowers the risk of developing cardiovascular disease (CVD) (Habauzit & Morand, 2011). The composition of carob fiber is distinct and contains a significant number of polyphenols. Consuming carob fiber, which is high in polyphenols, has been demonstrated to improve a person's blood profile. Particularly, the levels of total cholesterol and LDL were significantly lowered, although the LDL/HDL ratio was only slightly affected (Ruiz-Roso et al., 2010). Furthermore, triglycerides were also decreased (Zunft et al., 2001). Carob pods (pulp and seeds) have a variety of use in both the gastronomy and food industries. Carob flour's high sugar concentration makes it possible to think of it as a natural sweetener. The chemical composition of carob flour also reveals a significant concentration of insoluble fiber; therefore, the addition of carob flour to formulations increases the dietary fiber content of food products. Because carob flour has a similar flavor and looks like cocoa powder, it can be used as a replacement (Biernacka et al., 2017).

Nowadays, more and more food products are using carob powder to replace cocoa powder, and research focusing on the comprehensive analysis of the chemical and sensory characteristics of carob-based goods has been reported. The incorporation of carob flour at 5% boosts antioxidant activity and lowers protein and starch digestibility without changing the sensory qualities of food products. It was also suggested to be included up to 15% for GF bread (Seczyk et al., 2016). It was found out that this addition changed the rheology of the dough with a requirement to add more water as carob flour was added (Tsatsaragkou et al., 2014). Moreover, it has been suggested that carob flour can be used to lower the glycemic index of cookies. Nevertheless, research on the effect of adding carob flour on changes in the organoleptic quality of cakes or cookies or the effect of roasting levels of carob flour on altering the qualities of these baked goods is lacking (Román et al., 2017). According to Román et al. (2017), the carob flour-added cookies had a thinner and wider shape compared to the control cookies produced with rice flour.

Thus, carob cookies expanded less during baking. This was associated with higher fiber contents of carob flour and sugar, which both contribute to water retention in cookies, than other flours. The firmness analysis revealed that cookies made with rice flour were comparatively less hard than those made with carob flour, suggesting that the latter had a more compact structure. Together with increasing carob flour concentrations in cookie samples, the protein content of cookies also increased. It has been noted that moisture content of the cookies was the highest when 100% carob flour was used. This demonstrates that carob flour absorbs moisture more effectively. Moreover, cookies having carob powder at all levels (0, 20, 40, 50, and 100%) had strong antioxidant activity in comparison to the control group produced with wheat flour (Babiker et al., 2020).

According to Loullis & Pinakoulaki, (2017), carob powder offers additional advantages due to its high fiber and low-fat content, especially for those with severe dietary needs. Moreover, theobromine and caffeine, which are undesirable in some formulations, are reduced when carob powder is substituted for cocoa powder. Overall, carob is a very good contender to replace cocoa due to its nutritional benefits and financial advantages. In a variety of cocoa- and chocolate-based items, such as substitutes for chocolate and chocolate biscuits, carob can be used in place of cocoa. Several examples of the use of carob flour are shown in Table 2.2

Table 2.2. Literature findings about food products made with carob flour

Type of Flour	Findings	Reference
Wheat flour, carob flour	• The final product's ash content increased along with the amount of carob flour substituted in the tarhana recipe. • The reduction in carbohydrates as sugar led to a proportional rise in the dry matter of tarhana that cannot be fermented, including ash, protein, and mineral matter, particularly in terms of Ca, K, and Zn. • Because of its ability to gel, carob flour addition improved the tarhana soup's functionality.	Çaglar, A., Erol, N., & Elgun, M. S. (2012). Effect Of Carob Flour Substıtutıon On Chemıcal And Functıonal Propertıes Of Tarhana. *Journal of Food Processing and Preservation*, *37*(5), 670–675. https://doi.org/10.1111/j.1745-4549.2012.00708.x
Carob flour, banana flour, soy flour	• Cakes with high protein and dietary fiber content can be made using banana and soy flour, and carob flour can be used in place of cocoa powder. •The cakes' chemical composition showed higher amounts of dietary fiber and lower levels of fat, carbs, and calories. Carob flour was used in place of cocoa powder. •The texture investigations revealed that the elasticity, resilience, and cohesiveness were all reduced when cocoa powder was partially or entirely replaced by carob flour •The cakes with up to 75% substitution of carob flour for cocoa powder exhibited no variation in flavor, odor, or texture, proving that substitution up to this degree had no impact on sensory qualities.	Rosa, C. S., Tessele, K., Prestes, R. C., Silveira, M., & Franco, F. (2015). Effect of substituting of cocoa powder for carob flour in cakes made with soy and banana flours. International Food Research Journal, 22(5).

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Table 2.2 (cont.).

Type of Flour	Findings	Reference
Wheat flour, lentil flour, carob flour	•Wheat flour's rheological properties and bread qualities were changed by mixing it with carob seed or green lentil flour. •Carob soluble fiber's hydrophilicity and strong gelling capabilities contributed significantly to the carob flour blends' exceptional technical performances. •By including lysine-rich proteins, dietary fiber, and bioactive ingredients, carob flours and lentil flour, in particular, enhanced the nutritional value of bread..	Turfani, V., Narducci, V., Durazzo, A., Galli, V., & Carcea, M. (2017). Technological, nutritional and functional properties of wheat bread enriched with lentil or carob flours. LWT, 78, 361–366. https://doi.org/10.1016/j.lwt.2016.12.030
Rice flour, carob flour	•To help with minor modifications to the rheological qualities of their doughs and batters and in their physical features, such as specific volume or shape and texture, carob flour at levels of 15% can be used to create gluten-free cookies and cakes •Low-degree roasted carob flour is preferred over highly roasted carob flour since adding significantly changed the color and flavor of these items. •In terms of hardness, control cookies produced with rice flour were found to be less hard than those prepared with carob flour, which is suggestive of the cookies created with carob flour having a more compact structure.	Román, L., González, A., Espina, T., & Gómez, M. (2017). Degree of roasting of carob flour affecting the properties of gluten-free cakes and cookies. Journal of Food Science and Technology, 54(7), 2094–2103. https://doi.org/10.1007/s13197-017-2649-x
Carob pod powder	•The protein content was a little raised while the quantity of fiber and reduced sugars were significantly increased by increasing the amount of carob powder used as a substitute for cocoa in milk chocolate (25, 50, 75, and 100%). •Due to the increased carob powder proportions, the levels of potassium, calcium, sodium, and magnesium were greater than those observed in milk chocolate •The constant reduction in caffeine levels, which reached zero when 100% of carob powder was utilized, was one of the most noticeable benefits.	Salem, E. M., & Fahad, A. O. (2012). Substituting of cacao by carob pod powder in milk chocolate manufacturing. Australian Journal of Basic and Applied Sciences, 6(3), 572-578.

2.3. Hazelnut and Hazelnut Flour

The hazelnut tree, *Corylus maxima M.* and *Corylus avellana L.*, is a common nut tree found all over the world. Turkey dominates the hazelnut sector, providing 83% of the global production (Huntrods, 2013) and supplying 80% of hazelnut exports (FAO, 2010), even though its production is spread over from Turkey to some regions of the United States. Turkey offers ideal growth conditions for developing high-quality hazelnut cultivars. Moreover, Anatolia is the primary source of cultivated variants as well as the natural expansion region of the most prized wild species and hazelnut's genetic origin (Köksal et al., 2006). Parts of a hazelnut is shown in Figure 2.2.

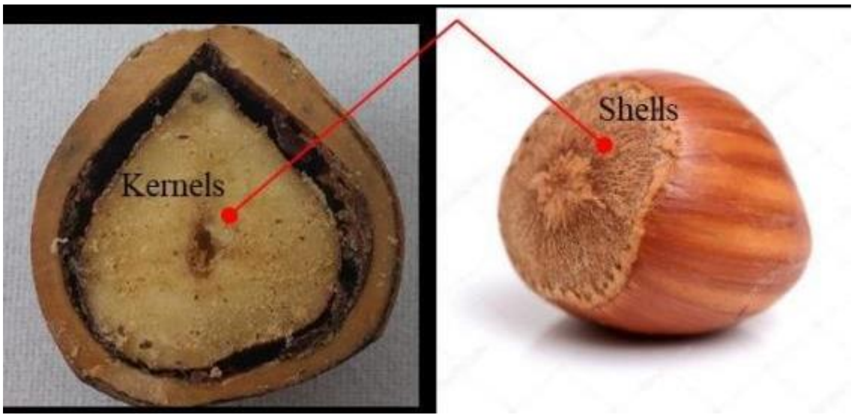

Figure 2.2. Parts of the hazelnut (Source: Chen et al., 2021)

Due to its unique nutritional combination of proteins (10–24%), carbohydrates (15–17%), fat (60–70%) and vitamins, hazelnut is one of the most significant nut species (Kirbaşlar & Erkmen, 2003). Compared to many proteins of plant origin, its protein quality is very good. Unsaturated fatty acids (linoleic, linolenic, oleic, acids) are crucial for human health and are present in hazelnut kernels with a high amount (50–73%)

(Garcia et al., 1994). For the most crucial elements for growth and development, such as iron (5.8 mg/100 g), calcium (160.0 mg/100 g), and zinc (2.2 mg/100 g), it seemed to be one of the finest sources of plant origin (Yagcı & Gogus, 2009). Hazelnut kernels are valuable sources of essential vitamins like vitamins B1, B6, niacin, and α-tocopherol in addition to their high mineral content. There is evidence that α-tocopherol, the active form of vitamin E, helps to lower the risk of some chronic illnesses (Köksal et al., 2006). Due to the presence of α-tocopherol, consumption of hazelnut also provides protection against conditions like heart disease (Iannuzzi et al., 2002), type 2 diabetes, hypertension, cancer (Boshtam, Rafiei, Sadeghi, &Sarraf-Zadegan, 2002), and Alzheimer's disease (Martin, 2003). While in smaller amounts, hazelnuts also contain organic acids, and malic acid is the most prevalent organic acid in hazelnut kernels (Botta et al., 2014).

Hazelnuts have a high ratio of unsaturated to saturated fatty acids, therefore adding them to processed foods can enhance their nutritional value (Köksal et al., 2006). Moreover, due to its organoleptic properties, hazelnut is one of the most significant raw ingredients for the pastry and chocolate industries (Fallico et al., 2003). A variety of hazelnut products, including sliced, chopped, flour, oil, and hazelnut butter, are consumed along with raw, blanched, and roasted hazelnut kernels (Köksal et al., 2006). One of the most crucial procedures that causes the essential changes in the product to become value-added nuts is roasting. Regarding both quality and safety, roasting time and temperature are key aspects in the hazelnut production process. Typically, hazelnuts are roasted for 5 to 60 minutes at temperatures between 100^{o}C and 180^{o}C. According to color characteristics, roasting at higher temperatures for longer periods of time produced more brown color as a result of Maillard reactions as well as the formation of hydroxymethyl furfural (HMF) (Turan et al., 2015).

Hazelnut flour is one of the most significant hazelnut products. The product known as hazelnut flour is made by properly crushing natural or roasted hazelnuts. In the food industry, hazelnut flour is used to make pastries, baked goods, ice cream, dairy products, confections, and chocolate products. It may also be used to season bread, cereals, yogurt, soups, salads, and main courses (Karaosmanoğlu & Üstün, 2020). Hazelnut flour can be regarded as advantageous when compared to other meals as a potential non-traditional source of proteins due to the high protein content of raw hazelnuts (Turan et al., 2015). The oil absorption capacity (OAC), or the quantity of oil absorbed per gram of sample, is a critical aspect in food compositions since it enhances the satiety, taste, and mouthfeel of food (Omosulis et al., 2011). The hazelnut flour has the potential to retain taste effectively, especially in matrices requiring high OAC. Protein, which is made up of both hydrophilic and hydrophobic components, is the major constituent factor controlling OAC. High OAC may be caused by partial protein denaturation and the exposure of highly hydrophobic proteins, which exhibit better binding to lipid hydrocarbon chains (Turan et al., 2015).

Due to the role that proteins and other amphoteric molecules play in the production of conventional or innovative meals, emulsifying properties are also important. Hazelnut flour's high emulsifying abilities may be particularly beneficial in food systems like salad dressings, drinks and meat substitutes (Ma et al., 2011). According to Turan et al. (2015), raw defatted hazelnut flour has an emulsion activity (EA) value that is higher than its emulsion stability (ES) value. While the EA of flours fell throughout the roasting process, the ES of flours increased after roasting. Heating can cause protein molecules to interact, as a result, protein aggregates that are large enough to capture oil in the three-dimensional matrix of the aggregates may form, creating an excellent emulsion. The ability of a substance to produce and maintain a foam is referred to as foaming capability. The study by Omosulis et al. (2011) found that hazelnut flour has a reasonably high foaming capacity and foaming stability, which implies that this flour may find use in goods like cakes, coffee whiteners and confectionary products where foaming properties are crucial (Turan et al., 2015).

Due to the challenges of use as well as the comparatively higher cost of natural hazelnut kernel, a variety of additives marketed as artificial hazelnut flavoring, natural similar hazelnut aroma, and natural hazelnut aroma are used in the food sector while making cookies. The addition of hazelnut testa greatly raises the product's overall acceptability, according to the sensory evaluation of the cookies conducted by Velioglu et al. (2017). Thanks to hazelnut unique flavor, hazelnut cake recipes are popular in both commercial ready-to-eat cake manufacturing and domestic dishes. Also, as anticipated, a greater hazelnut testa ratio in cake composition led to noticeably better smell scores. The inclusion of hazelnut testa in baking recipes was found to be acceptable. The sensory quality of cookies and cake, particularly in terms of smell and taste, was positively impacted by the addition of hazelnut testa (Velioğlu et al., 2017). Moreover, using flour blends fortified with hazelnut testa can lead to the production of nutritionally beneficial baked goods due to the high phenolic content (Anil, 2007). Findings from the literature for the products containing hazelnut flour is shown in Table 2.3.

Table 2.3. Literature findings about food products made with hazelnut flour

Type of Flour	Findings	Reference
Hazelnut flour	•The production of vanilla ice cream has effectively utilised hazelnut peel and flour. •Similar total solids, titratable acidity, overrun, and b-values were observed in hazelnut flour and hazelnut skin added samples. • The panelists provided samples of ice cream with hazelnut flour added better ratings for flavor, body and texture, and appearance than samples of ice cream with hazelnut skin added.	Dervisoglu, M. (2006, June). Influence of hazelnut flour and skin addition on the physical, chemical and sensory properties of vanilla ice cream. International Journal of Food Science and Technology, 41(6), 657–661. https://doi.org/10.1111/j.1365-2621.2005.01127.x
Durum clear flour, partially defatted hazelnut flour	•The extruded snacks' bulk density and water solubility index increased as the portion of partly defatted hazelnut flour (PDHF) increased, while their porosity and water absorption index decreased. •The morphological and functional characteristics of the generated snacks were impacted by changing process parameters. • Low PDHF level allowed for the development of expanded food products with acceptable sensory characteristics.	Yağcı, S., & Göğüş, F. (2008, May). Response surface methodology for evaluation of physical and functional properties of extruded snack foods developed from food-by-products. Journal of Food Engineering, 86(1), 122–132. https://doi.org/10.1016/j.jfoodeng.2007.09.018

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Table 2.3 (cont.).

Type of Flour	Findings	Reference
Wheat flour, hazelnut flouır	•Hazelnut testa addition has been observed to considerably change several quality parameters of doughs and breads in terms of ratio, particle size, and hydratation process. • The finest bread quality, measured as loaf volume, was found in control bread, breads containing 5% fine hazelnut testa, and breads containing 5% coarse hazelnut testa, except for hydrated hazelnut testa. •The greatest total sensory assessment ratings were achieved by control bread and bread containing 5% dry hazelnut testa, while adding 10% dry hazelnut testa also produced satisfactory results.	Anil, M. (2007, May). Using of hazelnut testa as a source of dietary fiber in breadmaking. Journal of Food Engineering, 80(1), 61–67. https://doi.org/10.1016/j.jfoodeng.2006.05.003
Defatted hazelnut flour (DHF), rice flour	• Gluten-free breads with addition DHF that contained 47.22% protein. •The qualities of the gluten-free dough were enhanced by adding DHF and other gums. The addition of DHF and gum to gluten-free formulations raised the values of the consistency index and flow behavior index • Gum was added to gluten-free recipes to enhance the volume of bread. The inclusion of DHF to gluten-free formulations did not significantly alter the specific volume of loaves with and without DHF.	Tunç, M. T., & Kahyaoglu, T. (2016, March 1). Improving Rheological and Baking Properties of Gluten-Free Breads Using Defatted Hazelnut Flour with Various Gums. International Journal of Food Engineering, 12(4), 343–353. https://doi.org/10.1515/ijfe-2015-0207

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

Cooked chickpea flour (CPF) and carob flour (CF) were obtained from Naturelka (Aydın, Turkey). Hazelnut flour (HF) produced from raw hazelnuts with skin and corn starch (COS) were purchased from Ingro (Karaman, Turkey). Other ingredients used in cookie formulations were obtained from the following suppliers: eggs (~60 g) from Ercanlar (Izmir, Turkey), margarine from Sana pastry (Turkey) brand, brown sugar from Takita (Turkey) and baking powder was from Dr. Oetker (Turkey).

3.2. Methods

All methods that’s used in the experiments were explained in the following sections.

3.2.1. Flour Properties

Experimental methods related to flour properties were mentioned.

3.2.1.1. Bulk Density

The flour samples were placed into a 5 mL graduated cylinder by constant tapping until there was no further change in volume. The contents were weighed, and then the bulk density of the samples was calculated (Narayana and Narasinga Rao, 1984; Turan et al., 2015). Results were reported as g/mL.

3.2.1.2. Water Retention Capacity

Water retention capacity (WRC) was determined by AACC Method 56-11. This value represents the weight of water held by flour after the centrifugation process as a percentage of the flour weight, on a 14% moisture basis. Firstly, weights of 50 mL centrifuge tubes were recorded, then 5.000 ± 0.050 g flours of known moisture content were weighed and poured into each tube. 25.00 ± 0.05 g water was added to each tube containing flour and the tubes were shaken vigorously to suspend the flour for 5 seconds. Contents of the tubes were allowed to dissolve and swell for 20 min, and they were shaken at the 5th, 10th, 15th, and 20th min (about 5 s each time). After the shaking process, tubes were immediately transferred to the centrifuge (SIGMA 2-16 KC Sigma Laborzentrifug, Germany) at 1000 × g for 15 min. Then, supernatants were decanted and the tubes were weighted. The weight of the gel is determined by subtracting the weight of the tube from the total weight of the tube and gel.

3.2.1.3. Oil Absorption Capacity

The oil absorption capacity (OAC) was determined by vortex mixing of 1 g of flour and 10 mL of sunflower oil for 30 s, and then they were allowed to stand for 30 min. The mixture was centrifuged at 3000 g for 20 min at 25°C. After the centrifugation process, the weights of the supernatants were determined. The volume (mL) of oil absorbed per gram of flour was reported according to the methods in literature (Abbey & Ibeh, 1988; Falade & Okafor, 2013).

3.2.1.4. Emulsifying Properties

The emulsifying activity (EA) and emulsion stability (ES) were determined by using methods described in the literature (Njintang et al., 2001; Vioque et al., 2000). 100 mL of 2% (w/v) sample solutions were homogenized at 9500 rpm for 30 seconds (621.11.001 ISOLAB GmbH, Germany) at room temperature. After that, 100 mL of corn oil was added to the solution, and the mixture was homogenized again at 9500 rpm for 1 minute. Finally, the emulsion (50 mL) was centrifuged at 1200 g for 5 minutes. The height of the emulsified layer was recorded and EA was calculated from the ratio of the height of the emulsified layer to the height of the contents of the tube. ES was determined by taking a ratio of the height of the remaining emulsified layer over the height of the original emulsified layer after the emulsions were heated at 80^{o}C for 30 minutes and re-centrifuged at 1200 g for 5 min.

3.2.1.5. Foaming Properties

The foaming capacity (FC) and the stability (FS) were determined by using a method defined by Njintang et al. (2001). 3% (w/v) solutions were prepared with flour samples and deionized water. The solutions (150 mL) were stirred in a homogenizer at 9500 rpm for 2 min and immediately transferred into a 250 mL graduated cylinder and the volume was recorded after whipping. FC was expressed as the percent volume (%) increased after whipping and determined from the calculation of volume after whipping subtracted from the volume before whipping and dividing this result by the volume before whipping. FS was determined from the foam volume changes in the graduated cylinder and these changes were recorded after 5, 10, 20, 30, 60 min of storage. FS was determined by subtraction of volume after standing from the volume before whipping and dividing this result into volume before whipping. All analyses were performed in duplicate.

3.2.1.6. Moisture Content

Moisture content was determined according to AOAC method, 925.05 with slight modifications (Anonymous, 1990). 2.5 ± 0.01 g flour samples were weighed and transferred into dried petri dishes. Then, petri dishes that contained flour samples were put in the laboratory oven (Binder, ED53, Tuttlingen, Germany). The drying process took place at 105 °C for 2 hours. After the drying process was finished, petri dishes were collected and put into a desiccator until no weight change was observed (approximately 30-60 min). Lastly, dishes were weighed by using a laboratory scale and to obtain moisture loss in grams, the petri dish tare was subtracted from the final weight. Moisture loss percentage was determined by the following formula (3.1):

$$\%\text{Moisture}=\frac{\text{Moisture Loss in grams}}{\text{Original Weight of flour}}\times 100 \qquad (3.1)$$

3.2.1.7. Protein Content

Protein content was determined according to the Kjeldahl Method (AOAC method, 950.48) with a conversion factor of 6.25 (Anonymous, 1990). This method consisted of three main stages, digestion, distillation and titration. First, approximately 1 gram of the sample was weighed and transferred in a test tube. Then, a catalyst tablet, antifoam reagent and concentrated sulphuric acid (appx. 15 mL) were added to each test tube. The same procedure was applied for the blanks with all chemicals and without samples. Samples were digested in a digestion unit. The system performs full automatic distillation, (Kjeldahl nitrogen/protein, ammonium, alkali direct, volatile acid-base distillations) in circulation with the potentiometric titration method. It has 20 combustion units. It works in the range of 0-430 ºC (GerhardtVapodest 50s, Germany). For the distillation and titration phase, test tubes were cooled down and entered the system.

3.2.1.8. Crude Fat Content

Crude fat content was determined according to the Soxhlet Method (AOAC method, 960.39) (Anonymous, 1990). Approximately 1 gram of the sample was weighed and transferred into a porous thimble. Then, the thimble with the sample was placed in the extraction chamber (Soxtherm multistat Gerhardt, Germany). With the reaching of filling level during the extraction, the solvent with extracted matter siphons back into the boiling flask. The sample is only extracted with a cold solvent. At the end of the process, the solvent is evaporated, and the boiling flask only contains the extracted matter which is fat.

3.2.1.9. Total Ash Content

Total ash content was determined according to AOAC method, 923.03 (Anonymous, 1990). Firstly, crucibles were dried in a laboratory oven for 2 hours at 130 °C and cooled in a desiccator (approximately for 60 minutes). Their weights were measured and recorded. About 3-5 gram flour samples were weighed in the crucibles. Then, crucibles that contained the flour samples were put in a laboratory oven (Binder, ED53, Tuttlingen, Germany) and the drying process took place at 105 °C for 2 hours. When the samples were cooled in a desiccator their weights were measured again and recorded. Crucibles were put in the muffle furnace and the ignition program was started. The furnace was reached to 550 ºC and then cooled to 90-95ºC. This process took around 8 hours. Crucibles were transferred to a desiccator at once, and they were cooled for at least 30 minutes. Then, total ash (%) on dry basis was calculated by using the following formula (3.2):

$$\%\text{Ash}=\frac{\text{Weight of the crucible with the ash-Weight of dry crucible}}{\text{Weight of the crucible with the dried sample-Weight of dry crucible}}\times 100 \quad (3.2)$$

3.2.1.10. Crude Fiber Content

Crude fiber contents were determined by using AOAC method 14.020 (Anonymous, 1990). Flour samples were weighed around 2 grams and transferred into a 1000 mL beaker. 200 mL H_2SO_4 (1.25%) solution was added into the same beaker and the beaker was placed on the hot plate. The mixture was boiled exactly for 30 minutes and mixed periodically to prevent solids from adhering to the sides of the beaker. After 30 minutes, beaker was removed and the contents were filtered through a cheesecloth. Beaker was rinsed with 50-75 mL H_2O (boiling) washed through the cheesecloth. Then, cheesecloth was washed with NaOH solution (up to 150 mL) and the remaining 50 mL was added. The boiling process continued exactly for 30 minutes. Contents were filtered again as described above; but this time, it was washed with 25 mL H_2SO_4 (1.25%), then with 50 mL H_2O, and 25 mL ethyl alcohol. In the end, all of the contents were transferred to a crucible and weighed. Crucibles were dried in the laboratory oven at 130°C for 2 hours, then cooled in a desiccator and weighed again. Lastly, the samples were ignited in a muffle furnace and cooled in a desiccator again. Their weights were recorded and fiber amount (%) was calculated using the following formula (3.3):

$$\%\ \text{Fiber}=\frac{\text{Weight of Dried Contents-Weight of Ash (final)}}{\text{ground sample}}\times 100 \qquad (3.3)$$

3.2.1.11. Carbohydrate Content

Carbohydrate contents were calculated as 100% - total% of other compounds (moisture + protein + fat + ash).

3.2.1.12. Total Phenolic Content (TPC)

The total phenolic contents of flours were determined using the methods in literature (Byanju et al., 2021; Maria do Socorro et al., 2010) with slight modifications. First, for the extraction process, 0.5 g flour samples were weighted and mixed with 7.5 mL 1% HCl solution. The mixture was held in the dark for 2 hours and transferred to a centrifuge at 2000 g for 10 minutes. After the centrifugation process, the supernatants were collected. Then, for the TPC determination, supernatants were diluted 10x times in eppendorf tubes. 50 µL diluted sample and 250 µL Folin-Ciocalteu reagent were mixed in eppendorf tubes and held in the dark for 5 minutes. Then, 200 µL Na_2CO_3 (8%) was added and kept in the dark for 60 minutes. As the last step, the samples were transferred to the well plate (96), and their absorbances were recorded at 760 nm. The following formula was used to obtain the TPC of the samples (GAE) (170.12 represents the gallic acid molecular weight) (3.4).

$$\text{PC}\ \left(\frac{\text{mg GAE}}{\text{L}}\right)=\frac{\text{Sample Absorbance-Blank Absorbance}}{0.0011}\times 10\times\frac{170.12}{1000} \qquad (3.4)$$

3.2.1.13. Color Measurements

The color of the flours in terms of L, a, b values were determined with a colorimeter (CR-400 Konica Minolta, Tokyo, Japan). In the triple scale consisting of CIE Color Values (L*, a*, b*), L*=100 white, L*=0 black; high positive a* red, high negative a* green; high positive b* yellow and high negative b* is rated as blue. The color of the three different points of the samples were recorded and average values were taken.

3.2.1.14. Scanning Electron Microscopy (SEM) Analysis

Microscale images of the flours were obtained with the scanning electron microscopy (Quanta 250 SEM, USA) at different magnitudes. Flour samples were dried at 105^{o}C for 3 hours in an oven before analysis.

3.2.1.15. Fourier Transform Infrared (FTIR) Spectroscopy Analysis of Flours

Mid-infrared spectroscopic profiles were collected with a Fourier transform infrared spectrometer (Spectrum 100, Perkin Elmer, USA) equipped with a DTGS detector. For this purpose, flours were mixed with KBr (3%) and mid-infrared spectra of flour-KBr pellets were obtained with 128 scans at 4 cm^{-1} resolution. Averages of 5 readings were taken.

3.2.2. Cookie Preparation

Table 3.1 and 3.2 list the cookie dough formulations. Cooked chickpea flour was used as a raw material, and it was replaced with carob and hazelnut flour based on different percentages to obtain the gluten-free cookies. Cookie formulations contain the following composite flours:

- Chickpea flour and hazelnut flour
- Chickpea flour and carob flour
- Chickpea flour, carob flour and hazelnut flour

A Kitchen Aid Professional KPM5 mixer (Kitchen Aid, St. Joseph, MI, USA) was used in mixing the ingredients. Firstly, margarine and sugar were creamed for 3 min long with scraping down. After that, egg was added and mixed at speed level 5 for 1 min. Flour blends and baking powder were added, followed by mixing for 1 min at speed level 3, with scraping down every 30 s. Approximately 20 g cookie dough pieces were slightly flattened with the palm of the hand. Cookie dough was cut with a circular cookie cutter (inside diameter 5 cm). Dough pieces were weighed and immediately transferred to a convection oven (Senox, Turkey) and baked at 175^{o}C for 10 min on a stamped steel baking tray with baking paper. The cookies were then allowed to cool at room temperature and subjected to further analysis. Gluten-free cookie production steps are shown in Figure 3.1.

As seen in Tables 3.1. and 3.2., 18 types of cookies were prepared by applying 18 different formulations. Cookie formulation design that contains 3 different flours was done by using Mixture Design Analysis.

Figure 3.1. Different steps of cookie preparation

Table 3.1. Cookie formulations containing only chickpea flour and combinations of chickpea + hazelnut and chickpea + carob flour

	Formulation Number								
Ingredients (g)	1	2	3	4	5	6	7	8	9
Chickpea Flour	90	45	60	75	30	45	60	75	30
Carob Flour	0	0	0	0	0	45	30	15	60
Hazelnut Flour	0	45	30	15	0	0	0	0	0
Corn Starch	10	10	10	10	10	10	10	10	10
Margarine	60	60	60	60	60	60	60	60	60
Sugar	40	40	40	40	40	40	40	40	40
Egg	60	60	60	60	60	60	60	60	60
Baking Powder	10	10	10	10	10	10	10	10	10

Table 3.2. Cookie formulations containing combinations of chickpea + hazelnut + carob flours set up according to a mixture design

	Formulation Number								
Ingredients (g)	10	11	12	13	14	15	16	17	18
Chickpea Flour	60	37.5	37.5	15	15	15	30	30	30
Carob Flour	15	37.5	15	60	37.5	15	30	30	30
Hazelnut Flour	15	15	37.5	15	37.5	60	30	30	30
Corn Starch	10	10	10	10	10	10	10	10	10
Margarine	60	60	60	60	60	60	60	60	60
Sugar	40	40	40	40	40	40	40	40	40
Egg	60	60	60	60	60	60	60	60	60
Baking Powder	10	10	10	10	10	10	10	10	10

3.2.3. Dough Properties

Experimental methods related to dough properties were mentioned.

3.2.3.1. Rheological Properties

Dough rheology was analyzed with back extrusion technique using a texture analyzer (model TA-XT2i, Stable Microsystems, U.K) with a 25-mm cylinder probe (P/25), while parameters were set at: pre-test speed 2 mm/s, test speed 3 mm/s, post-test speed 10 mm/s and trigger force 50 g. A standard size back-extrusion cylindrical container (50 mm-diameter, capacity of 115 g) and a backward extrusion rig (model A/BE) were used. The container was filled with ~50 g of cookie dough. Probe penetrated to a depth of 20 mm and then returned to starting position. Measurement parameters were chosen according to values given in the database of the equipment with slight modifications. Firmness (N), consistency (N.sec), viscosity index (N.sec) and cohesiveness (N) values were obtained from a graph generated as a result of the analysis (Figure 3.2).

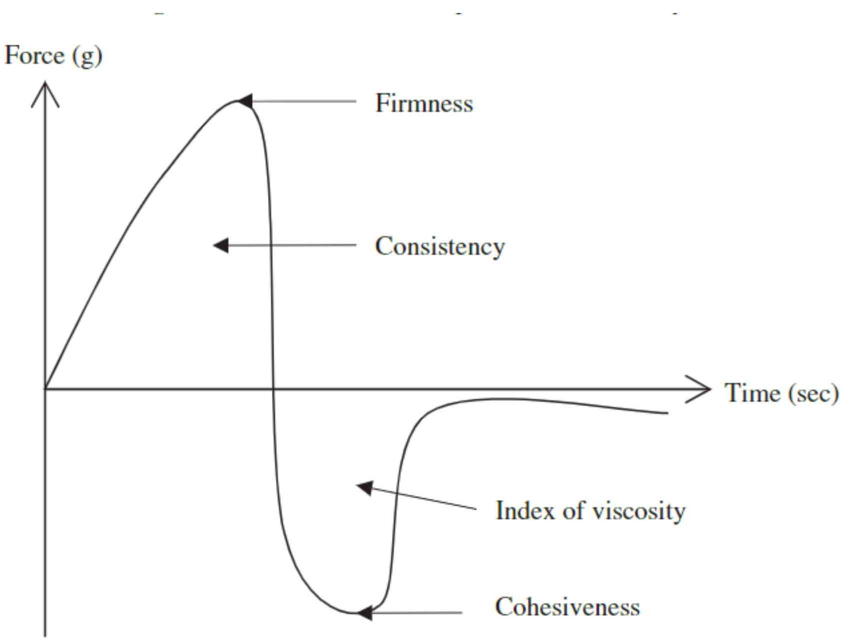

Figure 3.2. Example of time vs force curve of cookie dough textural properties using the back extrusion method (Source: Nasaruddin et al., 2012)

3.2.3.2. Fourier Transform Infrared (FTIR) Spectroscopy Analysis of Doughs

All infrared spectra of dough samples were collected between the range of 4000-650 cm^{-1} wavenumber by Perkin Elmer Spectrum 100 FTIR spectrometer (Perkin Elmer Inc., Wellesley, MA). FTIR spectra were obtained with attenuated total reflectance (ATR) accessory of FTIR spectrometer (Perkin-Elmer Spectrum 100, USA). Doughs were placed on ZnSe crystal and 96 scans were taken at 4 cm^{-1} resolution. Air spectra was obtained as background. In between each run, crystal was cleaned with hexane, ethanol and deionized water. Measurements were repeated two times.

3.2.4. Cookie Properties

Experimental methods related to flour properties were mentioned.

3.2.4.1 Moisture Content

Moisture content was determined according to AOAC method, 925.05 with slight modifications (Anonymous.1990). 6-9 grams of cookie samples were weighed and transferred into dried petri dishes. Petri dishes that contained cookie samples were put in a laboratory oven (Binder, ED53, Tuttlingen, Germany). Drying process took place at 105 °C for 2 hours. When the drying process was finished, petri dishes were removed and transferred into a desiccator until their weights do not change (approximately 30-60 min). Lastly, petri dishes with cookie samples were weighed by using the laboratory scale. Moisture loss in percentage was determined by the following formula (3.5)

$$\%\text{Moisture}=\frac{\text{Moisture Loss in grams}}{\text{Original Weight of flour}}\times 100 \qquad (3.5)$$

3.2.4.2. Baking Weight Loss (BWL) of Cookies

Baking weight loss (BWL) was determined by measuring the cookie weight before and after baking (Šarić et al., 2018). BWL was calculated from the subtraction of initial weight from the final weight and dividing this result to initial weight.

3.2.4.3. Size

Diameter and the height of ten cookies were determined individually with a digital caliper. Spread factor of the cookies were calculated by dividing the diameter of the baked cookie (D) by the height of the cookie (H).

3.2.4.4. Textural Properties

Textural properties of cookies were determined by using a texture analyzer (model TA-XT2i, Stable Microsystems, U.K). Hardness value was obtained via a 3-point bending test using a 3-point bending rig, trigger force of 5 g, and load cell of 5 kg. Also, the pre-test speed of 1.5 mm/s, test speed of 2.0 mm/s, post-test speed of 10 mm/s, and distance of 10 mm were used as measurement parameters, and the distance between the two bottom supports was adjusted to 50 mm. The peak value of force was recorded as hardness when the cookies were broken into two pieces (Chakraborty, Singh, Kumbhar, & Singh, 2009).

3.2.4.5. Color Analysis

Surface color of the cookies was measured by using a colorimeter (CR-400 Konica Minolta, Tokyo, Japan) and D65 illuminant. Color values were measured at 3 different points of each of the four cookies.

3.2.4.6. Sensory Analysis

For the sensory analysis, 40 people (average age: 28.86) evaluated 3 types of cookies that were chosen according to visual and handling properties. Panelists evaluated the color, flavor, texture, taste and overall acceptability in 1-7 scale. The sensory study was approved by Izmir Institute of Technology Scientific Research and Publication Ethics Committee (Number: 19.09.2022-E.96273).

3.2.4.7. *In Vitro* Starch Digestibility

The nutritionally significant starch components in gluten-free cookies were determined according to Englyst et al. (2000). Samples of the gluten-free cookies were mashed in a ceramic mortar. White bread was used as positive control during the analysis. These "as eaten" samples were weighed 0.25 g, and they contained 500–600 mg of starch before being treated for 30 min. at 37°C with a pepsin (Sigma EC 3.4.23.1)-guar gum (Sigma EC 232-536-8) mixture. Five glass balls and a 5 mL solution of 0.25 M sodium acetate buffer were then added. The tubes were incubated at 37 °C in a shaker incubator after the addition of a 5 mL enzyme combination containing pancreatin (Sigma EC 232-468-9), amyloglucosidase (Sigma EC 3.2.1.3), and invertase (Sigma EC 232-615-7). 0.1 mL samples were collected after 20 and 120 minutes, to determine the amounts of quickly digestible starch (RDS) and slowly digestible starch (SDS), respectively. Denaturation of the samples was performed for 5 min at 95^{o}C in a thermal heater after digestion. For free-sugar analysis, the same amount of the samples was weighted. Then, 1 M sodium acetate (pH 4.5) (0.25 mL) and distilled water (10 mL) were added to the sample tube. Tubes were placed into a water bath at 90^{o}C for 30 minutes. Then, tubes were removed from the water bath, and cooled to 37^{o}C and 0.2 mL invertase were added into each sample. Tubes again transferred to the water bath at 37^{o}C for 30 minutes. After digestion, for the denaturation of the samples, tubes were placed into a thermal heater at 95^{o}C for 5 minutes. For the starch fraction determination step, 50 µL of each sample was placed into 96 well-plate at appropriate dilutions. 100 µL glucose oxidase/ peroxidase reagent containing o-Dianisidine (GAGO20, Sigma was added and incubated at 37^{o}C for 30 minutes. After the incubation, 100 µL of 6 M H_2SO_4 was added into each well then, the absorbances of the samples were measured at 540 nm (37^{o}C)

3.3. Statistical Analysis

Analysis of variance (ANOVA) was used to determine the differences (Minitab Inc., Coventry, UK) in measurement parameters of the cookies containing dual composite flours. Tukey’s comparison test at 95% confidence interval was used for pairwise comparisons. A simple lattice mixture design was applied to three independent numeric factors, which are CPF (chickpea flour) (X1: 15-60%, flour basis, CF (carob flour) (X2: 15-60%, flour basis) and HF (hazelnut flour) (X3: 15- 60%, flour basis), was constructed. The lower (-1) and upper (1) levels were chosen according to the results of preliminary cookie making trials. The suitability of the model was evaluated by considering R^2, adjusted-R^2, p-value and lack of fit (LOF) of the model. Insignificant components were removed from the model to make it fit, and the resulting reduced models were used to calculate the presented responses for the best formulations. Minitab 19 software (Minitab Inc., Coventry, UK) was used for the construction of the experimental design and statistical evaluation of the data.

The spectroscopic profiles of all cookie doughs including both single, double and triple flours were evaluated with principal component analysis (PCA) which is an unsupervised chemometric analysis method. PCA was also applied to the results of the technological properties (rheological parameters, baking weight loss (BWL%), hardness, moisture, spread factor and color properties) of all gluten free cookies in order to investigate the differentiation of cookies. PCA models were built, and score and loading plots were created by using SIMCA 14.0 software (Sartorius, Goettingen, Germany). Score plots indicate the placement of the observations with respect to principal components (PCs), and loading plots reflect the original variants on a pair of PCs.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Chemical Compositions

The chemical compositions of the wheat, carob, hazelnut (with testa), pre-cooked and raw chickpea flour, and corn starch are given in Table 3.1. Corn starch and flours other than wheat and raw chickpea flour were used in cookie formulations which will be explained in the next chapter. Wheat and raw chickpea flours were added to the list for comparison purpose. According to the table, corn starch has the highest moisture content (8.48 g/100g) among the others and hazelnut flour has the lowest (1.06 g/100g). Comparing the two types of chickpea flour, pre-cooked chickpea flour has a significantly lower moisture content (3.31 g/100g) than raw chickpea flour (4.69 g/100g). Considering that wet heat treatment is applied during the cooking process, this is an expected result. During the heat treatment of chickpeas in water, starch is gelatinized, and this causes the entrapment of water in a gel matrix. Wheat flour has almost two times higher moisture content than pre-cooked chickpea flour, and its moisture content is much higher than carob and hazelnut flours. The moisture content of the flour directly affects the handling properties of the flour while producing bakery products.

According to Hemeda et al. (2010), dough consisting of chickpea flour and wheat flour had a lower moisture content than dough made with wheat flour alone. Quite a higher moisture content (10 %) of chickpea flour was reported compared to our results in a literature study (Wani et al., 2014). The differences in the chemical compositions of chickpea flours might be related to the variations in genetics, varieties, and growth settings (such as their geographic location and growing season) of chickpeas as the raw material. As far as the hazelnut flour is concerned, the moisture content of partially defatted hazelnut flour was found as 2.90 ± 0.06 (g/100g sample) which was a little bit higher than our result (Yagcı & Gogus, 2009). Hazelnut flour in our study has testa in it and it is not defatted. The moisture content of carob flour used in this study was higher than the studies in the literature (Rosa et al., 2015; Caglar et al., 2012).

Among all the flours used in this study, chickpea flours have the highest protein content. Raw chickpea flour (22.05 g/100g) has a slightly higher protein content than the pre-cooked (21.93 g/100g) one. Wheat flour was following them with 10.70 g/100g protein content which is about half of the chickpea flours.

Table 4.1. Chemical properties of flours

Properties	Wheat (WF)	Pre-Cooked Chickpea (N-CPF)	Carob (N-CF)	Hazelnut (I-HF)	Raw Chickpea (I-CPF)	Corn Starch (I-COS)
Moisture (g/100 g)	7.37 ± 0.50^{a}	3.31 ± 0.20^{c}	1.82 ± 0.26^{d}	1.06 ± 0.18^{d}	4.69 ± 0.12^{b}	8.48 ± 0.86^{a}
Protein (g/100g)	10.70 ± 0.34^{b}	21.93 ± 2.02^{a}	3.66 ± 0.75^{bc}	7.42 ± 4.63^{bc}	22.05 ± 2.14^{a}	0.60 ± 0.00^{c}
Fat (g/100g)	2.71 ± 0.17^{d}	10.06 ± 1.27^{b}	1.47 ± 1.11^{d}	69.34 ± 0.86^{a}	6.38 ± 1.19^{c}	0.38 ± 0.00^{d}
Carbohydrate (g/100g)	78.60	62.82	89.69	-	63.8	90.46
Total Ash (g/100 g)	0.62 ± 0.03^{c}	1.88 ± 0.10^{b}	3.36± 1.12^{a}	1.98 ± 0.04^{b}	3.08 ± 0.05^{a}	0.08 ± 0.02^{d}
Crude Fiber (g/100 g)	0.06 ± 0.01^{d}	1.96 ± 0.06^{c}	0.16 ± 0.09^{d}	22.59 ± 0.22^{a}	3.47 ± 0.19^{b}	0.05 ± 0.00^{d}
TPC (mg GAE/g flour)	0.35 ± 0.13^{b}	0.38 ± 0.05^{b}	24.14 ± 5.72^{b}	1.83 ± 0.00^{b}	0.54 ± 0.08^{b}	0.11 ± 0.1^{b}

(Values are mean ± SD. Means. Means having different letters in the same row are significantly different ($p < 0.05$).)

Corn starch has the lowest protein content among the others. According to Khan et al. (1995), the protein content of wheat flour ranges between 9.3-14.3 %, and chickpea flour varies between 24.4-25.4 %. Our results also coincide with the ranges given in this study. Lysine, leucine, aspartic acid, glutamic acid, and arginine are the prevalent amino acids in legume proteins. The type, the environment, the location, the growing season of the plant, and the heat treatment applied during flour production all have an impact on the protein content of the flour. Hazelnut and carob flours have lower protein contents compared to chickpea flour. The protein content of carob flour which was found as 3.66 g/100g is similar to the value reported as 4.62 g/100g in another study (Román et al., 2017). The small difference between them may be related to variety of carob or the process conditions during flour production. According to a study in literature, the protein content of raw hazelnut was found as 15.35 g/100g; therefore, hazelnut flour can be considered a good source of protein (Turan et al., 2015). Our results were lower than the literature findings (Ozdemir & Akinci, 2004; Kirbaslar & Erkmen, 2003).

The fat contents of different chickpea flours were found to be significantly different from each other. Raw chickpea flour has lower fat content with a value of 6.38 g/100g than the pre-cooked one which had 10.06g/100 g. Hazelnut flour has a fat content (69.34 g/100g) that is almost seven times higher than pre-cooked chickpea flour and also has the highest fat content among the others. The oil content of raw hazelnuts was reported as in the range of 57.65–69.4 % which is consistent with the results of the current study (Turan et al., 2015). Carob flour has the lowest fat content (1.47 g/100g) compared with the other flours; however, corn starch has the lowest fat content if all kinds are considered. According to a study in literature, the fat content of raw chickpea flour is also lower than the cooked one and the values match with the current results (de Almeida Costa et al., 2006). In another study, it was determined that chickpea flour obtained from raw seeds had also lower fat content than chickpea flour obtained from roasted and pressure-cooked chickpea seeds (Daur et al., 2008). Thermal treatment significantly reduces anti-nutritional elements that are present in legumes while enhancing the availability of other nutrients (Domene & Oliveira, 1993).

Carob flour has a very low-fat content since the carob fruit has a very low level of fat itself. It was reported that carob pod samples from eastern parts of Italy had very low-fat contents ranging between 0.4-0.8 % which matches with our findings (Ozcan et al., 2007). In the same study, it was also determined that Turkish carob samples had lower oil and higher sugar contents compared to Sicilian carob samples.

Carob flour stands out with its high carbohydrate content (89.69 g/100g), and it has even higher carbohydrate content than wheat flour (78.60 g/100g). Depending on the type of roaster being used and the desired end result, such as lightly, medium, or strongly roasted carob powder, different time-temperature combinations can be employed to roast the kibbled carob. Important chemical processes including sugar caramelization and the Maillard reaction occur during the roasting of carob powder, leading to noticeable changes in the final product's quality (Sahin et al., 2009). The carbohydrate content of carob flour which is almost the same amount as our result (89.69 g/100g) was determined as 88.88 g/100g in a literature study (Roman et al., 2017). The carbohydrate contents were determined as 63.8 and 62.82 g/100 g for raw and pre-cooked chickpeas flours, respectively. Raw one has a little bit higher carbohydrate content than pre-cooked one. This may be related to the cooking process that is applied to chickpea seeds before obtaining the flour. Chickpeas play a significant role in the diets of those who cannot afford animal proteins or who want to follow a vegetarian diet. The dry seed mass of chickpeas, which makes up around 80% of the total, is a rich source of both protein and carbohydrates (Chibbar et al., 2010). The main source of carbon storage in pulse seeds is starch, which corresponds to approximately 41 to 50% of the total carbohydrates. There are two main types of chickpeas as Desi and Kabuli and in comparison, to Desi types, Kabuli types contain more soluble sugars (sucrose, glucose, and fructose) (Singh et al., 1991). According to reports, chickpea seeds contain around 525 g of total starch per kilogram of dry mass, and roughly 35% of the starch is resistant starch while the remaining 65% is available starch (Miao et al., 2009). Compared to chickpeas, cereals like wheat have more starch; however, the amylose content of chickpea seeds is greater (30–40 vs. 25% in wheat) (Jukanti et al., 2012). Additionally, it was observed that the amount of carbohydrates in bread made with processed chickpea flours decreased significantly with increased amount of cooked chickpea flour (Ouazib et al., 2016). The availability of the carbohydrates in chickpea flour is lower than that of products made with wheat flour, and the glucose content after eating a meal made with chickpea flour is lower than that of products made with wheat flour. However, when a portion of wheat flour was substituted with chickpea flour in a study on a group of adults, there was little difference in the reduction of the glycemic index (GI). Moreover, the bread that included chickpea flour had a lower GI than bread made with wheat flour (Rachwa-Rosiak et al., 2015). Due to its high nutritional protein and fiber contents and low carbohydrate composition, hazelnut flour can successfully substitute wheat flour. The most often used functional recipes based on hazelnut flour include biscuits, muffins, and cookies, in which the hazelnut flour component can be substituted for different ratios (Poșta et al., 2022). The carbohydrate content of soft wheat flour was found as 83.60 g/100g in a study (David et al., 2015) and 74.22 g/100g carbohydrate content was reported in another one (Ahmed et al., 2012). Our result was calculated as 78.60 g/100g which is very close to the literature findings.

Higher ash content means that the flour is often less refined and has more endosperm and fine bran particles. Ash is, therefore, a commonly used indicator of the quality of the flour and the rate of its extraction during milling. Nutritionally speaking, it is preferable for the flour's ash content to rise along with its levels of dietary fiber, vitamins, and non-gluten proteins (Czaja et al., 2020). Carob flour has the highest ash content compared to the other types of flours with a value of 3.36 g/100g. Corn starch has the lowest ash content which is understandable due to its low nutritional content compared to the gluten-free flours. The ash content of pre-cooked chickpea and hazelnut flours were not significantly different and had similar results. Different types of chickpea flours have significantly different ash contents, raw one has higher ash content than pre-cooked one, and this can be attributed to the cooking step during flour production, which can cause the leaching of some compounds from chickpeas. This result is also supported by another study (Alajaji & El-Adawy, 2006), which reported a decrease in the ash contents of chickpea flours with cooking treatment. The findings in the literature are also in line with our result with the range of 3.15-3.72 g/100 g ash content (Almeida Costa et al., 2006; Alajaji & El-Adawy, 2006). It was determined that ash content decreased (-13 and -38%, respectively) for bread baked using toasted and cooked chickpea flours compared to bread made with raw chickpea flour in a literature study (Ouazib et al., 2016). When compared to bread made with raw flour, bread made with germinated chickpea flour had a slight reduction in the amount of ash, which was likely brought on by the leaching of minerals during soaking and cooking. Similar trend in the reduction of ash content brought on by germination and cooking in chickpea flour was also observed in two other studies (Mittal et al., 2012; Baik and Han 2012), According to a study in literature, partially defatted hazelnut flour has an ash content of 6.61 g/ 100 g, and this value is almost six times higher than our result (Yagcı & Gogus, 2009). In literature, the ash content of Turkish carob flour was reported as 2.89 g/100g which is very close to our result (Petkova et al., 2017).

Hazelnut flour has the highest crude fiber content (22.59 g/100g) among the others analyzed and is significantly different from the other flours and corn starch with a 22.59 g/100g crude fiber content. Wheat flour, carob flour, and corn starch have similar crude fiber contents which are not significantly different from each other’s. Moreover, raw chickpea flour has higher fiber content than pre-cooked chickpea flour. Dietary fiber is a part of the plants that are digested completely or partially in the large intestine but cannot be digested in the small intestine of humans (Meister, 1996). The testa of the hazelnut contains dietary fiber as well as certain phenolic compounds with antioxidant properties (Yurttas, Schafer, & Warthesen, 2000). According to literature, dietary fiber has an impact on the rheological characteristics of dough and bread quality (Anil, 2007). Moreover, the fiber content of wheat flour was found 2.7 g/100g, while the fiber content of hazelnut testa was 64.72 g/100g according to the aforementioned study. These findings support the recommendation of adding 5–10% of hazelnut testa to bread dough as a source of dietary fiber. Therefore, the testa fiber from hazelnuts could be useful for preparing bread. In another study, it was found that hazelnuts had a total dietary fiber level of 12.88 g/100 g and 2.21 g/100 g of this was soluble fiber (Alasalvar et al., 2003). The dietary fiber contents of six New Zealand-grown hazelnut cultivars were also investigated in a different study (Savage and McNeil, 1998). The findings (on a dry weight basis) varied from 9.8 to 13.2 g/100g. Müller et al. (2020) worked on 15 different hazelnut varieties and found dietary fiber content ranged from 13.4 to 22.2 g/100g for these varieties. “Webb’s Prize Cob” variety had the highest content of 22.2 g/100 g which is very close to our results.

The crude fiber content of chickpea flour was affected by the treatment that was applied to chickpea seeds (Mittal et al., 2012). Except for germination, in which it was reduced by 60.30%, all treatments considerably raised the crude fiber in chickpeas by

30% to 32%. The development of a protein-fiber complex was associated with this rise. However, crude fiber content was found lower than the raw one in our study. This may be related to the variety or treatment conditions of chickpea seeds.

Based on the findings of a study, it can be concluded that adding legumes, like peas and carob, to puffed snacks may increase their nutritional value by boosting their levels of protein and dietary fiber, particularly when compared to snacks made only with rice (Arribas et al., 2017). According to USDA dietary recommendations, the examined formula may be regarded as a healthier choice as gluten-free snack-like products with a balanced nutritional composition and an excellent source of dietary fiber, particularly the mixtures with larger amounts of pea (40%) and carob (10%).

Legumes' antioxidant capacity has a strong connection with their total phenolic content (TPC). TPC varies widely across various legumes and is influenced by the place of cultivation as well as the source of the bean seeds (Amarowicz & Pegg, 2008). It was reported that legumes with darker seeds have more TPC than those with lighter colors which is supportive for our results since the carob flour has the highest TPC value (24.14 mf GAE/g). TPC of the other flours were not significantly different from each other, and its range varied between 0.11-1.83 mg GAE/g flour. Lentils contain more TPC (4.86-9.60 mg GAE/g) than soybeans (1.57-5.57 mg GAE/g), chickpeas (0.98 mg GAE/g), yellow peas (0.85-1.14 mg GAE/g), and green peas (0.65-0.99 mg GAE/g) according to a study in literature (Xu et al., 2007), TPC differs greatly among popular bean types (0.57-6.99 mg GAE/g), with black turtle beans having the highest concentration and navy beans having the lowest (Xu et al., 2007).

4.1.1. Microstructure Analysis

Scanning electron microscopy (SEM) has shown to be a helpful technology for examining the microstructures of cereal grains, wheat flour, and related products. The textural abnormalities in seeds that have reduced the commercial value of legumes have been the main focus of research on the microstructure of legume seeds. The increasing cooking time, textural defects, or hard-shell legume seed problems present challenges to the consumption of legumes. In the current study, SEM pictures of all flours were obtained, and Figure 3.1.a and 3.1.b. are the micrographs of theses flours. Figure 3.1.a is the micrographs of the dry wheat, pre-cooked chickpea and raw chickpea flours., and micrographs of dry carob, hazelnut flour and corn starch can be seen in Figure 3.1.b. Starch granules can be observed in these graphs. According to the graphs, pre-cooked flour has larger granules due to the absorption of water and gelatinization. Moreover, wheat flour starch granules look larger than raw chickpea flour. Hazelnut flour contains very low or none starch, so does not have granule images. Also, carob granules have more of a rectangular shape and corn starch granules can be seen very clearly.

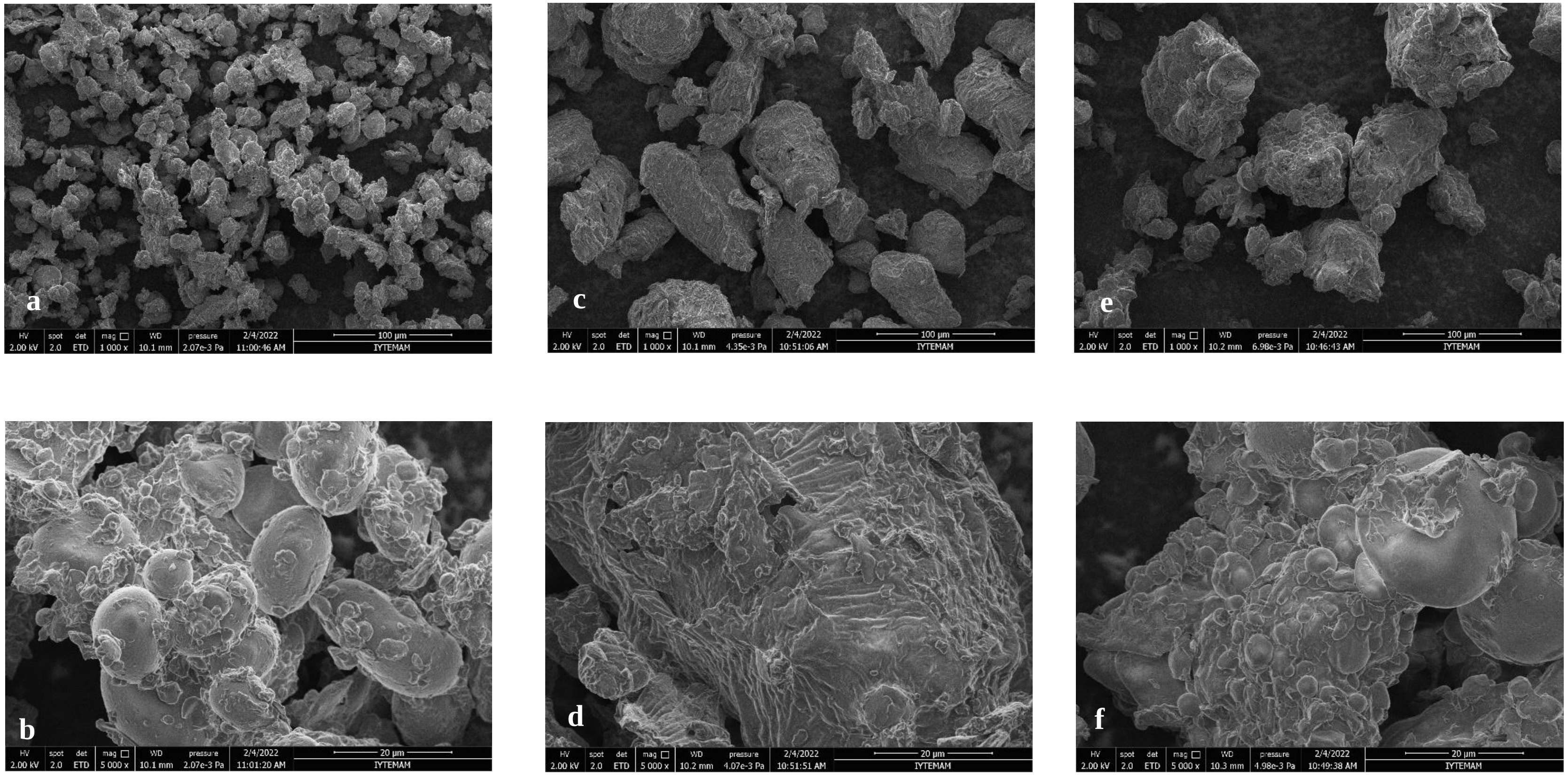

Figure 4.1. SEM Images of raw chickpea, pre-cooked chickpea and wheat flours with 1000x and 5000x magnitudes (a. Raw chickpea flour with 1000x magnitude, b. Raw chickpea flour with 5000x magnitude, c. Pre-cooked chickpea flour with 1000x mag, d. Pre-cooked chickpea flour with 5000x, e. Wheat flour with 1000x magnitude, f. Wheat flour with 5000x magnitude)

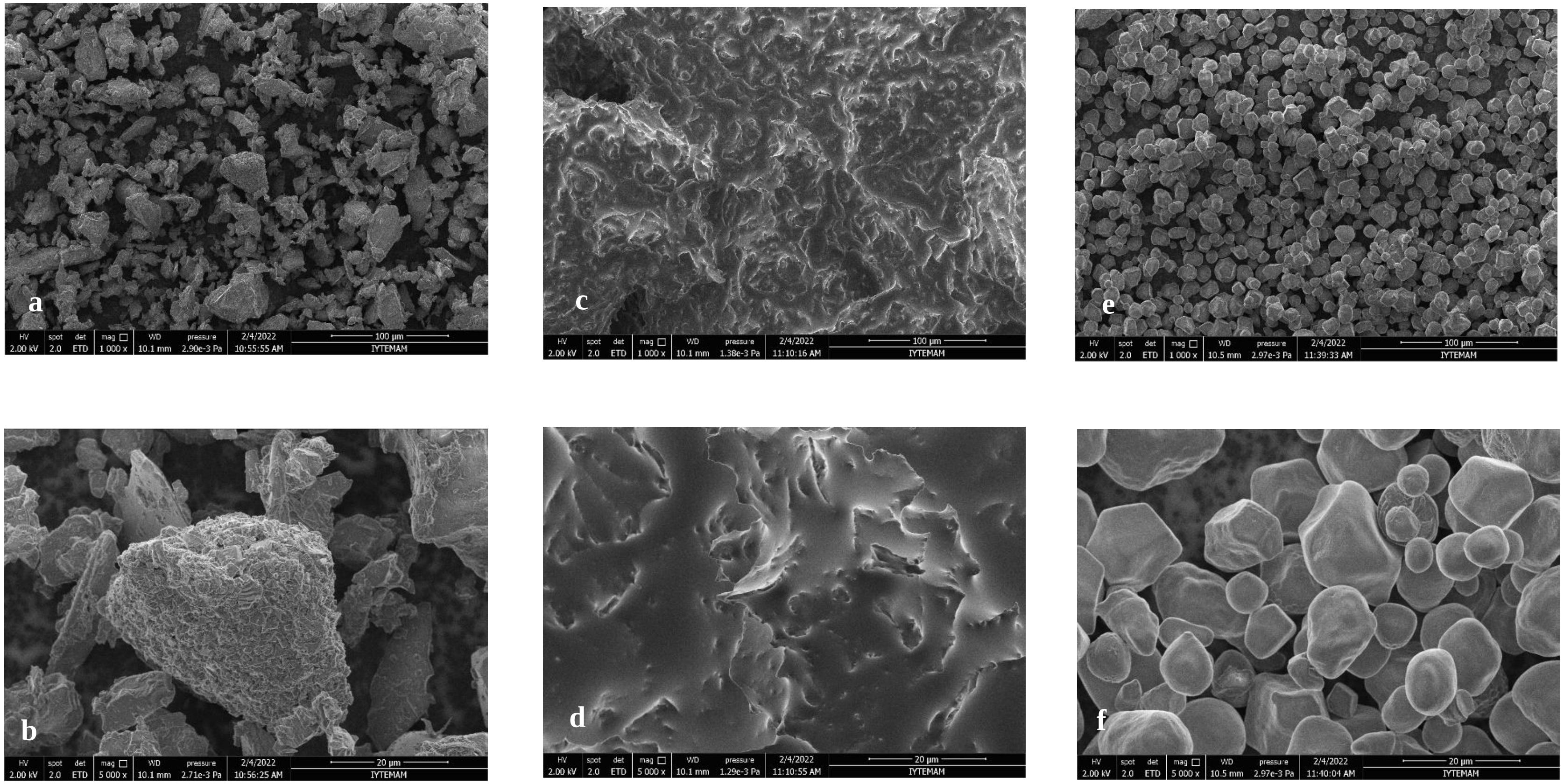

Figure 4.2. SEM Images of carob, hazelnut flours and corn starch with 1000x and 5000x magnitudes (a. Carob with 1000x magnitude, b. Carob flour with 5000x magnitude, c. Hazelnut flour with 1000x mag, d. Hazelnut flour with 5000x, e. Corn starch with 1000x magnitude, f. Corn starch with 5000x magnitude)

4.1.2. Fourier Transform Infrared (FTIR) Spectrometric Analysis

A variety of functional groups may be detected using the quick, non-destructive, and time-saving FTIR technique, which is also sensitive to changes in molecular structures. FTIR spectroscopy provides information based on the chemical composition and physical condition of the entire sample (Cocchi et al., 2004). Numerous parameters relating to the quality of flour have been measured using FTIR spectroscopy, which is a quick, precise, and nondestructive method.

FTIR spectra of all flours and corn starch are shown in Figure 4.3. Peaks at 1640 cm^{-1} and 3,300 cm^{-1} are attributed to water (Manley et al., 2002). The functional groups -H and -OH serve as the basis for absorption in these wavenumbers. Because of its -OH stretching and -H bending vibrations, water has a strong infrared absorption band. However, other OH-containing substances like alcohols, phenols, and hydroperoxides have also absorption in these regions (Dong et al. 2000). Amide I and amide II bands, two absorption bands that are crucial components of the protein, can be found at around 1700-1,600 cm^{-1} and 1570-1,550 cm^{-1}, respectively (Manley et al., 2002). Amide peaks for all the flours can be seen clearly in the spectra. Moreover, the peaks in the 3100−2800 cm^{-1} region are associated with C−H stretching, and the 1800−800 cm^{-1} region refers with CO and C−O−C stretching and also C−H bending. Since wheat and carob flours have low fat contents peaks associated with fat absorption are not significant for these flours. Since amylose and amylopectin are the two main components of starch, these vibrational modes are where the spectra of starch bands are primarily derived. The fingerprint region between 800 and 1,500 cm^{-1}, the C-H stretch region between 2,800 and 3,000 cm^{-1}, and lastly the O-H stretch zone between 3,000 and 3,600 cm^{-1}, belong to absorptions due to starch. Carob flour does not have significant peaks in the 900-500 cm^{-1} region as opposed to corn starch. This flour is richer in terms of sugars rather than starch.

To identify variations in peaks linked to chemical bonding, FTIR spectra of the flours were visually analyzed in Figure 4.3. Even though there were differences in transmittance values that can be attributed to compositional differences, the spectra of raw and pre-cooked chickpeas flours are quite similar in terms of the wavenumber ranges of the peaks. However, pre-cooked flour spectra had differences in some peaks compared to raw flour in the 1500–1400 cm^{-1} and 1100–1000 cm^{-1} regions of the peaks and these differences can be associated with the gelatinization of starch.

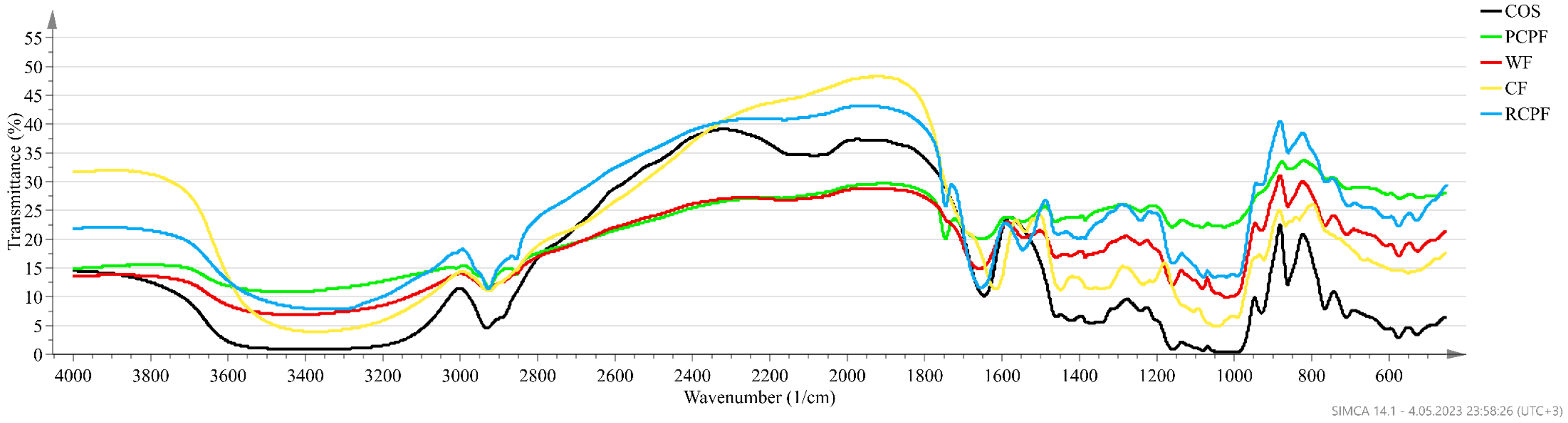

Figure 4.3. FTIR spectra of flour (COS: Corn starch, PCPF: Pre-cooked chickpea flour, WF: Wheat flour, CF: Carob Flour, RCPF: Raw chickpea flour)

Table 4.2. Physical properties of flours (Values are mean ± SD. Means. Means having different letters are significantly different ($p < 0.05$).)

Properties	Wheat (WF)	Pre-Cooked Chickpea (N-CPF)	Carob (N-CF)	Hazelnut (I-HF)	Raw Chickpea (I-CPF)	Corn Starch (I-COS)
Bulk Density (g/ml)	0.73 ± 0.03^{ab}	0.69 ± 0.00^{abc}	0.78 ± 0.04^{a}	0.48 ± 0.00^{d}	0.61 ± 0.00^{c}	0.68 ± 0.03^{bc}
Water Retention Capacity (%)	86.82 ± 1.50^{c}	300.76 ± 12.8^{a}	131.85 ± 6.30^{b}	-	137.26 ± 5.24^{b}	74.80 ± 3.01^{c}
Oil Absorption Capacity (g/g)	1.05 ± 0.00^{bc}	1.37 ± 0.13^{ab}	1.13 ± 0.10^{bc}	1.69 ± 0.21^{a}	0.90 ± 0.02^{bc}	0.84 ± 0.14^{c}
Emulsion Activity (%)	48.98 ± 0.00^{a}	51.00 ± 1.41^{a}	50.53 ± 3.68^{a}	54.01 ± 4.23^{a}	46.99 ± 2.81^{a}	50.50 ± 0.71^{a}
Emulsion Stability (%)	96.88 ± 1.48^{a}	95.16 ± 4.02^{a}	98.53 ± 2.08^{a}	91.73 ± 6.03^{a}	96.80 ± 1.38^{a}	96.52 ± 0.73^{a}
Foaming Capacity (%)	18.89 ± 4.71^{a}	17.29 ± 3.83^{a}	12.15 ± 5.15^{b}	12.00 ± 0.00^{b}	16.29 ± 2.82^{a}	-
Foaming Stability (%)	11.11 ± 0.00^{a}	8.16 ± 0.23^{ab}	6.87 ± 0.70^{ab}	2.00 ± 2.83^{b}	10.17 ± 2.35^{a}	-
L*	95.84 ± 3.84^{ab}	89.64 ± 0.01^{b}	58.68 ± 1.38^{d}	75.89 ± 0.58^{c}	91.13 ± 0.42^{ab}	98.22 ± 2.95^{a}
a*	-0.03 ± 0.00^{c}	0.91 ± 0.06^{c}	12.29 ± 0.12^{a}	5.92 ± 0.05^{b}	-5.12 ± 0.91^{e}	-2.50 ± 0.01^{d}
b*	16.52 ± 1.20^{d}	31.77 ± 0.23^{a}	29.26 ± 0.56^{b}	30.27 ± 0.13^{ab}	24.73 ± 0.21^{c}	12.19 ± 0.54^{e}

4.2. Physical Properties

Physical properties of the flours and starch are provided in Table 3.2. Bulk density of flours varied between 0.48 to 0.78 g/mL. Hazelnut flour has the lowest bulk density and is significantly different from the other types of flours; on the other hand, carob flour has the highest value. Bulk densities of pre-cooked and raw chickpea flour are very close to each other; however, pre-cooked one has a little higher than the raw chickpea flour. According to Kaur & Singh (2005), bulk density of desi chickpea ranged between 0.536 to 0.562 g/cm^3 and it was determined as 0.571 g/cm^3 for Kabuli chickpea. In the current study, bulk densities of raw (0.61 g/mL) and pre-cooked chickpea (0.69g/mL) flours are higher than the previously mentioned study. The bulk density of seed flours is primarily influenced by two variables: particle size and packing density. When lipids are present, particles may pack tighter because the triglycerides may function as adhesives in the agglomeration of protein and carbohydrate molecules (either individually or jointly), allowing for higher bulk densities (Chandra et al., 2014; Amandikwa et al., 2015). Although hazelnut flour has high fat content its bulk density is not that high, and this may be related with relatively large particle size of this flour.

Water retention capacity is an important techno-functional property for baking applications. Pre-cooked chickpea flour has the highest value among the others with 300.76 %. All flours have higher water retention capacity compared to wheat flour. Carob flour (131.85%) and raw chickpea flour (137.26%) are not significantly different from each other. Corn starch has the lowest water retention capacity (74.80%) and is significantly different from the other flours except wheat flour. According to Tagodoe & Nip (2007), the quantity and kind of hydrophilic components may affect this variation between the flours. According to a study, chickpea flour samples had water absorption capacity range from 1.66 to 2.44 g/g, and this value significantly increased with germination time (Sreerama et al., 2012). The rise in polar amino acid residues during germination was the cause of the increase in water absorption capacity, which significantly increases the attraction of germinated chickpea flour with water molecules. In our case, cooking treatment also increased the water retention capacity of the chickpea flour, and the pre-cooked chickpea flour has about 2.2 times higher water retention capacity than raw flour. Water holding capacity (WHC) is crucial from an industrial perspective. WHC varied between 73.89 and 107.96 g/100 g of flours, and Kabuli cultivar had the lowest value (Ghribi et al., 2015). The capacity to store water differs significantly between the two varieties. The existence of various hydrophilic carbohydrates and various protein structures may be the cause of the variable WHC. Additionally, the WHC of chickpea powders was low in comparison to the levels found in yellow pea seed flour, which typically swells to 3–4 times its original weight (Agboola et al., 2010). The presence of carbohydrates and the other substances that may prevent the proteins from swelling, dissociating, and unfolding could be the cause of the low WHC (Kinsella, 1979). Water retention capacity of hazelnut flour could not be determined most probably due to high fat content of this flour. Carob flour has about 52% higher water retention capacity than wheat flour. According to literature, because of the hydrophilicity and strong gelling abilities of the carob soluble fiber, carob flour blends shown very impressive technical capabilities. In comparison to wheat flour, these blends in particular absorbed more water (Turfani et al., 2017).

Oil absorption capacity (OAC) of the flours differs due to their type and varieties. Hazelnut flour has the highest oil absorption capacity (1.69 g/g). Wheat and two types of chickpea flours are not significantly different in terms of their oil absorption value. Corn starch has the lowest oil absorption capacity (0.84 g/g) among the others. For flavor retention and improved palatability, oil holding capacity (OHC) is critical. OHC ranged between 82.88 to 97.40 g per 100 g of analyzed flours in a study comparing the flours from desi and kabuli type of chickpeas from Tunisia (Ghribi et al., 2015). For Indian chickpeas, a higher OHC value of 105–124 g/100 g was reported in the literature (Sreerama et al., 2012). The existence of non-polar chains, which can interact with lipid hydrocarbon chains to produce hydrophobic interactions may be responsible for the variation in oil binding ability. Desi chickpea flours may be more suitable for use in recipes where fat retention is desired due to their increased fat absorption (Ghribi et al., 2015). For enhancing the mouthfeel and preserving the flavor of food items, the OAC of legume flour is important (Du et al., 2014). Capillary interaction, which is a part of the process for oil absorption, enables the absorption of oil to be retained. The primary factor in oil absorption is hydrophobic proteins (Du et al., 2014). The OACs of various legume flours are influenced by protein types, non-polar amino acid side chain ratios on the protein molecule surface, and particle sizes. More hydrophobic proteins exhibit superior lipid binding, indicating that non-polar amino acid side chains bind the paraffin chains of fats (Du et al., 2014). Oil absorption capacity of defatted raw hazelnut flour was determined as 1.11 g/g flour which was lower than our result (1.69 ± 0.21 g/g flour) (Turan et al., 2015). The difference may be related to defatting process. This finding points to the potential of hazelnut flour as a taste-stabilizing agent, a property for a high OAC system. Protein, which is made up of both hydrophilic and hydrophobic components, is the main chemical component controlling OAC. Higher OAC may be caused by partial protein denaturation and the exposure of highly hydrophobic proteins, which exhibit better binding to lipid hydrocarbon chains (Jitngarmkusol et al., 2008). OAC of carob flour was determined as 1.13 g/g. According to Caglar et al. (2012), OAC increased with the carob flour addition to tarhana samples.

Emulsion activity and stability values of all flours are not significantly different from each other statistically. Emulsion activity values vary between 46.99-54.01 % and emulsion stability values change between 91.73-98.53 %. Hazelnut flour has the highest emulsion activity among the other flours and raw chickpea flour has the lowest. According to a study in literature, the addition of carob flour to wheat flour improved foaming, water and oil absorption capabilities, and emulsifying activities of tarhana samples; nevertheless, it had a negative impact on foam stability. The tarhana having a high amount of carob flour had the most significant improvement in its ability to foam and emulsify (Caglar et al., 2012). According to Aguilar, Albanell, Mi˜narro, & Capellas, (2015), higher emulsion stability was observed in bread formulation due to the presence of chickpea protein compared to tiger nut flour. These properties of chickpea protein are critical in the production of chickpea-based bread because they provide the bread a high specific volume as well as boosting its nutritious qualities. Also, it was stated that the protein isolates of chickpea, fava bean, lentil, pea, lupin, and soy have exceptional emulsifying characteristics because of their capacity to adsorb at the surface of oil droplets, resulting in lower interfacial tension and prevention of coalescence (Karaca et al., 2011).

Wheat flour has the highest foaming capacity (18.89%) among all the flours. However, foaming capacity of the flours are not significantly different from each other. Corn starch did not show any foaming behavior. Pre-cooked chickpea flour has a slightly higher foaming capacity (17.29%) than raw chickpea flour (16.29%). Hazelnut and carob flours have very close foaming capacity results. Foaming stability was also investigated for all flours and corn starch. According to the results given in Table 3.2, wheat flour has the highest foaming stability (18.89%) and the hazelnut has the lowest (2%). Although it is not a statistically significant difference raw chickpea flour has higher foaming stability value (10.17%) than pre-cooked one (8.16%). This value for raw chickpea flour is very close to the one for wheat flour. The amount of interfacial area that a protein can form between air and continuous phase is referred to as the protein's foam capacity (Fennama 1996). A particle made up of numerous gas bubbles that have been trapped in a liquid or solid called foam. Thin liquid coatings wrap tiny air bubbles. Foam capacities of various flours including wheat and combinations of wheat, rice, green gram and potato flours were determined as in the range of 12.92 to 17.60% in a study (Chandra et al., 2014). In comparison to flour blends, wheat flour had a lower foam capacity value (12.92%). The term "foam stability" (FS) refers to a protein's capacity to withstand mechanical and gravitational stresses (Fennama, 1996). According to Table 3.2, the highest foaming stability was observed for wheat flour (11.11%). Raw chickpea flour and pre-cooked chickpea flour were followed by 10.17% and 8.16%, respectively, and they were not significantly different from each other. Hazelnut flour has the lowest foaming stability (2%) among the other flours and corn starch did not have any foaming behavior. Significant variations in the foaming abilities (FC) and foam stabilities (FS) of the flours produced from various chickpea cultivars were reported (Kaur & Singh, 2005). Flours from all chickpea cultivars produced relatively thick foams with low foam volumes but high foam stabilities. All chickpea flours were found to have concentration-dependent foaming ability. With an increase in solids content, the foaming ability of all flour samples gradually increased. Foam stability is an important property since the effectiveness of whipping agents depends on their capacity to sustain the whip for an extended period of time (Lin et al., 1974). All of the chickpea flours had excellent foam stability, and this suggests that the natural proteins in chickpea flour are highly surface-active and soluble in water (Kaur & Singh, 2005).

The tristimulus color measure of flour uses a numerical approach to assess a sample's lightness (L*) on a scale of 0 to 100 as well as its "chromaticity," or hue, on two scales, each ranging from -60 to +60 for green-red (a*) and blue-yellow (b*). Brighter colors are denoted by high L* values, while more yellow is denoted by high b* values. The color of the flour is an important factor that determines the color of the final product containing this flour, and the flour color is affected by the color of the raw material, particle size, and ash concentration (Gwirtz, 2020). According to the color parameters of the flours, wheat flour and corn starch have the highest L* value due to their bright white color. Raw chickpea flour has a higher L* value than pre-cooked chickpea flour, and this may be related to the cooking treatment applied to chickpea before the process. Carob flour has the lowest L* value due to its dark brown color, and it has also the highest a* value and was significantly different from the others. Moreover, hazelnut flour has the highest b* value which is very close to b* value of carob flour. Corn starch has the lowest b* value and wheat flour followed it.

4.3 Cookie Properties Prepared with Dual and Triple Legume and/or Nut Flours

Results of cookie properties were mentioned.

4.3.1. Cookies Prepared with Dual Flour Mixtures

In comparison to the other vegetable-based food products, legumes are noted for having a higher protein content. They are also high in fiber and bioactive substances such as enzyme inhibitors, lecithin, folates, and phenolic compounds. Consuming legumes benefits human health by preventing obesity, diabetes, cancer, and cardiovascular disorders (Ferreira et al., 2020). Despite the challenges with their usage and consumption, interest in the usage of legume flours in baked products has grown. One of these issues is related with the presence of anti-nutrients such as trypsin inhibitors, phytic acid, and other non-digestible oligosaccharides that cause digestive pain. Another issue with using chickpea flour in baked goods is the possibility of undesirable flavors which might make the finished items objectionable for some consumers. Conventional approaches usually include masking them with sugar, salt, acids, or fragrances (Torra et al., 2021). For this reason, hazelnut and carob flours were used to suppress the undesirable taste and odor created by chickpea flour in the current study.

The testa of the hazelnut contains dietary fiber as well as certain phenolic compounds having antioxidant properties (Anil, 2007; Taş & Gökmen, 2017). Due to their organoleptic properties, hazelnuts rank among the most vital raw ingredients for the baking and chocolate industries. Additionally, hazelnuts enhance the flavor and texture of baked goods, sweets, cereal, dairy, salads, entrées, sauces, and desserts (Turan et al., 2015).

Carob pods are processed as the flour that resembles cocoa and is then marketed as "carob cocoa." As a drink, milled flour is frequently mixed with hot or cold milk. Carob also has rich phenolic content and gallic acid is the most prevalent phenolic acid in the pods (Román et al., 2017). Carob pods are also a good source of K, Ca, and Mg (Loullis

& Pinakoulaki, 2017). Carob can be a good alternative due to its cacao-like flavor for masking the undesirable taste of chickpea flour.

In this study, double and triple composite flours were used in gluten-free cookie formulations. Double composite flours included chickpea-hazelnut flours and chickpea-carob flours combinations. Detailed explanation of flour amounts that were used in cookie formulations are given Table 4.1.1. Flour ratios were determined according to personal experiences while making cookies. Triple combinations have chickpea, hazelnut and carob flours and a mixture design was used in the formulations for this case (Table 4.2.1). Corn starch was used for all formulations in a fixed amount which was 10 % of dry material. Handling properties, stickiness, and softness of the dough were important properties affecting the decisions. Pictures of baked cookies are presented in Appendix.

Table 4.3. Dual composite flour ratios used in cookie formulations (% of dry material)

Sample	Pre-Cooked Chickpea	Carob	Hazelnut	Corn Starch
1	90	0	0	10
2	45	0	45	10
3	60	0	30	10
4	75	0	15	10
5	30	0	60	10
6	45	45	0	10
7	60	30	0	10
8	75	15	0	10
9	30	60	0	10

4.3.1.1. Rheological Properties of Cookie Doughs Prepared with Dual Flour Mixtures

Table 4.4. represents the measured rheological properties of cookie doughs for dual flour combinations. Firmness, consistency, viscosity index and cohesiveness were determined by using back extrusion method.

Table 4.4. Rheological properties of cookie doughs for dual flour combinations

Sample	Firmness (N)	Consistency (N.sec)	Cohesiveness (N)	Viscosity Index (N.sec)
1	37.72 ± 4.34^{a}	119.02 ± 8.06^{a}	16.94 ± 2.01^{a}	14.61 ± 1.44^{a}
2	7.33 ± 1.93^{e}	29.78 ± 7.45^{d}	3.27 ± 1.43^{de}	2.55 ± 0.61^{e}
3	7.35 ± 0.54^{e}	28.43 ± 5.58^{d}	3.75 ± 1.02^{de}	5.41 ± 1.39^{d}
4	11.70 ±0.71^{d}	42.41 ± 4.47^{d}	5.65 ± 0.80^{cde}	5.66 ± 0.41^{d}
5	3.54 ± 0.12^{e}	12.69 ± 0.78^{e}	2.72 ± 0.10^{e}	2.42 ± 0.09^{e}
6	20.03 ± 1.34^{c}	66.14 ± 5.91^{c}	8.72 ± 1.02^{bc}	8.77 ± 1.18^{c}
7	27.46 ± 1.05^{b}	90.61 ± 4.37^{b}	9.61 ± 0.95^{b}	10.04 ± 2.01^{bc}
8	22.85 ± 2.41^{c}	69.47 ± 4.27^{c}	10.02 ± 1.88^{b}	11.58 ± 2.08^{b}
9	7.17 ± 0.64^{e}	28.85 ± 6.12^{d}	5.97 ± 2.53^{cd}	4.66 ± 0.91^{de}

(Values are mean ± SD. Means in the same column having different letters are significantly different ($p < 0.05$)).

The rheological properties of gluten-free doughs, which range widely in consistency from batter to dough, have received relatively less research. It is still necessary to investigate the connections between dough rheology and structure as well as the behavior of dough during mechanical handling and baking in gluten-free systems. Therefore, research on the rheological characteristics of food is relevant and valuable for applications such as food handling and processing, quality control, and sensory evaluation (Buresova et al., 2014). When hydrated, the gluten in wheat flour creates a viscoelastic network that holds onto the gas created during fermentation and proofing as well as the growth of the dough as a result of its expansion during baking. Gluten is commonly referred to as the "structural" protein in bread. Contrarily, because of variations in their protein characteristics, gluten-free doughs are unable to build a comparable protein network. Baking without gluten causes significant difficulty (Matos and Rosell, 2013). The production method, dough rheology, and the quality of the finished gluten-free goods are all significantly impacted by the absence of gluten in the dough. Doughs without gluten are more elastic, cohesive, and less viscous than dough with gluten (Matos and Rosell, 2015).

Back extrusion involves compressing a sample within a cylindrical cell with a plunger that fits loosely until the sample passes through the annulus between the plunger and the cell wall. The test was utilized to determine how well the "liquid-like" materials' viscoelastic characteristics were performed. The disk continued to penetrate during the tests at a speed of 1 mm/s to a depth of 30%. The probe returns to its initial location at this time, which is most likely the moment of maximum force. In terms of firmness, the "peak" or maximum force is used as a criterion; the greater the value, the stiffer the sample. The consistency of the sample is measured by the area under the curve up to this point; the greater the value, the thicker the consistency of the sample. The weight of the sample is raised largely on the upper surface of the disk on return, which is due to back extrusion. This causes the negative area of the graph, generated on probe return, and it provides a measurement of the viscosity (resistance to flow off the disk). The sample's cohesiveness is determined by its greatest negative force, hence the higher negative the number, the more cohesive the sample is. The area under the negative region curve is sometimes referred to as the "work of cohesion," and the greater the value, the more resistant the sample is to withdrawal, which is a measure of the sample's cohesiveness and viscosity. For accurate findings, every measurement should be performed frequently enough (Ronda et al., 2017).

According to Table 4.4, sample 1 (90% chickpea flour) has the highest firmness value (37.72 N) and is significantly different from the other formulations. On the other hand, sample 5 has the lowest firmness value among the others and it has the highest hazelnut content (60%). Due to its high fat content, hazelnut gives softer texture to the end product. If the effects of hazelnut and carob flour additions on the firmness of the cookie samples are compared, it can be said that the samples with carob and chickpea flour combination have higher firmness values than the samples with hazelnut flour. Addition of carob flour up to 60 % was tested and sample 9 which has the highest carob flour has the lowest firmness value with 7.17 N among all carob containing doughs and it is almost 3 times lower than the other carob flour containing samples. According to this result, it could be suggested that carob flour addition should be in the range of 15-45 % for desirable cookie dough firmness.

The consistency of the samples varies between 12.69 to 119.02 N.sec. Sample 1 has the highest consistency value while the sample 5 has the lowest one and is significantly different from the other formulations. Since the consistency was obtained from the positive area under the curve results have similar distribution with the firmness results. Samples 2, 3, 4 and 9 are not significantly different from each other. Therefore, highest carob containing dough sample has similar consistency with hazelnut containing samples except 60% one (Sample 5).

Cohesiveness value obtained from negative peak force of the back extrusion graph. Sample 1 having only chickpea flour has the highest cohesiveness value (16.94 N) and is significantly different from the other doughs with the composite flours. Sample 5 with the highest level of hazelnut flour has the lowest cohesiveness value with 2.72 N value. If the addition of hazelnut and carob flours is compared carob flour containing formulations have higher cohesiveness value.

The negative area of the back extrusion graph gives the viscosity index value. Sample 1 has the highest viscosity index (14.61 N.sec) and is significantly different from the others. On the other hand, sample 5 has the lowest viscosity index value (2.42 N.sec).

The addition of chickpea flour increases all types of rheological properties of gluten-free cookie doughs. However, addition of hazelnut and carob flour causes decrease of the rheological properties. When creating a cookie formulation, the rheology of the dough is a factor that needs careful consideration. A dough that is too soft or too firm is difficult to work with; as a result, the dough must be sufficiently cohesive to hold together during the process and allow for easy lamination without becoming overly sticky to the point where it sticks to the rolling mill (Torra et al., 2021).

4.3.1.2. Physical Properties of Cookies Prepared with Dual Composite Flours

Table 4.5. shows the physical properties of cookie samples which are moisture, baking weight loss, spread ratio, hardness, and color properties. According to Table 4.5., carob flour containing samples 6, 8, and 9 has the highest moisture content values and these values are very close to each other. Sample 5 with the highest hazelnut flour content has the lowest moisture content with 7.55 %, and is significantly different from the others. When all nine formulations are examined, it can be concluded that formulations with hazelnut flour have a lower moisture percentage than formulations that contain carob flour. Since hazelnut flour has high fat content, this is an expected result. According to Manley (2000), dough often contains a mixture of protein and starch particles, with the fat appearing as big globules or massive interconnected masses. For instance, fat can either form a more continuous phase or be distributed depending on the amount present in the system (Baltsavias et al., 1999). Compared to cakes and bread, cookies have lower moisture levels and rely more on fat for tenderness and mouthfeel (Lai and Lin, 2006).

The cookie dough undergoes a lot of changes during baking. Changes in dimensions, moisture loss, and the development of color and flavor are the most significant of these (Pareyt & Delcour, 2008). According to Table 4.5, sample 2 (45% hazelnut flour) has the highest baking weight loss (BWL) with 15.82 %, which is significantly different from the others and sample 5 with the highest hazelnut flour has the lowest BWL value. The mass transfer continued until the end of baking (9 min), but the formation of a dry surface layer caused a reduction in water vapor flow, increasing the weight loss percentage (as reported in earlier studies), which was the greatest in the first few minutes of baking (5 min) (Thorvaldsson & Skjoldebrand, 1998). According to a study by Schouten et al. (2023), lupin biscuits lost considerably more weight after baking compared to wheat samples, but no significant differences were observed between biscuits samples of chickpeas and lupins. Moreover, it was reported that gluten-free cookies made from rice flour and corn starch have a 13.59 % BWL value and the addition of blueberry and raspberry pomace increased the BWL value up to 17.33 % in another study (Šarić et al., 2018).

Table 4.5. Physical properties of cookies prepared with dual flour mixtures

Sample	Properties						
	Moisture (%)	Baking Weight Loss (BWL)	Spread Ratio	Hardness (N)	L*	a*	b*
1	9.94 ± 0.71^{bc}	12.05± 0.60cde	3.89± 0.33c	4.76 ±1.52ef	72.71 ± 0.84a	-1.46 ± 0.42d	40.48 ±0.84a
2	8.26 ± 1.47^{cd}	15.82 ± 0.86a	4.36 ± 0.58b	5.50 ± 1.09def	67.00 ± 2.12c	1.41 ± 1.09b	40.68 ± 0.81a
3	8.79 ± 0.41^{bcd}	13.62 ± 1.08b	3.86 ± 0.20c	5.95 ± 0.74de	69.28 ± 1.55b	-0.25± 0.54c	38.94 ± 0.70b
4	9.45 ± 0.57^{bcd}	12.83 ± 0.68bc	3.66 ± 0.20c	7.19 ± 0.99cd	69.75 ± 1.52b	0.17 ± 0.96c	41.24 ± 1.02a
5	7.55 ± 0.55^{d}	11.04 ± 1.23e	4.94 ± 0.62a	3.70 ± 1.04f	62.08 ± 1.33d	2.02 ± 1.27b	38.13 ± 1.52b
6	12.31 ± 0.82^{a}	12.25 ± 0.79cd	3.60 ± 0.11c	10.37 ± 1.41b	31.79 ± 1.10g	8.46 ± 0.58a	18.63 ± 0.78e
7	10.60 ± 1.97^{ab}	11.67 ± 0.67cde	3.73 ± 0.30c	10.71 ± 2.53ab	34.67 ± 2.06f	9.12 ± 0.95a	22.09 ± 0.88d
8	12.02 ± 1.46^{a}	11.96 ± 0.84cde	3.66 ± 0.28c	8.18 ± 1.11c	43.24 ± 1.85e	8.35 ± 0.86a	27.68 ± 0.85c
9	12.24 ± 0.76^{a}	11.29 ± 0.59de	3.76 ± 0.22c	12.50 ± 1.15a	28.26 ± 1.17h	8.59 ± 1.69a	16.46 ± 0.97f

(Values are mean ± SD. Means. Means having different letters are significantly different ($p < 0.05$)).

The spread ratio was obtained by dividing the diameter of the cookie to its height. According to the results, sample 5 has the highest spread ratio value (4.94) and is significantly different from the others (Table 4.5.). Sample 2 followed sample 5 with a spread ratio value of 4.36 and the spread ratio increased with increasing hazelnut flour content. Other formulations have spread ratio values between 3.60 to 3.89 and they are not significantly different from each other. An opposite trend was observed in another study and the spread ratio decreased as the chestnut flour fraction increased (Torra et al., 2021). Cookie height has a significant impact on this parameter; it was higher in cookies with a chickpea flour of 50% or higher compared to cookies with a chickpea flour of 25% or less. The difference in cookie height between cookies prepared using mixes of flour and cookies made with chestnut flour was less, and this difference was underlined (Torra et al., 2021). Fat melts and sugars lower the dough's viscosity during the initial stage of baking, allowing the dough to relax and expand. Moreover, when chestnut flour was added in higher quantities compared to rice flour, it was observed a decrease in cookie diameter (Demirkesen, 2016). The spread ratio characteristics, however, were not significantly affected by the addition of chickpea flour, and while the spread ratio decreased in flour mixtures made with amaranth or buckwheat, it did not do so in those made with wheat flour. Therefore, based on the findings of the study by Torra et al. (2021), chestnut flour appeared to have a greater lowering effect of the spread factor than chickpea flour, which may be related to the rheology of the dough. Similar findings were also found in our study, the addition of hazelnut flour has a greater but opposite impact on the spread ratio than chickpea and carob flour. The opposite trend can be related with very different chemical properties of hazelnut compared to chestnut flour. Hazelnut flour has high oil and low carbohydrate content while chestnut flour is rich in terms of carbohydrates.

The hardness of the cookies is directly affected by the type of the flour. Both hazelnut and carob flour containing cookies have a downward trend for hardness with increasing level of these flours in their own group. According to our results, sample 5 (60% hazelnut flour) has the lowest hardness value with 3.70 N and is significantly different from the others (Table 4.5). Since sample 5 has the highest level of hazelnut flour, this result is expected due to its high-fat content. On the other hand, cookie formulations that contain carob flour have higher hardness values than hazelnut-containing ones. Also, samples 2, 3 and 4 have higher hardness values than sample 1 with only chickpea flour. This is not expected, but can be explained with the observation that sample 1 has a very rigid cookie form and can be sliced into two pieces easily compared to hazelnut-containing samples. Samples 2, 3, and 4 have more bread-like structure and are hard to cut into pieces. It was determined that a slight amount of chestnut flour caused the hardness of the rice flour cookies to decrease (Torra et al., 2021). This situation may be due to the cookie formulation, which contains more fat than sugar and differs from the formulation utilized in this study, or to the influence of the flour particle size distribution, which was not assessed. In general, cookies with a compact structure and a low spread factor have greater hardness value.

One of the key characteristics that influences whether a consumer will accept the finished product is the surface color of the cookies. Lightness value (L*) decreased with the addition of carob flour. According to Table 4.5., sample 1 which has only chickpea flour has the highest L* value (72.71) and is significantly different from the others. Conversely, sample 9 (60% carob flour) has the lowest L* value (28.26) due its high carob flour content. Parameters a* also increased (more reddish) and b* decreased (less yellowish) as the amount of carob flour increased. Samples 6, 7, 8 and 9 have similar a* values, and they are not significantly different from each other. Sample 1 has the lowest a* value with -1.46 and is significantly different from the others. Sample 9 has the lowest b* value with 16.46 and sample 4 has the highest b* value with 41.24. Surface color of the cookies is mostly influenced by sugar caramelization and Maillard reaction, which takes place when proteins and reducing sugars interact. Additionally, the color of the cookie can vary depending on the initial color of the flour. Since hazelnut and chickpea flour contain light color tones, the reactions that occur during baking are what cause cookies to become darker. Despite the high protein level of chickpea flour, which can affect the Maillard processes, high sugar content of carob flour may affect the caramelization reactions. Depending on the type of sugar, this reaction generally takes place at temperatures above 120 °C which is a lower temperature value than baking temperature (Chevallier et al., 2000).

4.3.2 Cookies Prepared with Triple Flour Mixtures

Each type of flour (chickpea, carob and hazelnut flours) has its own taste, smell and aroma. Considering the results obtained with the cookie samples containing dual flour mixtures in the first part, formulations containing all three types of flours were also prepared. The mixture design approach was used to investigate the triple formulations. Due to its capability to offer useful information from a limited number of tests and to analyze the interactions among variables, the mixture design methodology is frequently used to solve the optimization challenges in the food industry (Buruk Sahin et al., 2016). In this study, it was thought that the use of three flours together would contribute to the general taste, textural and rheological properties of the cookies. Table 4.2.1 shows the cookie formulations by using the triple flour combinations, pre-cooked chickpea, carob and hazelnut flours. Pictures of baked cookies are presented in Appendix.

Table 4.6. Flour ratios used in triple cookie formulations (% of dry material)

Sample	Pre-Cooked Chickpea Flour	Carob Flour	Hazelnut Flour	Corn Starch
10	60	15	15	10
11	37.5	37.5	15	10
12	37.5	15	37.5	10
13	15	60	15	10
14	15	37.5	37.5	10
15	15	15	60	10
16	30	30	30	10
17	30	30	30	10
18	30	30	30	10

4.3.2.1. Rheological Properties of Cookie Doughs Made with Triple Flour Mixtures

The continuous protein network that gluten offers helps to retain the gas produced by yeast fermentation and oven rise. As a result, the volume of baked goods made without gluten is poor. Producing high-quality gluten-free foods has become one of the most difficult problems for manufacturers, cereal technologists, and scientists. In response to the expanding need for high-quality products from celiac patients, numerous studies on the rheological properties of dough/batter as well as quality parameters of gluten-free baked goods have been carried out to date (Yazar & Demirkesen, 2022).

Table 4.7. Rheological properties of cookie dough prepared with triple flour mixtures

Sample	Firmness (N)	Consistency (N.sec)	Cohesiveness (N)	Viscosity Index (N.sec)
10	7.37 ± 0.48	24.55 ± 1.37	4.19 ± 0.23	4.13 ± 0.06
11	5.44 ± 0.23	18.46 ± 0.26	3.34± 0.04	3.66 ± 0.17
12	5.17 ± 1.40	19.32 ± 2.11	3.29 ± 1.05	3.10 ± 1.28
13	6.62 ± 0.74	21.91 ± 3.70	3.92 ± 0.47	4.22 ± 0.47
14	2.66 ± 0.14	9.33 ± 0.82	1.85 ± 0.12	1.93 ± 0.13
15	1.23 ± 0.03	4.43 ± 0.09	0.90 ±0.00	0.95 ± 0.04
16	5.88 ± 0.19	20.03 ± 1.22	3.80 ± 0.19	3.93 ± 0.21
17	5.39 ± 0.31	19.31 ± 1.39	3.30 ± 0.25	3.45 ± 0.31
18	5.31 ± 0.24	18.16 ± 1.61	3.39 ± 0.22	3.67 ± 0.30

In addition to the type of protein incorporated, the type of starch used as the dough's basis also affects the rheological properties of the dough. Mancebo et al. (2016) evaluated the effects of starch and/or protein addition on the quality of rice flour gluten-free cookies and the impact of protein on the rheological behavior of gluten-free dough in the presence of starch was also investigated. While maize starch addition decreased hydration qualities, the introduction of protein in formulations boosted the hydration properties of the mixture and the viscoelastic properties of dough. Compared to cookies with more starch and no protein addition, cookies with higher protein content demonstrated higher acceptance.

The rheological properties of cookie doughs prepared with triple flour mixtures are shown in Table 4.7. Sample 15 has the lowest firmness (1.23 N), consistency (4.43 N.sec), cohesiveness (0.90 N), and viscosity index (0.95 N.sec) values. Since hazelnut content of this dough is the highest among all formulations, low rheological properties are expected. Hazelnut has very high fat content, and this provides softer texture to cookie dough.

Sample 10 which consists of 60% pre-cooked chickpea, 15% hazelnut flour and 15% carob flour has the highest firmness (7.37N), consistency (24.55 N.sec), and cohesiveness (4.19 N). Sample 13 with 15 % chickpea, 60% carob and 15% hazelnut flours has also very high rheological properties. Considering all these information, it can be said that hazelnut flour makes the dough handling properties more difficult. Due to its high-fat content, it makes the dough sticky and difficult to shape. On the other hand, carob flour with high sugar content, makes the cookie dough firmer and non-sticky which is easier to handle and shape. Pre-cooked chickpea flour addition also increased the rheological properties of cookie dough, especially firmness and consistency values. According to the results, the cookie dough with the highest amount of pre-cooked chickpea flour (sample 1) has a texture which is almost 7 times firmer than the cookie dough with the highest percentage of hazelnut flour (sample 15).

A simple lattice mixture design was applied to the results of rheological properties which are firmness, cohesiveness, consistency, and viscosity index (Appendix). According to regression results, one of the linear terms which is chickpea and hazelnut flour interaction (cpf*hf) was insignificant for all four properties, so it was dropped from the model. After that, all linear, quadratic and cubic terms became significant for all rheological properties. Firstly, the result of a model summary of firmness gave us R-sq as 96.57, R-sq(adj) as 95.71% and R-sq (pred) as 93.76 % which are very good values and especially R-sq prediction value provides information on how successfully a regression model predicts outcomes for new observations. Our model is predicted the 93.76 % of the firmness values. Figure 4.4. shows the contour plots of rheological properties and in the graph 4.4.a, firmness is explained. The dark blue color refers to the smallest values which are smaller than 2 N and the dark green refers to values greater than 7 N. According to the contour plot, increased hazelnut flour content causes lower firmness results. Moreover, higher chickpea content brings the highest firmness values.

Secondly, the result of a model summary of cohesiveness determined as R-sq as 94.77, R-sq(adj) as 93.46% and R-sq (pred) as 91.31 % (Appendix). The model predicted 91.31 % of the cohesiveness values and according to analysis of variance, all terms are signicant (P value <0.05). In the Figure 4.4, graph b represents the cohesiveness value of cookie doughs. The darkest blue is explained by values lower than 1 N, and the tone of green becomes darker while the cohesiveness value is increased. According to the contour plot of cohesiveness, when the amount of hazelnut flour increased up to 60%, the cohesiveness value become lower. The increased amounts of carob and chickpea flour make cookie dough more cohesive.

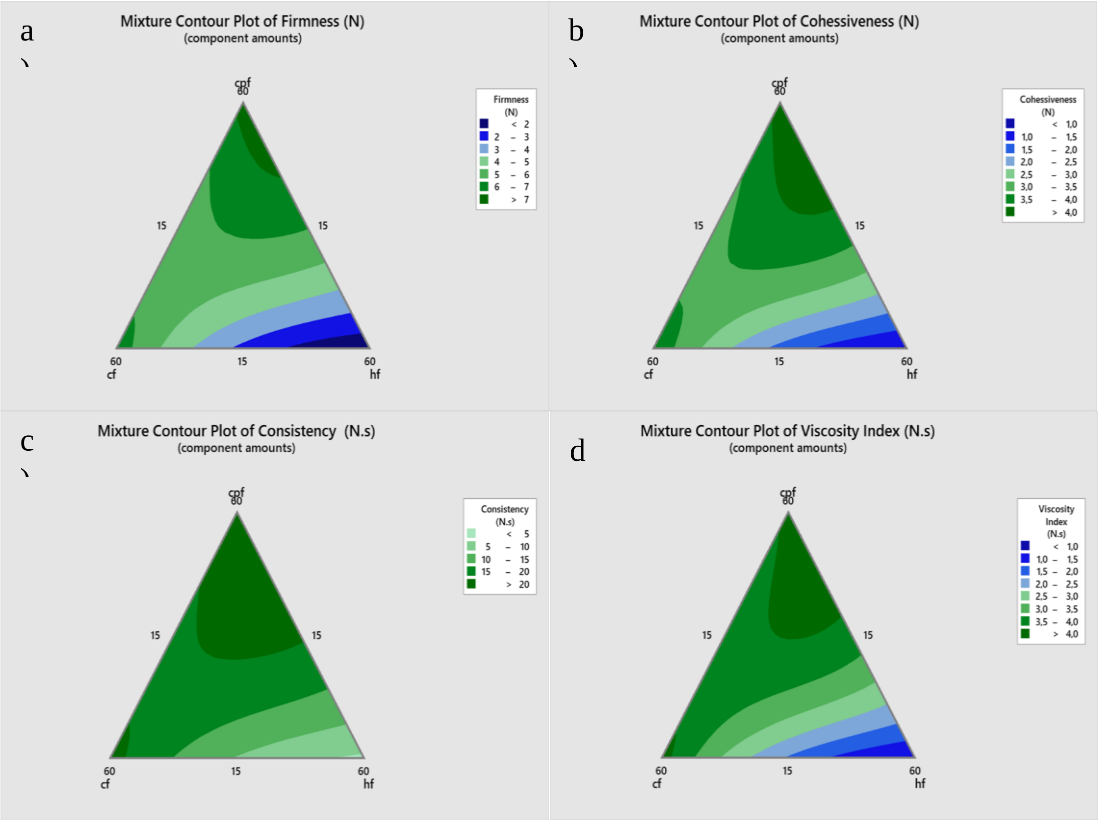

Figure 4.4. Mixture contour plot of rheological properties of cookie dough made with triple flour mixtures (cpf: pre-cooked chickpea flour, cf: carob flour, hf: hazelnut flour)

Thirdly, the result of a model summary of consistency determined as R-sq as 94.02, R-sq(adj) as 92.52% and R-sq (pred) as 89.01 % (Appendix). The model predicted 89.01 % of the consistency values, also both linear and quadratic terms are significant. In the third graph (c) of Figure 4.4., the contour plot of consistency values of cookie dough is shown. The lightest green refers to consistency values lower than 5 N.sec, the green color becomes darker and darker while the consistency value is increasing. The high amounts of carob and chickpea flour addition (up to 60%) cause cookie dough samples to become more consistent. On the other hand, the high amount of hazelnut flour (up to 60%) results in lower consistency values.

Lastly, the result of a model summary of viscosity index was shown as R-sq as 94.50, R-sq(adj) as 93.13% and R-sq (pred) as 91.08 % (Appendix). The model predicted 91.08 % of the viscosity index values and according to analysis of variance all terms are signicant (P value <0.05). Moreover, the fourth plot (d) of Figure 4.4. represents the contour plot of viscosity index of cookie doughs. The dark blue color indicates the lowest viscosity index which is lower than 1 N.sec and the darkest green is the viscosity index values that are higher than 4 N.sec. According to all four contour plots, the use of hazelnut flour between 15 and 45 % will be better for improving the rheological properties of cookie dough. The use of chickpea and carob flours in the range of 30-60 % provides more ideal results for the rheological properties of the cookie dough since it is easier to handle these doughs.

4.3.2.2. Physical Properties of Cookies Made with Triple Flour Mixtures

Moisture, baking weight loss (BWL), spread ratio, hardness, and color properties are determined as physical properties for the baked cookies (Table 4.8). A simple lattice mixture design shown in Table 4.8. was applied to the results of the physical properties of cookies which are moisture, baking weight loss (BWL), spread ratio, and hardness.

The texture of cookies and their customer acceptance are significantly influenced by the moisture content of the cookie-type of products. A summary of model results for the moisture content of cookies shows R-sq as 61.88%, R-sq(adj) as 58.77%, and R-sq (pred) as 57.55 % (Appendix). The model predicted 57.55 % of the moisture content values and according to the analysis of variance, all terms are significant (P value <0.05). Due to the low reproducibility of the experiment and non-homogeneous structure of cookies, our R^2 values are quite low. According to Table 4.8., sample 13 has the highest and sample 10 has the lowest moisture content. However, there was not much difference between the moisture contents of the cookies formed with the triple flour formulations. The moisture contents of cookies ranged between 7.16-10.28 %. Figure 4.5. represents the contour plots of the results of the mixture design, and in the contour plot a), the dark blue color shows the percent moisture content lower than 7.5% and dark green indicates the moisture content higher than 10%. According to this plot, the high amounts of hazelnut flour and chickpea flour caused lower moisture content for cookies. The high amount of carob flour, on the other hand, is brought higher moisture content. Higher protein and starch content of chickpea flour could lead to an interaction between these compounds and water, and water can be entrapped in 3D matrix. While high oil content of hazelnut oil can cause repelling effect and evaporation of water. Carob flour, on the other hand, is richer in terms of mono- and oligosaccharides which have the capability to interact with water but not through 3D-networks. According to a study in literature, cookies made with composite flours (germinated triticale, kidney bean, and chickpea) have a higher moisture content than wheat flour cookies (Singh Sibian & Singh Riar, 2020).

Table 4.8. Physical Properties of Cookies Prepared with Triple Flour Mixture

	Properties						
Sample	Moisture (%)	Baking Weight Loss (%) (BWL)	Spread Ratio	Hardness (N)	L*	a*	b*
10	7.16 ± 0.56	13.05 ± 0.58	3.77 ± 0.15	3.92 ± 0.55	41.42 ± 1.32	9.06 ± 0.80	13.77 ± 0.67
11	9.13 ± 0.23	12.87 ± 0.80	3.87 ± 0.17	4.82 ± 0.58	30.16 ± 1.74	9.70 ± 0.40	9.72 ± 0.56
12	7.77 ± 0.30	12.85 ± 1.13	4.43 ± 0.30	2.86 ± 0.53	39.43 ± 1.72	9.15± 0.72	12.91 ± 1.01
13	10.28 ± 0.13	13.59 ± 0.75	3.37 ± 0.14	8.26 ± 1.21	25.68 ± 1.51	8.95 ± 0.35	6.73 ± 0.74
14	8.49 ± 0.25	16.46 ± 0.87	4.92 ± 0.32	5.84 ± 0.82	28.18 ± 0.76	9.55 ± 0.24	8.28 ± 0.86
15	7.24 ± 0.17	19.93 ± 1.10	7.47 ± 0.38	3.45 ± 0.89	34.27 ± 1.53	8.88 ± 0.57	11.30 ± 1.27
16	8.94 ± 0.19	12.60 ± 0.92	4.05 ± 0.20	3.75 ± 0.70	32.68 ± 1.23	9.98 ± 0.31	10.45 ± 0.51
17	8.69 ± 0.35	13.87 ± 1.10	4.27 ± 0.15	3.61 ± 0.63	31.15 ± 1.50	9.92 ± 0.43	10.11 ± 0.65
18	10.04 ± 0.37	11.73 ± 0.65	4.15 ± 0.20	2.56 ± 0.26	31.03 ± 1.09	9.76 ± 0.62	10.33 ± 0.98

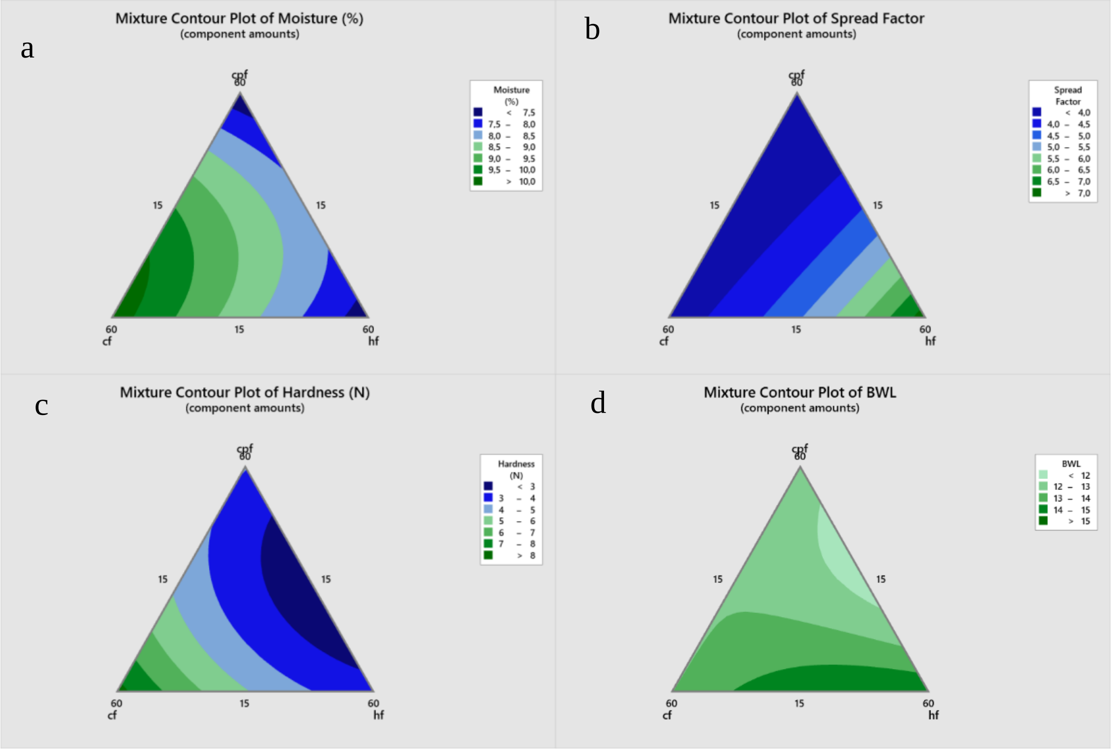

Figure 4.5. Mixture contour plots of physical properties of cookies made with triple flour mixtures (cpf: pre-cooked chickpea flour, cf: carob flour, hf: hazelnut flour)

One of the factors which help to estimate cookie quality is the spread ratio. A higher spread ratio is ideal for better cookies (Mudgil et al., 2017). Dough viscosity appears to be an important factor in cookie spread rate. Therefore, a correlation between viscosity index and spread ratio values are investigated and R^2 value is determined as 0.88 (Figure 4.6). A good correlation was not observed in the doughs obtained with the dual flour mixture, but a good correlation was established between the viscosity index and the spread ratio for the doughs obtained with the triple flour mixture, with a value of 0.88 R^2. More sugar is dissolved during mixing when there is more water in the dough. Due to the reduced initial dough viscosity, the cookie can spread more quickly while being heated. The amount of water available to dissolve the sugar in the recipe is decreased by flour components that absorb a lot of water. As a result, the dough has a higher initial viscosity and spreads less while baking. Cookies with a greater spread are made with flours with poor hydration qualities (Hoseney & Rogers, 1994). In a study, it was concluded that the viscosity of the dough affected how quickly cookies spread when baking (Miller et al., 1997). The rate at which cookies spread increased with water content in formulation, probably because of the decrease in the dough's viscosity and the cooking time was also shortened at the same time. The diameter of cookies made with soft wheat flour and a low water level was significantly larger than those made with hard wheat flour and a high-water content (Miller & Hoseney, 1997).

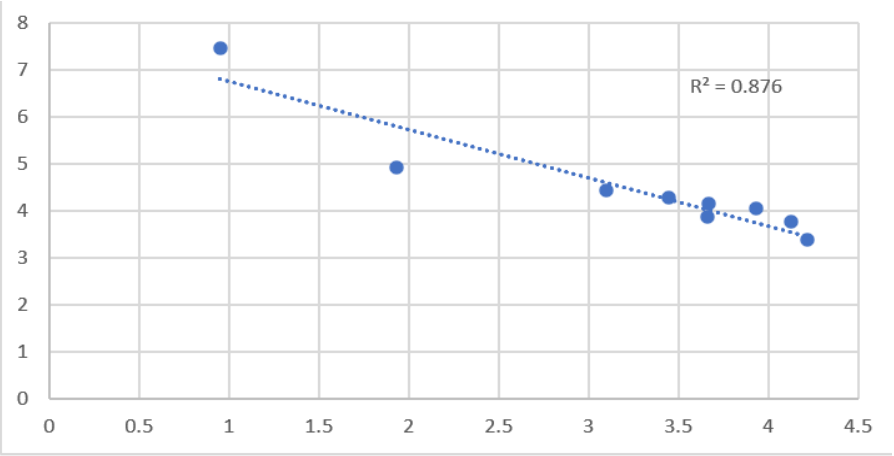

Figure 4.6. Correlation plot of viscosity index vs spread rate for the cookies having triple flour combination

In our study, the spread ratio values ranged between 3.37 to 7.47. Only sample 15 which is a cookie consisting of 60% hazelnut flour together with 15% of chickpea and 15% carob flours has a spread ratio value with a large difference compared to the other samples. Sample 13 has the lowest spread ratio which consists of 60% carob flour. Other cookie samples have similar spread ratio results. A model with R-sq as 95.71%, R-sq(adj) as 95.53%, and R-sq (pred) as 95.12 % are obtained as a result of statistical analysis of the spread ratio results (Appendix). Our model predicted 95.12 % of the spread ratio values and according to the analysis of variance, all terms (linear and quadratic) are significant (P value <0.05). According to the contour plot in Figure 4.5.b. which represented the result of the mixture design of spread factor, the dark blue color indicates values lower than 4 and the darkest green color indicates a value greater than 7. An almost linear relationship can be observed between the amount of hazelnut flour and the spread ratio of the cookies. While the amount of hazelnut flour increased, the spread ratio of the cookie also increased. The opposite is true for the relationship between carob flour and the spread ratio. There is an inverse relation between the amount of carob flour and the spread ratio, and as the amount of carob flour increases, the spread factor of the cookie decreases. According to a study by Hadinezhad & Butler (2009), the relationship between cookie spread rate and ultimate diameter was strong and significant. However, there was a weak and non-significant association between cookie set time and final diameter. The diameter of the cookie increases as the spread rate and setting time increase. It should be noted that the researchers tested samples of soft and hard wheat flour as two distinct kinds of flour. It is commonly known that soft wheat flour works best for baking biscuits, whereas hard wheat flour is not ideal for producing biscuits of high quality. Given that the flour samples were all from the soft wheat flour class, it might help to explain why the association between cookie set time and cookie diameter was poor.

The hardness values of the cookies made with triple flour mixtures were determined and are shown in the Table 4.8. The hardness values of cookies range between 2.56 N and 8.26 N. Sample 13 which consists of 60% of carob flour has the highest hardness value (8.26 N) and the sample 15 which had 60% of hazelnut flour has the second highest hardness value (5.84 N). However, their cookie textures were very different, since the sample 15 had high amount of hazelnut flour, its fat content was also high. This situation caused the cookie to have a texture that can hardly be divided into two pieces, like bread. The result of a model summary of the hardness values of cookies shows R-sq as 71.63%, R-sq(adj) as 70.08%, and R-sq (pred) as 67.90 %. Our model predicted 67.90 % of the hardness values of cookies and according to the analysis of variance, all terms (linear and quadratic) are significant (P value <0.05). Since our samples have low repeatability, R square values were a little bit low. According to the contour plot of hardness in Figure 4.5, the dark blue color indicates the hardness value smaller than 3 N, and the darkest green represents the hardness value greater than 8 N. It is observed that as the amount of carob flour increases up to 60%, the hardness value also increases and even reaches its highest values. If the amounts of chickpea flour and carob flour are increased at the same time, this causes a decrease in the hardness value of the cookie. According to a study, it was found that it took greater force to break cookies made with legume flour (Lee et al., 1991). This may have happened as a result of the addition of protein-rich flour, which requires more water to make a nice cookie dough and causes formation of extremely tough cookies when baked. As the butter content grew, the hardness reduced, which is consistent with the idea that one of the purposes of employing fats in cookies is to soften and tenderize the texture in addition to improving flavor and facilitating leavening (Chakrabarti et al., 2017). One of the key elements affecting the eating quality of cookies is their texture, and one of the most significant textural criteria for cookies is hardness, which is measured as the peak force required to break the cookie. According to a study by Mancebo et al. (2015), the size of the flour particle had a significant impact on cookie hardness. For instance, cookies created with fine-grained flour required a higher peak force than cookies made with coarse-grained flour of the same wheat type. This might be because cookies made with fine-grained flour have a denser structure. According to another study, cookies made with buckwheat, teff, and maize flours had the highest hardness values (Maache-Rezzoug et al., 1998). Since it was noticed how the effective force increased with protein content while examining the mechanical properties of cookies manufactured from wheat flour, the high protein content of teff and buckwheat flours may be the cause of the cookies' high hardness values. Contrarily, it was observed that switching from rice to buckwheat flour resulted in a reduction in the hardness of the cookies due to the fact that used rice flour had a finer consistency than buckwheat flour (Hadnadev et al., 2013).

Baking weight loss is an important quality parameter for baked products to understand how much loss takes place from dough to baked product. During baking, cookies loose moisture; therefore, there is a change in structure and texture, and an increase in volume. The primary mechanisms in the formation of crumbs are generally recognized to be moisture losses and starch retrogradation. A dry crust may form if too much moisture is lost, which will make the product underweight and make packaging the goods more difficult. Additionally, the water lost during baking has a negative impact on the freshness of baked items, causing them to age more quickly (Kotoki & Deka, 2010). It was concluded that reduced water requirements in the dough were achieved by substituting raspberry fiber concentrate for the gluten-free flour mixture in a literature study (Šarić et al., 2018). Since the amount of water in each formulation was kept constant, extra water developed in the rice flour dough sample, which led to a lower BWL during baking and a greater end-product moisture content. Higher levels of free water caused the sucrose to dissolve more quickly, which resulted in a more noticeable volume rise during baking (Laguna et al., 2011). Low BWL may also be correlated with the presence of amorphous starch zones, which have a significant impact on water absorption in cookie doughs containing rice flour (Aparicio-Saguilá et al., 2007). Since there was more water in the system due to the rice flour, the amorphous region in the starch granules swelled as a result.

In our study, BWL values had a range between 11.73 to 19.93%. The highest BWL was observed for sample 15 which was a cookie consisting of 60% hazelnut flour. The results of the other samples were close to each other. The result of a model summary of the baking weight loss (BWL %) values of cookies shows R-sq as 64.20%, R-sq(adj) as 62.65%, and R-sq (pred) as 61.16% (Appendix). Our model predicted 61.16% of the BWL (%) values of cookies and according to the analysis of variance, all terms (linear and quadratic) are significant (P value <0.05). According to mixture contour plot of BWL in Figure 4.5.d, the lightest green indicates that BWL (%) lower than 12 and the darkest green shows the BWL (%) greater than 15. If the amount of hazelnut flour was increased BWL (%) also increased. In addition, high amount of carob flour usage also causes the higher BWL (%) values.

The surface color of the cookies is one of the major quality factors that determines whether a customer will accept the finished product. L* indicates the lightness of the sample. According to Table 4.8., sample 10 has the highest L* value (41.42) which is an expected result since the sample 10 has the highest pre-cooked chickpea flour content (60%) and chickpea flour has the lightest color compared to hazelnut and carob flours. Conversely, sample 13 has the lowest L* value (25.68) since it has the highest carob flour content. In general, cookies made with triple flour mixtures have a lower L* (lightness) value compared to cookies made with dual flour mixtures since all triple flour ones contain carob flour having a light brown color. Redness is shown with a* values and yellowness with b* values in color parameter determination of samples. Values of a* were found similar according to Table 4.8. However, sample 16 has the highest a* value (9.98) among others but is very close to samples 17 (9.92) and 18 (9.76) which have the same compositions in mixture design. Sample 10 which consists of the highest amount of chickpea flour has the highest b* value (13.77) and the sample 13 which have the high amount of carob flour has the lowest b* value (6.73). Besides the color of the raw material, the reactions that take place while baking also make cookies darker.

4.4. Principal Component Analysis (PCA) of Cookies with Respect to the Physical and the Spectroscopic Properties

PCA related to physical and spectroscopic properties were mentioned.

4.4.1. Fourier Transform Infrared (FTIR) Spectrometric Analysis of Cookie Doughs Made with Dual & Triple Flour Mixtures

Figure 4.2.5.1 and 4.2.5.2 show FTIR spectral profiles of cookie doughs made with dual and triple composite flours, respectively. The absorption region of 1300-800 cm^{-1} in an FTIR spectrum is primarily associated with the vibrations of C-C, C-O, and C-OH bonds and can be mainly attributed to starch structure. Two peaks at 1022 and 1047 cm^{-1} in particular, represent the amorphous and short-range order structures of starch, respectively, the saccharide group correlates to an absorbance band at 1150-900 cm^{-1}, which reveals variations between the samples that might be attributed to their starch crystallinity (Pulatsu et al., 2021). The FTIR spectra of the chickpea, carob, and hazelnut flours varied because they included various amounts of fat, protein, and sugar. For cookie doughs, spectral profiles have variations depending on the formulations. Clear peaks can be observed in 3700-2600 cm^{-1} and 1800-800 cm^{-1} regions. In general, the absorptions in 3000-2800 cm^{-1} and 1200-800 cm^{-1} region can be associated with lipids and carbohydrates, respectively. Amide I and amide II regions are located between 1700 and 1450 cm^{-1}. By analyzing the amide I band (1720-1570 cm^{-1}), Fourier transform spectroscopy (FT-IR) and Fourier transform Raman spectroscopy (FT-Raman) are mostly utilized to examine the secondary structure of proteins.

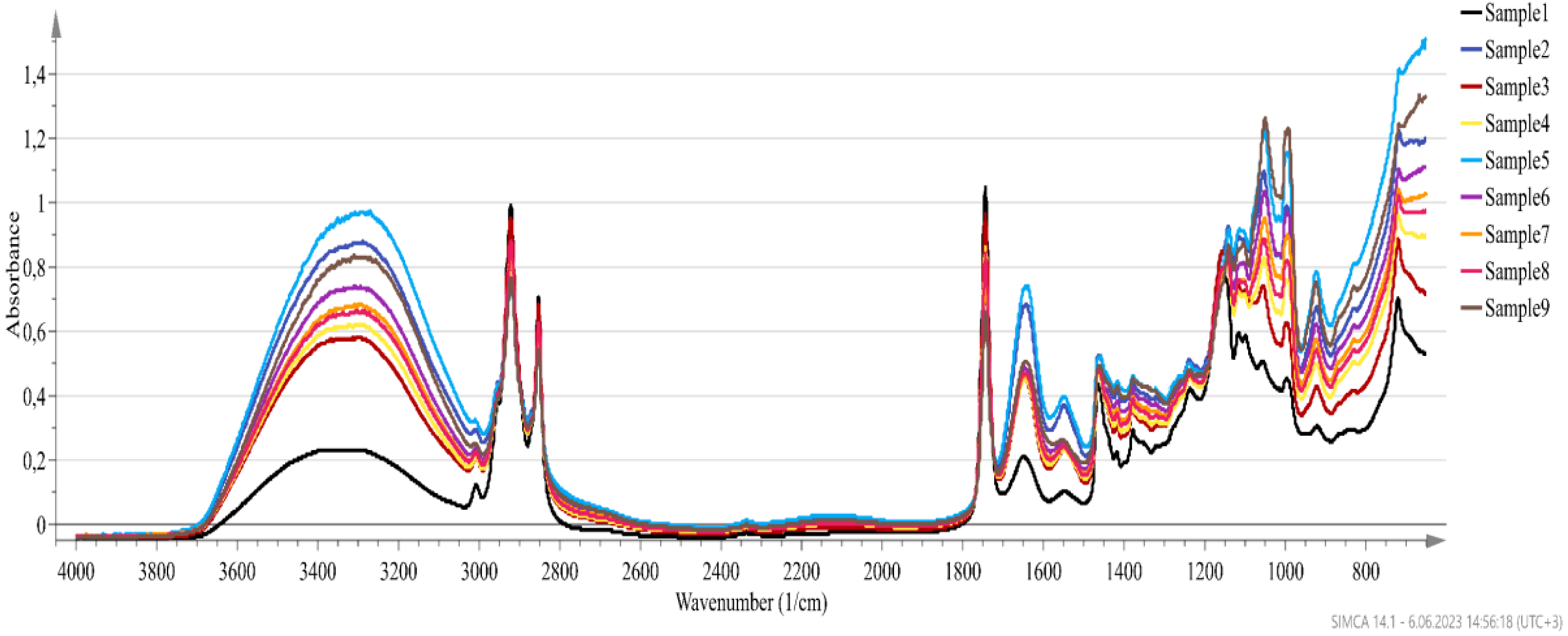

Figure 4.7. FTIR spectra of cookie doughs with dual flour mixtures (Sample 1: 90% cpf, Sample 2: 45%cpf 45%hf, Sample 3: 60% cpf 30%hf, Sample 4: 75%cpf 15%hf, Sample 5: 30%cpf 60%hf, Sample 6:45%cpf 45%cf, Sample 7: 60%cpf 30c% cf, Sample 8: 75%cpf 15%cf, Sample 9: 30%cpf 60%cf)

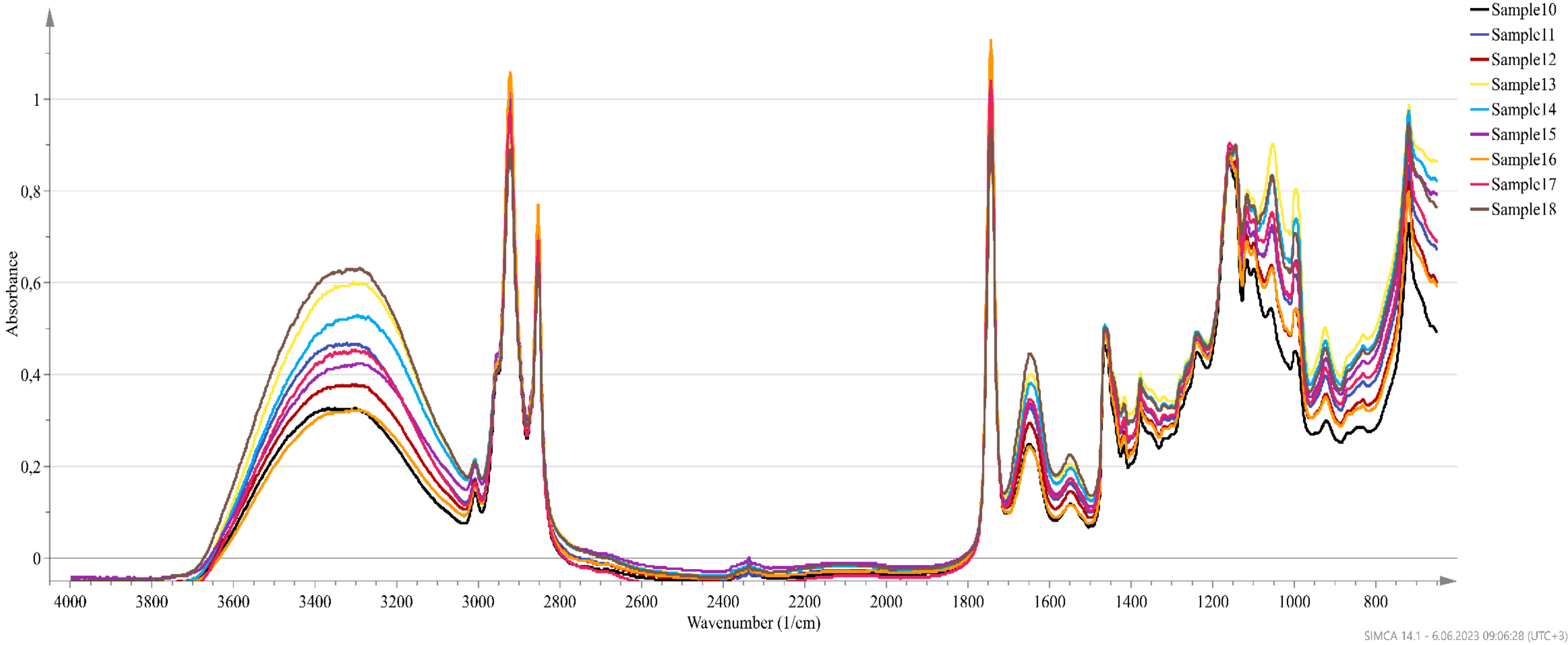

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Figure 4.8. FTIR spectra of cookie doughs with dual flour mixtures (Sample 10: 60% cpf 15% cf 15% hf, Sample 11: 37.5% cpf 37.5% cf 15% hf, Sample 12: 37.5% cpf 15% cf 37.5% hf, Sample 13: 15% cpf 60% cf 15% hf, Sample 14: 15% cpf 37.5% cf 15% hf, Sample 15: 15% cpf 15% cf 60% hf, Sample 16: 30% cf 30% hf, Sample 17: 30% cpf 30% cf 30% hf, Sample 18: 30% cpf 30% cf 30% hf)

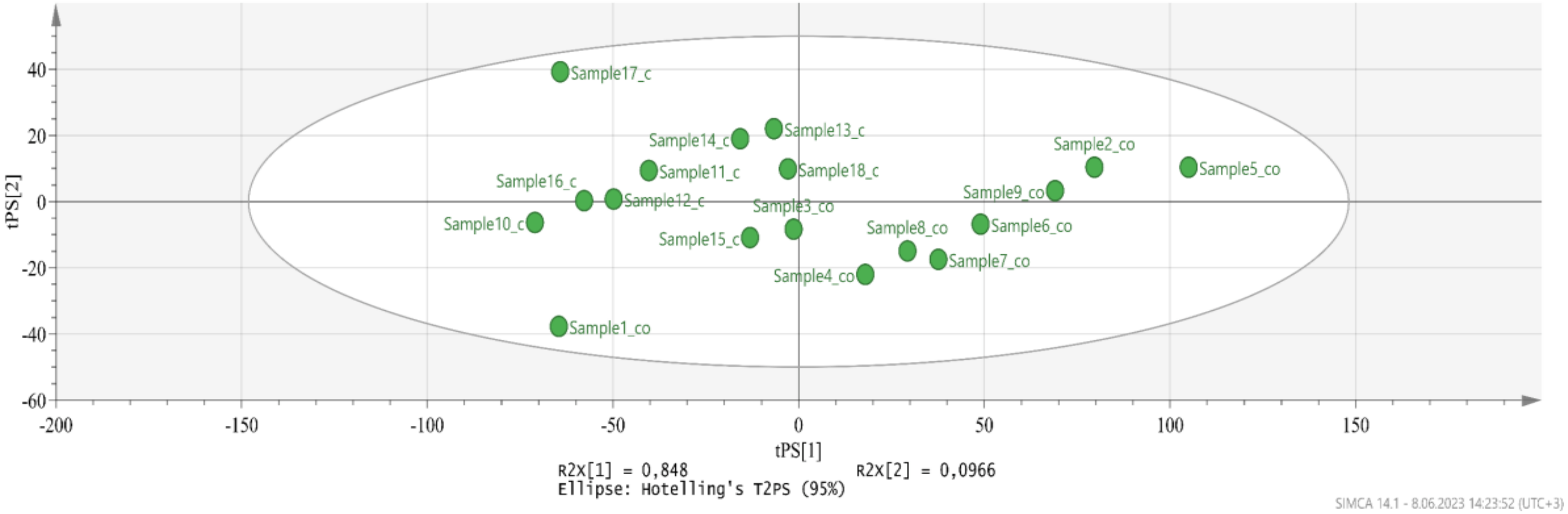

Figure 4.9. Score plot for PCA of FTIR spectra of cookie doughs with dual & triple flour mixtures (Sample 1: 90% cpf Sample 2: 45%cpf 45%hf, Sample 3: 60% cpf 30%hf, Sample 4: 75%cpf 15%hf, Sample 5: 30%cpf 60%hf, Sample 6:45%cpf 45cf, Sample 7: 60%cpf 30% cf, Sample 8: 75%cpf 15%cf, Sample 9: 30%cpf 60%cf , Sample 10: 60% cpf 15% cf 15% hf, Sample 11: 37.5% cpf 37.5% cf 15% hf, Sample 12: 37.5% cpf 15% cf 37.5% hf, Sample 13: 15% cpf 60% cf 15% hf, Sample 14: 15% cpf 37.5% cf 15% hf, Sample 15: 15% cpf 15% cf 60% hf, Sample 16: 30% cf 30% hf, Sample 17: 30% cpf 30% cf 30% hf, Sample 18: 30% cpf 30% cf 30% hf,)

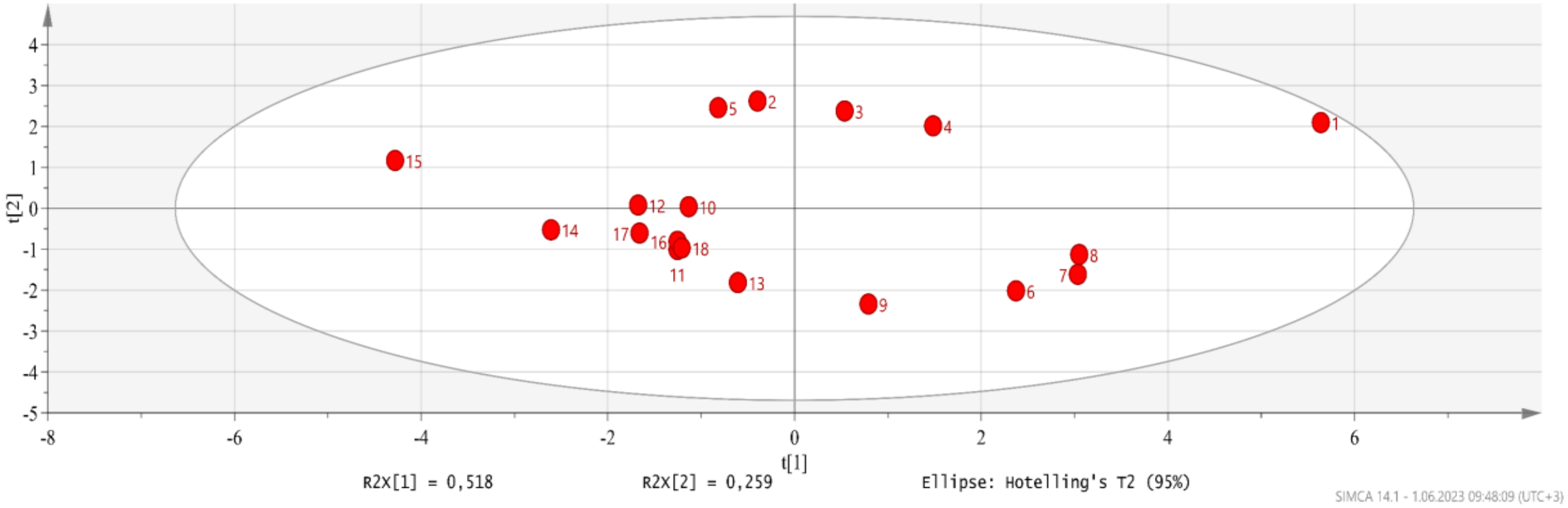

Figure 4.10. Score plot for PCA of physical properties of cookies with dual & triple flour mixtures (Sample 1: 90% cpf Sample 2: 45%cpf 45%hf, Sample 3: 60% cpf 30%hf, Sample 4: 75%cpf 15%hf, Sample 5: 30%cpf 60%hf, Sample 6:45%cpf 45cf, Sample 7: 60%cpf 30c% cf, Sample 8: 75%cpf 15%cf, Sample 9: 30%cpf 60%cf, Sample 10: 60% cpf 15% cf 15% hf, Sample 11: 37.5% cpf 37.5% cf 15% hf, Sample 12: 37.5% cpf 15% cf 37.5% hf, Sample 13: 15% cpf 60% cf 15% hf, Sample 14: 15% cpf 37.5% cf 15% hf, Sample 15: 15% cpf 15% cf 60% hf, Sample 16: 30% cf 30% hf, Sample 17: 30% cpf 30% cf 30% hf, Sample 18: 30% cpf 30% cf 30% hf,)

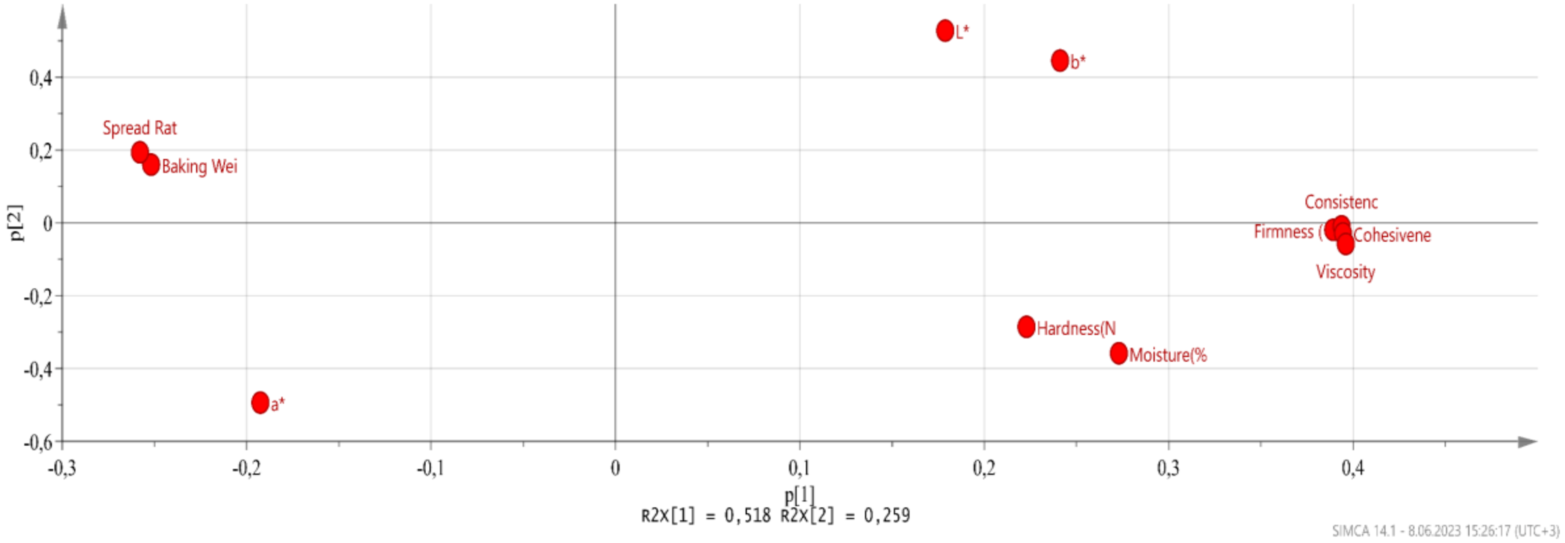

Figure 4.11. Loading plot for PCA of physical properties of cookies with dual & triple flour mixtures (Sample 1: 90% cpf Sample 2: 45%cpf 45%hf, Sample 3: 60% cpf 30%hf, Sample 4: 75%cpf 15%hf, Sample 5: 30%cpf 60%hf, Sample 6:45%cpf 45cf, Sample 7: 60%cpf 30c% cf, Sample 8: 75%cpf 15%cf, Sample 9: 30%cpf 60%cf, Sample 10: 60% cpf 15% cf 15% hf, Sample 11: 37.5% cpf 37.5% cf 15% hf, Sample 12: 37.5% cpf 15% cf 37.5% hf, Sample 13: 15% cpf 60% cf 15% hf, Sample 14: 15% cpf 37.5% cf 15% hf, Sample 15: 15% cpf 15% cf 60% hf, Sample 16: 30% cf 30% hf, Sample 17: 30% cpf 30% cf 30% hf, Sample 18: 30% cpf 30% cf 30% hf,)

FT-IR offers data on water concentrations in the bread dough (Nawrocka et al., 2018). Furthermore, it can be used in research on small amounts of dry and wet materials because it is non-destructive. The relationship between protein structure, rheological qualities of doughs, and technological aspects of wheat bread has already been highlighted using this technique (Sivam et al., 2013). It was also used to investigate how adding dietary fiber preparations and fiber polysaccharides to wheat dough affected the gluten's structural alterations (Nawrocka et al., 2018). The backbone vibrations of the CO, CN, and CC bonds that are usually assigned to polysaccharides are characteristic of another spectral region (800-1200 cm^{-1}). Since it is difficult to compare the spectral profile (which are shown in Figure 4.7 and 4.8) of all 18 cookie formulations together with visual analysis FTIR spectra of the dough samples having double and triple flour mixtures were analyzed using PCA, and the results are given in Figure 4.9. One of the most popular data mining approaches in the sciences, PCA, is used to analyze a variety of datasets (such as sensory, instrumental, and chemical data) (Cozzolino et al., 2019). PCA is employed to give users a general understanding of the interconnectedness and complexity of multivariate data sets. Among other uses, this technique is typically used to extract and compress multivariate data sets, uncover relationships between the variables and the samples, find and quantify patterns and trends, and locate outliers (Bro and Smilde, 2014).

According to Figure 4.9 that represents the score plot of FTIR spectroscopy results of all cookie dough samples, it can be said that the cookie dough samples are separated according to their contents. However, it was not observed a highly successful separation because it was a low repeatability analysis due to non-homogeneous structure of doughs. However, it is possible to say that the samples of cookie doughs containing hazelnut flour are in the upper right part of the graph, while those containing carob flour are concentrated in the lower right. Moreover, some spectral filters like reprocessing the data by using derivatives were applied to better distinguish the cookie dough samples but it did not improve the results. All rheological and physical properties of all cookies were also analyzed with PCA. When score plot in Figure 4.10 is examined, it could be seen how the cookie samples show a distribution according to their physical properties, which are moisture, spread ratio, baking weight loss and hardness. Sample 1 which is the reference cookie containing chickpea flour is separated from the others with composite flours as expected. The samples containing chickpea and hazelnut flours (2, 3, 4, 5) are positioned in the upper middle and upper right part of the graph. As the amount of hazelnut flour in the cookie samples increases, the distribution of the samples starts to shift from the right to the middle of the graph. Cookies containing carob and chickpea flour (6, 7, 8, 9) are located in the lower right part of the graph. This time, the position of the samples is towards the middle as the carob content in the cookie increases. For example, sample 9 is the cookie sample containing the most carob flour with 60% and is located in a region close to the middle compared to the other samples. In addition, cookies with triple flour formulations (chickpea, carob and hazelnut) are located in the middle-left part of the graph. Sample 15 is separated from the group containing triple flour formulation due to its high hazelnut flour content and low chickpea flour content (60% hazelnut flour, 15% carob flour, 15% chickpea flour) and is located in the upper left part of the graph.

In Figure 4.11, the loading plot of the PCA for physical properties of the cookie samples are presented. The regions in the data set that had the biggest effects on each factor that contributed to the separation of the samples are found using the loadings. Loadings can be in the range of 1 to -1, with loadings near to 1 or -1 indicating that the variable have a significant impact on the primary component. However, loadings around 0 show that the variable has only a little impact on that primary component (Cozzolino et al., 2019). If the score and loading plots are placed on top of each other it can be seen that the cookie samples located in the lower right part of the graphic stand out with their hardness and moisture properties. From another point of view, it is possible to say that the cookie samples positioned towards the upper left of the graph are positioned according to the spread ratio and baking weight loss properties. The positioning of sample 15, which has a high hazelnut flour content, is logical since the spread ratio value of the cookies increased as the amount of hazelnut flour increased.

4.5. Sensory Evaluation of Cookie Samples

40 panelists (29 women, 11 men) with ages ranging from 21 to 56 attended the sensory panel of gluten-free cookies among the personnel and students of the Department of Food Engineering at Izmir Institute of Technology. The method of sensory evaluation was known to all participants. The two cookies selected to be tasted in the sensory analysis were chosen based on test results and personal experience during their preparation. Parameters such as the handling properties of the dough and the texture of the cookie played an important role in this selection. The sensory evaluation was conducted in a sensory evaluation facility in the same day with the baking process. Individual panel booths that were lit with white light were used during testing. Each sample of the cookies was coded with a distinct letter and placed on white plastic plates. The panelists were also given a glass of water to rinse their palates. The panelists were asked to rate the following attributes: color, odor, texture, taste, and general acceptability using a 7-point hedonic scale (7, like extremely; 1, dislike extremely).

Table 4.9. Average results of sensory analyses (* Sample 16: 30% chickpea flour-30% carob flour-30% hazelnut flour-10% corn starch, Sample 10: 60% chickpea flour-15% carob flour-15% hazelnut flour-10% corn starch, Sample 1: 90% chickpea flour-10% corn starch)

Sample*	**Color**	**Flavor**	**Texture**	**Taste**	**Overall Acceptability**
Sample 16	5.80 ± 1.36^{a}	5.40 ± 1.33^{a}	5.43 ± 1.44^{a}	5.55 ± 1.17^{a}	5.63 ± 1.05^{a}
Sample 10	5.43 ± 1.28^{a}	5.33 ± 1.25^{a}	5.50 ± 0.98^{a}	5.43 ± 1.03^{a}	5.28 ± 1.11^{ab}
Sample 1	5.60 ± 1.15^{a}	4.50 ± 1.43^{b}	5.48 ± 1.06^{a}	4.55 ± 1.41^{b}	4.78 ± 1.19^{b}

According to Table 4.9, sample 16 has the highest scores among all parameters except texture. Sample 1 which contains 90% chickpea flour has the highest texture score; however, it has the lowest flavor score. This is an expected result considering the undesirable flavor of chickpea flour by consumers. Sample 1 also has the lowest scores for taste and overall acceptability parameters. From the consumer point of view, sample 16 has the highest overall acceptability.

Considering that sample 1 is the reference cookie, it can be concluded that the other two cookie samples are more acceptable. Therefore, the addition of carob and hazelnut flour to chickpea flour-containing formulation increases the appreciation and preference of the consumer compared to the sample of cookies containing only chickpea flour.

4.6. Predicted Nutritional Value Calculation of Cookie Samples

Gluten-free cookie samples that were also used in the sensory evaluation were investigated regarding to their predicted nutritional value. Atwater et al. (1900) established the system for calculating the energy value of foods at the USDA Agricultural Experiment Station (Storrs, Connecticut) hundred years ago. The Atwater general factors are still often used to assess food's energy content more than a century later. This method was used to calculate total energy of 100 g cookie in kcal. For this calculation, amount of carbohydrate, protein, fat and fiber are considered as 4 kcalories per gram, 4 kcalories per gram, 9 kcalories per gram and 2 calories per gram, respectively. According to Table 4.2.4, sample 1 which consists of 90% of chickpea flour provides 476.5 kcal/100g and 24.7% of this energy comes from protein which is quite a high amount. Considering the high protein content of chickpea flour, this is an expected outcome. It is thought that the 47.2 kcal energy coming from protein in 100 g cookies will make this product a very good protein source in the eyes of the consumer.

Table 4.10. Predicted nutritional values of sample 1 (90% chickpea flour) (For energy calculation; carbohydrate = 4 kcalories per gram, protein = 4 kcalories per gram, fat = 9 kcalories per gram, fiber = 2 calories per gram)

Component	**g/100 g Cookie**	**Energy (kcal/100 g Cookie)**	**Total Energy (kcal/100 g cookie)**	**Energy% from protein**
Fat	26.1	235.1	476.5	*24.7*
Protein	11.8	47.2		
Moisture	9.9	0.0		
Ash	2.8	0.0		
Fiber	1.6	3.2		
Carbohydrate (except fiber)	47.7	190.9		

Table 4.11. Predicted nutritional values of sample 10 (60% chickpea flour, 15% carob flour, 15% hazelnut flour) (For energy calculation; carbohydrate = 4 kcalories per gram, protein = 4 kcalories per gram, fat = 9 kcalories per gram, fiber = 2 calories per gram)

Component	**g/100 g Cookie**	**Energy (kcal/100 g Cookie)**	**Total Energy (kcal/100 g cookie)**	**Energy% from protein**
Fat	29.8	268.1	496.9	*22.6*
Protein	10.4	41.4		
Moisture	8.9	0.0		
Ash	2.9	0.0		
Fiber	2.3	4.5		
Carbohydrate (except fiber)	45.7	182.9		

According to Table 4.11, sample10 which consists of 60% of chickpea flour, 15% carob flour and 15% hazelnut flour has a 496.9 kcal/100g and 22.6% of this energy comes from protein. Sample 10 has higher total energy than sample 1 which is predictable because the addition of carob and hazelnut flour affect the amount of fat and carbohydrate contents. 60% of chickpea flour is pretty high amount and considering the high protein content of chickpea flour, high energy comes from protein is expected. Moreover, it was observed that the addition of hazelnut flour increased the fiber content in 100 g cookie and in relation to this energy that comes from fiber source.

Table 4.12. Predicted nutritional values of sample 16 (30% chickpea flour, 30% carob flour, 30% hazelnut flour) (For energy calculation; carbohydrate = 4 kcalories per gram, protein = 4 kcalories per gram, fat = 9 kcalories per gram, fiber = 2 calories per gram)

Component	**g/100 g Cookie**	**Energy (kcal/100 g Cookie)**	**Total Energy (kcal/100 g cookie)**	**Energy% from protein**
Fat	32.9	296.0	510.9	*19.9*
Protein	8.7	34.8		
Moisture	8.9	0.0		
Ash	3.0	0.0		
Fiber	2.9	5.7		
Carbohydrate (except fiber)	43.6	174.4		

Table 4.12 shows the predicted nutritional values of sample16 which consists of 30% of chickpea flour, 30% carob flour and 30% hazelnut flour and this cookie has 510.9 kcal/100g and 19.9% of this energy comes from protein. Sample 16 has the highest total energy among the other samples, which is predictable because the added amounts of carob and hazelnut flour were increased and this affects the amount of fat and carbohydrate content directly. However, sample 16 has the lowest energy % comes from protein which is also expected since it has the lowest chickpea flour content among the others. Moreover, it was observed that if the amount of hazelnut flour increased fiber content in 100 g cookie sample and in relation to this energy that comes from fiber source also increased.

4.7. *In vitro* Starch Digestibility Analysis

The primary source of carbohydrates in the human diet is starch, which causes a spike in blood glucose levels after eating a starchy dish and up to 40% of the calories in a normal western diet come from starch (Bustos et al., 2017). Consuming foods high in rapidly digestible starch (RDS) increases the risk of obesity and incurable illnesses such as type II diabetes and cardiovascular disease. Rapid starch digestion in the small intestine creates a large and sudden postprandial glycemic peak. Consuming slowly digested starch (SDS), on the other hand, results in a slower release of energy, which aids in preserving glucose homeostasis (Ells et al., 2005). The degree of starch digestion in the human small intestine depends on both the intrinsic factors such as granular vs. gelatinized physical structures and extrinsic factors such as food viscosity, surrounding food matrix factors, amylose/amylopectin ratio, and morphology (Butterworth et al., 2011). Cookies often have moderate glycemic indices (GIs), ranging from 40 to 58, due to their high sugar content. The GI of the product is also affected by starch, and modifying how starch is digested may be able to further reduce the GI of starch-rich foods like cookies (Mulargia et al., 2022).

In our study, sample 16 was chosen to be investigated for *in vitro* starch digestibility since it collected the highest score from the sensory analysis. Sample 16 consists of 30% chickpea, 30% carob and 30% hazelnut flours. As a reference, cookie having only chickpea flour was also evaluated for *in vitro* digestibility. Starch digestibility can be considerably influenced by the type of ingredients, product composition, and food processing conditions, which has an impact on its metabolic conditions.

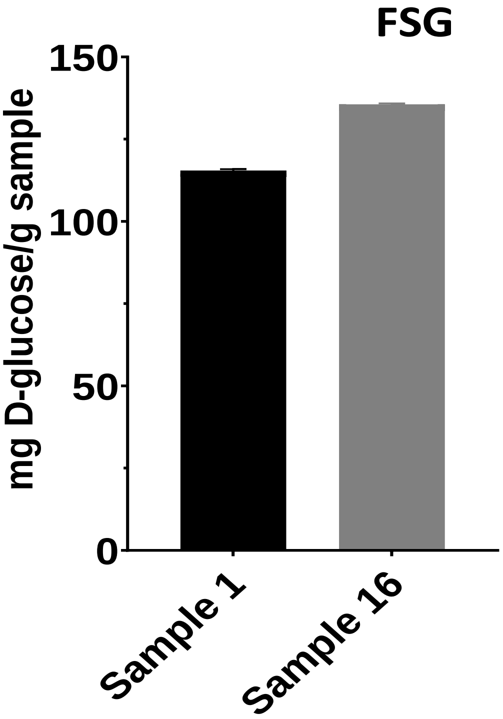

Figure 4.12. Free sugar glucose amount of Sample 16 and Sample 1 in terms of mg D-glucose/ g sample

According to Figure 4.12, The amount of free sugar glucose (FSG) of sample 16 is around 135 mg D-glucose/g sample. FSG indicates the sum of free glucose and glucose from the sucrose in the product. FSG of cookies made with 90% chickpea flour is lower which is around 115 mg D-glucose/g sample. Free sugars are defined as monosaccharides (like glucose and fructose) and disaccharides (like sucrose or table sugar) added to foods and beverages as well as sugars naturally present in honey, syrups, fruit juices, and fruit juice concentrates, according to the terminology and classification used by the WHO (World Health Organization) (Te Morenga et al., 2012). Since sample 16 contains 30% of carob flour, which have a relatively higher sugar content, a higher FSG compared to the sample having 90% chickpea flour (sample 1) is expected.

The lowest free sugar glucose values have been reported in legumes, which are also low in free sugar and low in the amount of rapidly digestible starch. It is likely that a combination of the starch granules being encapsulated by cell walls (dietary fiber) and not being fully gelatinized is what causes the slow and incomplete digestion of legume starch. Because of their solid structure, foods like spaghetti, macaroni, and pearled barley have a moderate free sugar glucose value (Englyst et al., 2000). Moreover, according to study by Fattore et al. (2017), there is convincing evidence that free sugars do not increase body weight or blood pressure when they are iso-energetically substituted for complex carbohydrates.

Figure 4.13 indicates the mg D-glucose amount/gram sample during digestion stages for the reference cookie (sample 1) and the sample 16. Firstly, in the gastric phase sample 16 has the lowest amount, which is around 126 mg D-glucose, compared to the intestinal phases. The intestinal phase amount is increased up to around 340 mg/g in the first 20 minute and then around to 405 mg in 120 minutes. This increase between phases is expected due to fact that the rapidly digestible (RDS) and slowly digestible (SDS) fractions together represent the amount of starch that is likely to be completely absorbed in the small intestine of a human. Any remaining starch is referred to as the resistant starch (RS) fraction, which is available for the fermentation in the large intestine (Englyst et al., 2000).

Firstly, at the end of the 20 minutes, result indicates the rapidly available glucose released from starch and sugars, and for determining rapidly digestible starch amount of cookie sample, the free sugar glucose amount should be subtracted from the amount of glucose at the 20th min. Moreover, for determining the amount of slowly digestible starch, available glucose amount at 20 min should be subtracted from the available glucose amount at the end of 120 minute (Englyst et al., 2018). Same trend also applies to digestion phases of cookie made with 90% chickpea flour which is sample 1. However, it has lower glucose level, around 93 mg/g in gastric phase but higher glucose levels of around 420 mg/g and 511 mg/g after 20 min and 120 min digestion in intestine, respectively. Also Figure 4.14 indicates the RDS (rapidly digestible glucose) and SDS (slowly digestible glucose) amount of reference cookie (sample 1) and sample 16. All these results indicate that, although the glucose value measured at the end of the gastric phase of sample 1 is lower than that of sample 16, it can be seen that the amount of glucose released in intestinal phase, glucose level of reference cookie (sample 1 which consists of 90% chickpea flour) is higher than sample 16, both at the end of the 20th minute and at the end of the 120th minute. This situation directly affects the RDS and SDS values of the samples. When we examine Figure 4.14, sample 1, known as the reference cookie sample, has a higher RDS value than sample 16. In addition, when we examine the SDS values, sample 1 still has a higher SDS value than sample 16. According to a study in literature, it was stated that it is important to note that increased SDS concentration is related to higher gelatinization enthalpy, average particle size, and relative crystallinity degree of starches (Ji, 2018). The reason for the differences between RDS and SDS values may be the differences in the contents of the cookie samples. Since Sample 1 contains 90% chickpea flour, it has a much higher protein content than sample 16. Also, since sample 16 contains 30% carob flour, 30% hazelnut flour and 30% chickpea flour, especially the fat and carbohydrate contents are higher than sample 1. Such differences may have directly affected the *in vitro* digestion results of the cookies.

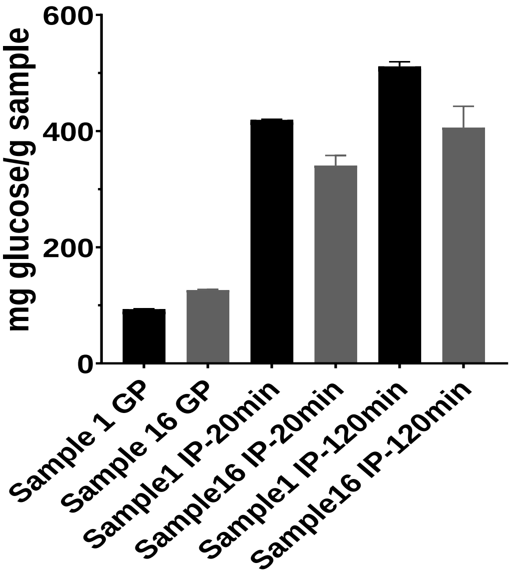

Figure 4.13. mg D-glucose / g sample amount of cookie sample 1 and 16 after gastric phase (GP), intestinal phase 20th min (IP-20) and 120th min (IP-120)

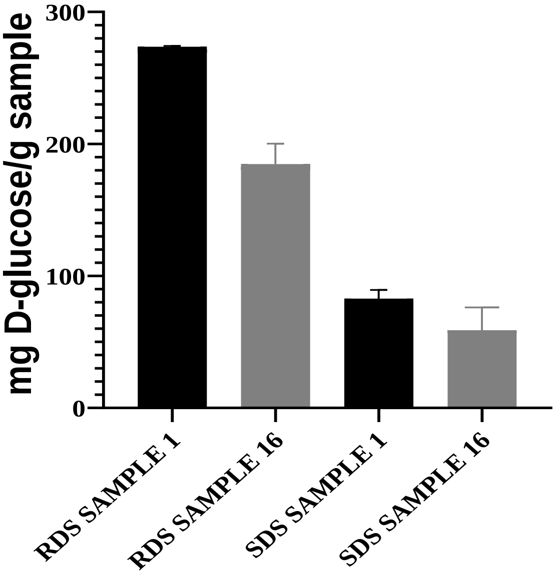

Figure 4.14. mg D-glucose / g sample amount of cookie sample 1 and in terms of rapidly digestible starch (RDS) and slowly digestible starch

CHAPTER 5

CONCLUSIONS

The aim of this study is the investigation of the rheological, spectroscopic and technological properties of gluten-free cookie formulations suitable for the consumption of patients with celiac and non-celiac gluten sensitivity. For this purpose, chickpea flour was used instead of wheat flour, and chickpea flour was substituted with carob and hazelnut flours in various proportions for different formulations. Physical, sensory, textural, and spectroscopic properties of developed cookies were determined. Moreover, the flours used in the production of gluten-free cookies and the doughs of these cookie samples were also examined in terms of physical, chemical, textural, and spectroscopic properties.

According to the results of the flour analyses, raw and pre-cooked chickpea flours have significantly higher protein content than wheat flour (almost two times higher). Hazelnut flour stands out with its high fat content, and it has approximately 35 times more fat than wheat flour and 6 times more than chickpea flour. Compositional differences directly affect both the sensory and physical properties of the cookie samples to which it is added. Also, hazelnut flour has very high fiber content which is one of the most important parameters affecting the consumer’s preference. Carob flour differs from the other flours with its high carbohydrate and phenolic content. It contains 25 times higher phenolics, which also affect the antioxidant capacity of the flour, than wheat flour and chickpea flour. When the physical properties of flours used in gluten-free cookie formulations were examined, pre-cooked chickpea flour stands out with its high-water retention capacity. It has approximately 3.5 times higher water retention capacity than wheat flour due to cooking treatment which boosted the chickpea flour's ability to hold onto water. Pre-cooked chickpea flour has also 2.2 times higher water retention capacity than raw chickpea flour.

In this research, gluten-free cookie blends included double and triple composite flours. Double composite flours are the blends of chickpea-hazelnut and chickpea-carob flours. According to the rheological properties of cookie doughs, sample containing 90% chickpea flour has the highest firmness value (37.72 N) and has the greatest difference from the other formulations. However, dough having the highest hazelnut content (60%) has the lowest firmness value of all the samples. Hazelnut provides the cookie product a softer texture because of its high fat content. Dough having 90% chickpea also has the highest consistency and viscosity index value among the others. Moreover, dough having the highest hazelnut flour in triple flour mixtures has the lowest firmness (1.23 N), consistency (4.43 N.sec), cohesiveness (0.90 N), and viscosity index (0.95 N.sec) values. As a result of evaluation of the rheological measurements, it can be concluded that the chickpea flour is added to gluten-free cookie dough increases all types of rheological parameters. In opposite, the rheological properties of cookie doughs are reduced when hazelnut and carob flour are added. Since these doughs are easier to work with, using chickpea and carob flours in the range of 30 to 60% provides more optimal outcomes for the rheological characteristics of the cookie dough. According to the physical properties, cookie which contains 60% hazelnut flour has the highest spread ratio value especially compared to cookie having only 90% of chickpea flour. A direct relation between increasing amounts of hazelnut flour and spread ratio was found while carob flour caused a decrease in the same parameter. Cookies made with carob and hazelnut flours indicate a decrease in hardness as the amounts of hazelnut flours increase. According to triple flour mixtures, the hardest sample is the one with 60% carob flour. The second-hardest sample is the cookie with 60% hazelnut flour high hazelnut flour level and high-fat percentage of this cookie resulted in a quite distinct cookie texture which made it difficult to break into two pieces, much like bread. Conversely, cookie recipes that use carob flour have a higher hardness value than those that use hazelnut flour.

All measured cookie parameters and spectroscopic profiles were also evaluated using a principal component analysis (PCA). According to PCA, all cookie dough samples containing double and triple composite flours are separated based on their formulations and cookie having only chickpea flour is distinguished from the others.

Considering all properties measured and personal experiences about the ease of handling of doughs, two cookie formulations were tested through sensory analysis compared to cookie containing only chickpea flour. From the sensory analysis of the cookies, it can be concluded that the addition of hazelnut and carob flour has a positive effect on the consumer preferences. *in vitro* digestion study was performed with the cookie sample that received the highest appreciation as a result of sensory analysis, and the reference cookie having only chickpea flour. According to the results of this analysis, it was determined that the reference cookie sample had a lower glucose value than the cookie with triple composite flour at the end of the gastric phase, while it had a higher glucose level than triple flour cookie at both the 20th and 120th minutes in the intestinal phase. In addition, RDS and SDS values were also calculated, the reference cookie has a higher RDS and SDS value. This can be explained by the fact that triple composite flour cookie has different flour types (chickpea, carob and hazelnut) content and the reference cookie has a high protein value due to 90% chickpea flour content.

In the light of this information, new usage areas of chickpea, carob and hazelnut flours used in the study can be investigated. In addition, thanks to its high protein content, gluten-free products to be produced with chickpea flour can replace gluten-free products with low nutritional values in the market.

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APPENDIX A

IMAGES OF COOKIE SAMPLES

Figure A. 1. Sample images of 1,2,3 and 4 respectively.

Figure A. 2. Sample images of 5,6,7 and 8 respectively.

Figure A. 3. Sample images of 9,10,11 and 12 respectively.

Figure A. 4. Sample images of 13,14,15 and 16 respectively.

Figure A. 5. Sample images of 17 and 18 respectively.

APPENDIX B

RESULTS OF MIXTURE DESIGN OF THE COOKIES MADE WITH TRIPLE FLOUR

Regression for Mixtures: Consistency (N.s) versus cpf; cf; hf

Estimated Regression Coefficients for Consistency (N.s) (component proportions)

Term	Coef	SE Coef	T-Value	P-Value	VIF
cpf	47,97	9,19	*	*	95,60
cf	66,85	8,72	*	*	89,69
Hf	5,24	9,19	*	*	95,60
cpf*cf	-209,9	49,4	-4,25	0,000	241,63
cpf*hf	-50,0	53,2	-0,94	0,359	256,79
cf*hf	-195,0	49,4	-3,95	0,001	241,63
cpf*cf*hf	802	224	3,57	0,002	365,41

Model Summary

S	R-sq	R-sq(adj)	PRESS	R-sq(pred)
1,74648	94,28%	92,48%	127,303	87,44%

Analysis of Variance for Consistency (N.s) (component proportions)

Source	DF	Seq SS	Adj SS	Adj MS	F-Value	P-Value
Regression	6	955,90	955,898	159,316	52,23	0,000
Linear	2	771,90	307,509	153,755	50,41	0,000
Quadratic	3	145,08	166,305	55,435	18,17	0,000
cpf*cf	1	10,12	55,052	55,052	18,05	0,000
cpf*hf	1	126,06	2,695	2,695	0,88	0,359
cf*hf	1	8,90	47,520	47,520	15,58	0,001
Special Cubic	1	38,91	38,913	38,913	12,76	0,002
cpf*cf*hf	1	38,91	38,913	38,913	12,76	0,002
Residual Error	19	57,95	57,953	3,050		
Total	25	1013,85				

Estimated Regression Coefficients for Consistency (N.s) (component amounts)

Term	Coef
cpf	0,532947
cf	0,742733
hf	0,058271
cpf*cf	-0,025909
cpf*hf	-0,006174
cf*hf	-0,024071
cpf*cf*hf	0,001100

Fits and Diagnostics for All Observations

Obs	StdOrder	Consistency (N.s)	Fit	SE Fit	Resid	Std Resid	
1	1	23,572	24,546	1,008	-0,974	-0,68	
2	2	18,679	18,459	1,008	0,220	0,15	
3	3	25,609	21,905	1,008	3,704	2,60	R
4	4	10,022	9,329	1,008	0,693	0,49	
5	5	4,516	4,426	1,008	0,090	0,06	
6	6	21,114	19,168	0,582	1,946	1,18	
7	7	20,749	19,168	0,582	1,581	0,96	
8	8	16,446	19,168	0,582	-2,722	-1,65	
9	9	26,110	24,546	1,008	1,564	1,10	
10	10	18,533	18,459	1,008	0,074	0,05	
11	11	21,707	19,710	1,235	1,997	1,62	
12	12	21,904	21,905	1,008	-0,001	-0,00	
13	13	9,537	9,329	1,008	0,208	0,15	
14	14	4,415	4,426	1,008	-0,011	-0,01	
15	15	20,272	19,168	0,582	1,104	0,67	
16	16	17,984	19,168	0,582	-1,184	-0,72	
17	17	19,631	19,168	0,582	0,463	0,28	
18	18	23,955	24,546	1,008	-0,591	-0,41	
19	19	18,165	18,459	1,008	-0,294	-0,21	
20	20	17,713	19,710	1,235	-1,997	-1,62	
21	21	18,203	21,905	1,008	-3,702	-2,60	R
22	22	8,429	9,329	1,008	-0,900	-0,63	
23	23	4,346	4,426	1,008	-0,080	-0,06	
24	24	18,712	19,168	0,582	-0,456	-0,28	
25	25	19,202	19,168	0,582	0,034	0,02	
26	26	18,406	19,168	0,582	-0,762	-0,46	

R Large residual

Regression for Mixtures: Firmness (N) versus cpf; cf; hf

Estimated Regression Coefficients for Firmness (N) (component proportions)

Term	Coef	SE Coef	T-Value	P-Value	VIF
cpf	13,80	2,11	*	*	95,60
cf	20,03	2,00	*	*	89,69
hf	0,75	2,11	*	*	95,60
cpf*cf	-60,0	11,3	-5,29	0,000	241,63
cpf*hf	-9,0	12,2	-0,73	0,472	256,79
cf*hf	-55,3	11,3	-4,88	0,000	241,63
cpf*cf*hf	210,8	51,5	4,09	0,001	365,41

Model Summary

S	R-sq	R-sq(adj)	PRESS	R-sq(pred)
0,400941	96,66%	95,61%	6,62083	92,77%

Analysis of Variance for Firmness (N) (component proportions)

Source	DF	Seq SS	Adj SS	Adj MS	F-Value	P-Value
Regression	6	88,461	88,4612	14,7435	91,71	0,000
Linear	2	71,932	29,8116	14,9058	92,72	0,000
Quadratic	3	13,838	15,8541	5,2847	32,87	0,000
cpf*cf	1	1,643	4,4932	4,4932	27,95	0,000
cpf*hf	1	10,795	0,0867	0,0867	0,54	0,472
cf*hf	1	1,401	3,8261	3,8261	23,80	0,000
Special Cubic	1	2,691	2,6908	2,6908	16,74	0,001
cpf*cf*hf	1	2,691	2,6908	2,6908	16,74	0,001
Residual Error	19	3,054	3,0543	0,1608		
Total	25	91,516				

Estimated Regression Coefficients for Firmness (N) (component amounts)

Term	Coef
cpf	0,153319
cf	0,222502
hf	0,008317
cpf*cf	-0,007402
cpf*hf	-0,001107
cf*hf	-0,006830
cpf*cf*hf	0,000289

Fits and Diagnostics for All Observations

Obs	StdOrder	Firmness (N)	Fit	SE Fit	Resid	Std Resid	
1	1	6,868	7,370	0,231	-0,502	-1,53	
2	2	5,288	5,443	0,231	-0,155	-0,47	
3	3	7,422	6,620	0,231	0,802	2,45	R
4	4	2,764	2,663	0,231	0,101	0,31	
5	5	1,204	1,230	0,231	-0,026	-0,08	
6	6	6,080	5,525	0,134	0,555	1,47	
7	7	5,658	5,525	0,134	0,133	0,35	
8	8	5,100	5,525	0,134	-0,425	-1,13	
9	9	7,834	7,370	0,231	0,464	1,42	
10	10	5,713	5,443	0,231	0,270	0,82	
11	11	6,377	5,935	0,284	0,442	1,56	
12	12	6,472	6,620	0,231	-0,148	-0,45	
13	13	2,723	2,663	0,231	0,060	0,18	
14	14	1,217	1,230	0,231	-0,013	-0,04	
15	15	5,848	5,525	0,134	0,323	0,85	
16	16	5,054	5,525	0,134	-0,471	-1,25	
17	17	5,572	5,525	0,134	0,047	0,12	
18	18	7,407	7,370	0,231	0,037	0,11	
19	19	5,329	5,443	0,231	-0,114	-0,35	
20	20	5,493	5,935	0,284	-0,442	-1,56	
21	21	5,966	6,620	0,231	-0,654	-2,00	
22	22	2,502	2,663	0,231	-0,161	-0,49	
23	23	1,270	1,230	0,231	0,040	0,12	
24	24	5,708	5,525	0,134	0,183	0,48	
25	25	5,462	5,525	0,134	-0,063	-0,17	
26	26	5,246	5,525	0,134	-0,279	-0,74	

R Large residual

Regression for Mixtures: Viscosity Index (N.s) versus cpf; cf; hf

Estimated Regression Coefficients for Viscosity Index (N.s) (component proportions)

Term	Coef	SE Coef	T-Value	P-Value	VIF
cpf	5,92	1,56	*	*	95,60
cf	11,18	1,48	*	*	89,69
hf	-0,05	1,56	*	*	95,60
cpf*cf	-27,67	8,41	-3,29	0,004	241,63
cpf*hf	0,56	9,06	0,06	0,951	256,79
cf*hf	-29,93	8,41	-3,56	0,002	241,63
cpf*cf*hf	117,1	38,2	3,06	0,006	365,41

Model Summary

S	R-sq	R-sq(adj)	PRESS	R-sq(pred)
0,297323	94,50%	92,77%	3,57590	88,30%

Analysis of Variance for Viscosity Index (N.s) (component proportions)

Source	DF	Seq SS	Adj SS	Adj MS	F-Value	P-Value
Regression	6	28,8843	28,8843	4,81405	54,46	0,000
Linear	2	22,2374	9,5447	4,77233	53,99	0,000
Quadratic	3	5,8168	5,2726	1,75753	19,88	0,000
cpf*cf	1	0,0074	0,9570	0,95699	10,83	0,004
cpf*hf	1	5,4749	0,0003	0,00034	0,00	0,951
cf*hf	1	0,3345	1,1194	1,11941	12,66	0,002
Special Cubic	1	0,8301	0,8301	0,83005	9,39	0,006
cpf*cf*hf	1	0,8301	0,8301	0,83005	9,39	0,006
Residual Error	19	1,6796	1,6796	0,08840		
Total	25	30,5639				

Estimated Regression Coefficients for Viscosity Index (N.s) (component amounts)

Term	Coef
cpf	0,065756
cf	0,124267
hf	-0,000570
cpf*cf	-0,003416
cpf*hf	0,000069
cf*hf	-0,003694
cpf*cf*hf	0,000161

Fits and Diagnostics for All Observations

Obs	StdOrder	Viscosity Index (N.s)	Fit	SE Fit	Resid	Std Resid	
1	1	4,071	4,126	0,172	-0,055	-0,23	
2	2	3,470	3,662	0,172	-0,192	-0,79	
3	3	4,722	4,218	0,172	0,504	2,08	R
4	4	2,057	1,935	0,172	0,122	0,50	
5	5	0,999	0,953	0,172	0,046	0,19	
6	6	4,169	3,683	0,099	0,486	1,73	
7	7	3,794	3,683	0,099	0,111	0,40	
8	8	3,336	3,683	0,099	-0,347	-1,24	
9	9	4,189	4,126	0,172	0,063	0,26	
10	10	3,790	3,662	0,172	0,128	0,53	
11	11	4,204	3,794	0,210	0,410	1,95	
12	12	4,133	4,218	0,172	-0,085	-0,35	
13	13	1,952	1,935	0,172	0,017	0,07	
14	14	0,923	0,953	0,172	-0,030	-0,12	
15	15	3,763	3,683	0,099	0,080	0,29	
16	16	3,205	3,683	0,099	-0,478	-1,70	
17	17	3,908	3,683	0,099	0,225	0,80	
18	18	4,117	4,126	0,172	-0,009	-0,04	
19	19	3,726	3,662	0,172	0,064	0,26	
20	20	3,384	3,794	0,210	-0,410	-1,95	
21	21	3,799	4,218	0,172	-0,419	-1,73	
22	22	1,795	1,935	0,172	-0,140	-0,58	
23	23	0,937	0,953	0,172	-0,016	-0,07	
24	24	3,851	3,683	0,099	0,168	0,60	
25	25	3,346	3,683	0,099	-0,337	-1,20	
26	26	3,772	3,683	0,099	0,089	0,32	

R Large residual

Regression for Mixtures: Cohessiveness (N) versus cpf; cf; hf

Estimated Regression Coefficients for Cohessiveness (N) (component proportions)

Term	Coef	SE Coef	T-Value	P-Value	VIF
cpf	6,09	1,48	*	*	95,60
cf	10,57	1,40	*	*	89,69
hf	-0,92	1,48	*	*	95,60
cpf*cf	-28,21	7,93	-3,56	0,002	241,63
cpf*hf	4,45	8,54	0,52	0,608	256,79
cf*hf	-25,65	7,93	-3,23	0,004	241,63
cpf*cf*hf	101,1	36,0	2,80	0,011	365,41

Model Summary

S	R-sq	R-sq(adj)	PRESS	R-sq(pred)
0,280501	94,84%	93,22%	3,05552	89,46%

Analysis of Variance for Cohessiveness (N) (component proportions)

Source	DF	Seq SS	Adj SS	Adj MS	F-Value	P-Value
Regression	6	27,4958	27,4958	4,58264	58,24	0,000
Linear	2	20,7546	10,2281	5,11404	65,00	0,000
Quadratic	3	6,1226	5,7471	1,91571	24,35	0,000
cpf*cf	1	0,2089	0,9947	0,99471	12,64	0,002
cpf*hf	1	5,6817	0,0214	0,02136	0,27	0,608
cf*hf	1	0,2320	0,8227	0,82270	10,46	0,004
Special Cubic	1	0,6186	0,6186	0,61858	7,86	0,011
cpf*cf*hf	1	0,6186	0,6186	0,61858	7,86	0,011
Residual Error	19	1,4949	1,4949	0,07868		
Total	25	28,9908				

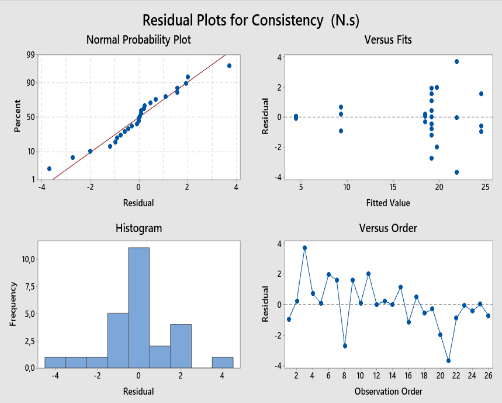
Estimated Regression Coefficients for Cohessiveness (N) (component amounts)

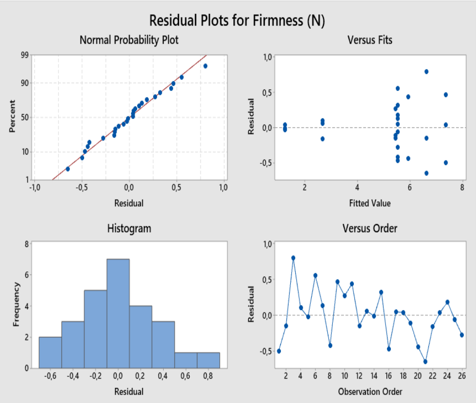
Term	Coef
cpf	0,067632
cf	0,117400
hf	-0,010210
cpf*cf	-0,003483
cpf*hf	0,000550
cf*hf	-0,003167
cpf*cf*hf	0,000139

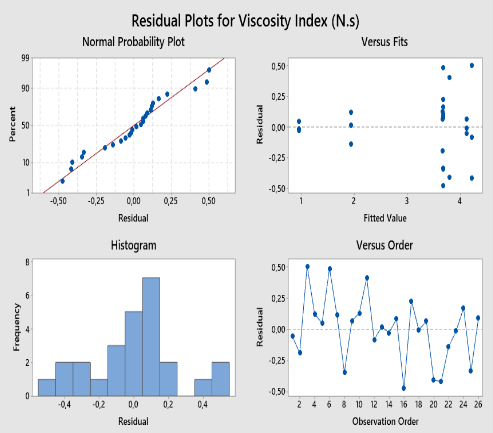
Fits and Diagnostics for All Observations

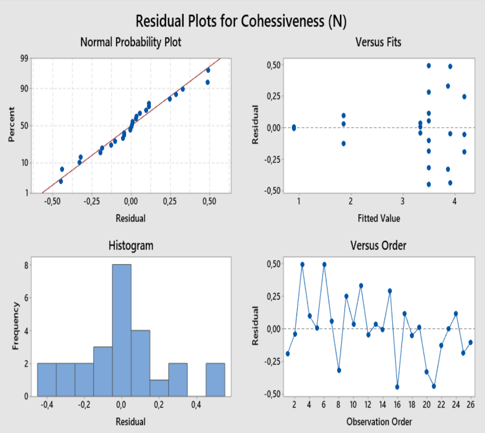
Obs	StdOrder	Cohessiveness (N)	Fit	SE Fit	Resid	Std Resid
1	1	3,990	4,185	0,162	-0,195	-0,85
2	2	3,296	3,340	0,162	-0,044	-0,19
3	3	4,405	3,916	0,162	0,489	2,14 R
4	4	1,952	1,855	0,162	0,097	0,42
5	5	0,899	0,895	0,162	0,004	0,02
6	6	3,991	3,498	0,094	0,493	1,87
7	7	3,554	3,498	0,094	0,056	0,21
8	8	3,176	3,498	0,094	-0,322	-1,22
9	9	4,432	4,185	0,162	0,247	1,08
10	10	3,375	3,340	0,162	0,035	0,15
11	11	4,203	3,871	0,198	0,332	1,67
12	12	3,869	3,916	0,162	-0,047	-0,20
13	13	1,886	1,855	0,162	0,031	0,14
14	14	0,890	0,895	0,162	-0,005	-0,02
15	15	3,784	3,498	0,094	0,286	1,08
16	16	3,048	3,498	0,094	-0,450	-1,70
17	17	3,610	3,498	0,094	0,112	0,43
18	18	4,133	4,185	0,162	-0,052	-0,23
19	19	3,349	3,340	0,162	0,009	0,04
20	20	3,539	3,871	0,198	-0,332	-1,67
21	21	3,473	3,916	0,162	-0,443	-1,93
22	22	1,726	1,855	0,162	-0,129	-0,56
23	23	0,896	0,895	0,162	0,001	0,00
24	24	3,610	3,498	0,094	0,112	0,43
25	25	3,312	3,498	0,094	-0,186	-0,70
26	26	3,393	3,498	0,094	-0,105	-0,40

R Large residual









Regression for Mixtures: Moisture (%) versus cpf; cf; hf

Estimated Regression Coefficients for Moisture (%) (component proportions)

Term	Coef	SE Coef	T-Value	P-Value	VIF
cpf	2,02	1,41	*	*	22,80
cf	10,95	1,13	*	*	14,53
hf	4,45	1,13	*	*	14,53
cpf*cf	12,98	5,64	2,30	0,026	30,77
cpf*hf	15,48	5,64	2,74	0,008	30,77

Model Summary

S	R-sq	R-sq(adj)	PRESS	R-sq(pred)
0,796323	61,88%	58,77%	34,6033	57,55%

Analysis of Variance for Moisture (%) (component proportions)

Source	DF	Seq SS	Adj SS	Adj MS	F-Value	P-Value
Regression	4	50,442	50,442	12,6104	19,89	0,000
Linear	2	41,762	23,920	11,9602	18,86	0,000
Quadratic	2	8,680	8,680	4,3398	6,84	0,002
cpf*cf	1	3,903	3,359	3,3591	5,30	0,026
cpf*hf	1	4,776	4,776	4,7760	7,53	0,008
Residual Error	49	31,072	31,072	0,6341		
Lack-of-Fit	2	2,983	2,983	1,4916	2,50	0,093
Pure Error	47	28,089	28,089	0,5976		
Total	53	81,514				

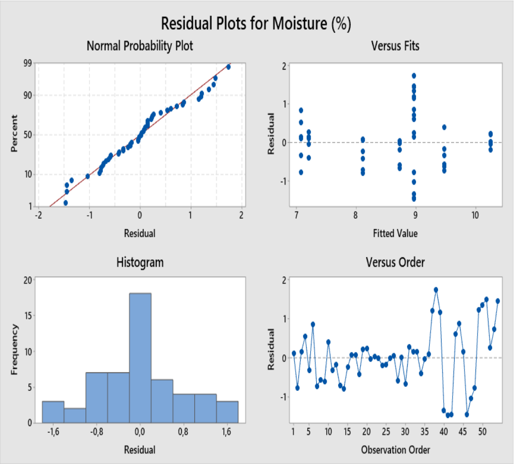
Estimated Regression Coefficients for Moisture (%) (component amounts)

Term	Coef
cpf	0,022446
cf	0,121682
hf	0,049416
cpf*cf	0,001602
cpf*hf	0,001911

Fits and Diagnostics for All Observations

Obs	StdOrder	Moisture (%)	Fit	SE Fit	Resid	Std Resid
1	1	7,177	7,075	0,322	0,102	0,14
2	2	6,302	7,075	0,322	-0,773	-1,06
3	3	7,220	7,075	0,322	0,145	0,20
4	4	7,605	7,075	0,322	0,531	0,73
5	5	6,739	7,075	0,322	-0,336	-0,46
6	6	7,918	7,075	0,322	0,843	1,16
7	7	8,738	9,474	0,279	-0,736	-0,99
8	8	8,895	9,474	0,279	-0,579	-0,78
9	9	8,847	9,474	0,279	-0,627	-0,84
10	10	9,874	9,474	0,279	0,400	0,54
11	11	9,140	9,474	0,279	-0,334	-0,45
12	12	9,298	9,474	0,279	-0,176	-0,24
13	13	7,391	8,108	0,279	-0,717	-0,96
14	14	7,302	8,108	0,279	-0,806	-1,08
15	15	7,868	8,108	0,279	-0,240	-0,32
16	16	8,178	8,108	0,279	0,070	0,09
17	17	8,182	8,108	0,279	0,073	0,10
18	18	7,675	8,108	0,279	-0,433	-0,58
19	19	10,463	10,251	0,295	0,212	0,29
20	20	10,483	10,251	0,295	0,232	0,31
21	21	10,211	10,251	0,295	-0,039	-0,05
22	22	10,267	10,251	0,295	0,016	0,02
23	23	10,223	10,251	0,295	-0,027	-0,04
24	24	10,056	10,251	0,295	-0,195	-0,26
25	25	8,540	8,729	0,186	-0,188	-0,24
26	26	8,714	8,729	0,186	-0,015	-0,02
27	27	8,764	8,729	0,186	0,035	0,05
28	28	8,137	8,729	0,186	-0,592	-0,76
29	29	8,741	8,729	0,186	0,012	0,02
30	30	8,053	8,729	0,186	-0,676	-0,87
31	31	7,473	7,207	0,295	0,266	0,36
32	32	7,356	7,207	0,295	0,149	0,20
33	33	7,351	7,207	0,295	0,144	0,19
34	34	6,794	7,207	0,295	-0,413	-0,56
35	35	7,166	7,207	0,295	-0,041	-0,05
36	36	7,300	7,207	0,295	0,093	0,13
37	37	10,165	8,968	0,140	1,197	1,53
38	38	10,711	8,968	0,140	1,744	2,22 R
39	39	10,125	8,968	0,140	1,157	1,48
40	40	7,607	8,968	0,140	-1,360	-1,74
41	41	7,492	8,968	0,140	-1,476	-1,88
42	42	7,513	8,968	0,140	-1,454	-1,86
43	43	9,572	8,968	0,140	0,604	0,77
44	44	9,836	8,968	0,140	0,868	1,11
45	45	9,119	8,968	0,140	0,151	0,19
46	46	7,515	8,968	0,140	-1,453	-1,85
47	47	7,925	8,968	0,140	-1,043	-1,33
48	48	8,191	8,968	0,140	-0,777	-0,99
49	49	10,177	8,968	0,140	1,209	1,54
50	50	10,320	8,968	0,140	1,352	1,72
51	51	10,450	8,968	0,140	1,482	1,89
52	52	9,214	8,968	0,140	0,246	0,31
53	53	9,686	8,968	0,140	0,718	0,92
54	54	10,420	8,968	0,140	1,452	1,85

R Large residual



Regression for Mixtures: Spread Factor versus cpf; cf; hf

Estimated Regression Coefficients for Spread Factor (component proportions)

Term	Coef	SE Coef	T-Value	P-Value	VIF
cpf	4,321	0,249	*	*	14,63
cf	3,560	0,244	*	*	14,46
hf	13,245	0,304	*	*	22,83
cpf*hf	-16,11	1,23	-13,15	0,000	30,97
cf*hf	-9,63	1,21	-7,93	0,000	30,73

Model Summary

S	R-sq	R-sq(adj)	PRESS	R-sq(pred)
0,231717	95,71%	95,53%	5,62109	95,12%

Analysis of Variance for Spread Factor (component proportions)

Source	DF	Seq SS	Adj SS	Adj MS	F-Value	P-Value
Regression	4	110,320	110,320	27,5799	513,66	0,000
Linear	2	96,933	83,615	41,8073	778,64	0,000
Quadratic	2	13,387	13,387	6,6934	124,66	0,000
cpf*hf	1	10,012	9,286	9,2863	172,95	0,000
cf*hf	1	3,375	3,375	3,3747	62,85	0,000
Residual Error	92	4,940	4,940	0,0537		
Lack-of-Fit	2	0,083	0,083	0,0415	0,77	0,467
Pure Error	90	4,857	4,857	0,0540		
Total	96	115,259				

Estimated Regression Coefficients for Spread Factor (component amounts)

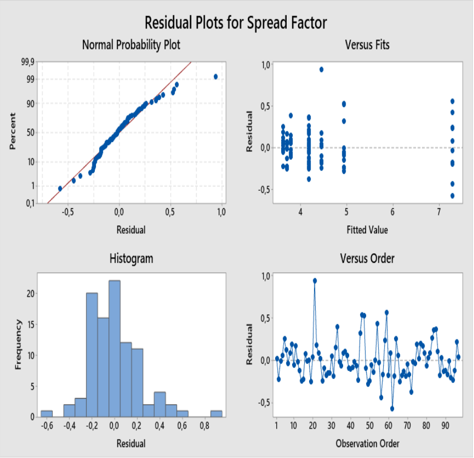
Term	Coef
cpf	0,048015
cf	0,039559
hf	0,147172
cpf*hf	-0,001989
cf*hf	-0,001188

Fits and Diagnostics for All Observations

Obs	StdOrder	Spread Factor	Fit	SE Fit	Resid	Std Resid
1	1	3,6419	3,6243	0,0665	0,0176	0,08
2	2	3,3920	3,6243	0,0665	-0,2324	-1,05
3	3	3,6122	3,6243	0,0665	-0,0122	-0,05
4	4	3,6742	3,6243	0,0665	0,0498	0,22
5	5	3,8733	3,6243	0,0665	0,2489	1,12
6	6	3,7468	3,6243	0,0665	0,1225	0,55
7	7	3,5871	3,6243	0,0665	-0,0372	-0,17
8	8	3,7072	3,6243	0,0665	0,0829	0,37
9	9	3,8113	3,6243	0,0665	0,1869	0,84
10	10	3,5669	3,6243	0,0665	-0,0575	-0,26
11	11	3,8664	3,7044	0,0412	0,1621	0,71
12	12	3,6851	3,7044	0,0412	-0,0193	-0,08
13	13	3,5757	3,7044	0,0412	-0,1287	-0,56
14	14	3,4581	3,7044	0,0412	-0,2463	-1,08
15	15	3,4771	3,7044	0,0412	-0,2272	-1,00
16	16	3,7730	3,7044	0,0412	0,0687	0,30
17	17	3,6879	3,7044	0,0412	-0,0164	-0,07
18	18	3,7007	3,7044	0,0412	-0,0037	-0,02
19	19	3,4522	3,7044	0,0412	-0,2521	-1,11
20	20	3,7432	3,7044	0,0412	0,0389	0,17
21	21	5,3871	4,4474	0,0601	0,9397	4,20 R
22	22	4,6214	4,4474	0,0601	0,1740	0,78
23	23	4,5321	4,4474	0,0601	0,0848	0,38

24	24	4,4615	4,4474	0,0601	0,0141	0,06	
25	25	4,2014	4,4474	0,0601	-0,2460	-1,10	
26	26	4,3483	4,4474	0,0601	-0,0991	-0,44	
27	27	4,2690	4,4474	0,0601	-0,1784	-0,80	
28	28	4,2897	4,4474	0,0601	-0,1577	-0,70	
29	29	4,2902	4,4474	0,0601	-0,1572	-0,70	
30	30	4,4894	4,4474	0,0601	0,0420	0,19	
31	31	4,2604	4,4474	0,0601	-0,1870	-0,84	
32	32	3,9358	3,7844	0,0640	0,1514	0,68	
33	33	4,1727	3,7844	0,0640	0,3883	1,74	
34	34	3,7599	3,7844	0,0640	-0,0245	-0,11	
35	35	3,7204	3,7844	0,0640	-0,0640	-0,29	
36	36	3,8624	3,7844	0,0640	0,0780	0,35	
37	37	3,8878	3,7844	0,0640	0,1034	0,46	
38	38	3,8388	3,7844	0,0640	0,0544	0,24	
39	39	3,6863	3,7844	0,0640	-0,0981	-0,44	
40	40	3,6757	3,7844	0,0640	-0,1087	-0,49	
41	41	3,6981	3,7844	0,0640	-0,0863	-0,39	
42	42	3,7599	3,7844	0,0640	-0,0245	-0,11	
43	43	4,8600	4,9328	0,0601	-0,0728	-0,33	
44	44	4,6978	4,9328	0,0601	-0,2350	-1,05	
45	45	5,2480	4,9328	0,0601	0,3152	1,41	
46	46	5,4677	4,9328	0,0601	0,5349	2,39	R
47	47	5,4549	4,9328	0,0601	0,5221	2,33	R
48	48	4,8396	4,9328	0,0601	-0,0932	-0,42	
49	49	4,6481	4,9328	0,0601	-0,2846	-1,27	
50	50	4,6852	4,9328	0,0601	-0,2476	-1,11	
51	51	4,8760	4,9328	0,0601	-0,0568	-0,25	
52	52	4,7863	4,9328	0,0601	-0,1465	-0,65	
53	53	4,9264	4,9328	0,0601	-0,0064	-0,03	
54	54	7,7105	7,2843	0,0693	0,4262	1,93	
55	55	7,2500	7,2843	0,0693	-0,0343	-0,16	
56	56	6,8411	7,2843	0,0693	-0,4432	-2,00	R
57	57	7,1089	7,2843	0,0693	-0,1754	-0,79	
58	58	7,5155	7,2843	0,0693	0,2311	1,05	
59	59	7,8454	7,2843	0,0693	0,5610	2,54	R
60	60	7,1068	7,2843	0,0693	-0,1775	-0,80	
61	61	7,3650	7,2843	0,0693	0,0807	0,36	
62	62	6,7056	7,2843	0,0693	-0,5787	-2,62	R
63	63	7,0900	7,2843	0,0693	-0,1943	-0,88	
64	64	7,5316	7,2843	0,0693	0,2472	1,12	
65	65	4,2379	4,1828	0,0302	0,0551	0,24	
66	66	3,9257	4,1828	0,0302	-0,2571	-1,12	
67	67	4,0000	4,1828	0,0302	-0,1828	-0,80	
68	68	4,0493	4,1828	0,0302	-0,1334	-0,58	
69	69	3,9934	4,1828	0,0302	-0,1894	-0,82	
70	70	4,1336	4,1828	0,0302	-0,0492	-0,21	
71	71	4,0069	4,1828	0,0302	-0,1759	-0,77	
72	72	3,8026	4,1828	0,0302	-0,3802	-1,65	
73	73	4,1655	4,1828	0,0302	-0,0173	-0,08	
74	74	4,1379	4,1828	0,0302	-0,0449	-0,20	
75	75	4,3714	4,1828	0,0302	0,1886	0,82	
76	76	4,1979	4,1828	0,0302	0,0151	0,07	
77	77	4,3777	4,1828	0,0302	0,1949	0,85	
78	78	4,3464	4,1828	0,0302	0,1636	0,71	
79	79	4,2643	4,1828	0,0302	0,0815	0,35	
80	80	4,1181	4,1828	0,0302	-0,0647	-0,28	
81	81	4,2049	4,1828	0,0302	0,0221	0,10	
82	82	4,2660	4,1828	0,0302	0,0832	0,36	
83	83	4,4424	4,1828	0,0302	0,2597	1,13	
84	84	4,5401	4,1828	0,0302	0,3574	1,56	
85	85	4,5481	4,1828	0,0302	0,3654	1,59	
86	86	4,2837	4,1828	0,0302	0,1009	0,44	
87	87	4,0033	4,1828	0,0302	-0,1795	-0,78	
88	88	4,2100	4,1828	0,0302	0,0272	0,12	
89	89	4,0503	4,1828	0,0302	-0,1325	-0,58	
90	90	4,0600	4,1828	0,0302	-0,1228	-0,53	
91	91	4,0132	4,1828	0,0302	-0,1695	-0,74	
92	92	4,1701	4,1828	0,0302	-0,0127	-0,06	
93	93	3,9700	4,1828	0,0302	-0,2128	-0,93	
94	94	3,9470	4,1828	0,0302	-0,2358	-1,03	
95	95	4,0608	4,1828	0,0302	-0,1220	-0,53	
96	96	4,3993	4,1828	0,0302	0,2165	0,94	
97	97	4,2183	4,1828	0,0302	0,0355	0,15	

R Large residual



Regression for Mixtures: Hardness (N) versus cpf; cf; hf

Estimated Regression Coefficients for Hardness (N) (component proportions)

Term	Coef	SE Coef	T-Value	P-Value	VIF
cpf	9,02	1,48	*	*	24,88
cf	16,03	1,44	*	*	24,15
hf	5,77	1,44	*	*	24,54
cpf*cf	-24,53	5,70	-4,30	0,000	31,55
cpf*hf	-22,40	5,60	-4,00	0,000	31,07
cf*hf	-12,87	5,55	-2,32	0,023	30,91

Model Summary

S	R-sq	R-sq(adj)	PRESS	R-sq(pred)
1,05667	71,63%	70,08%	114,985	67,90%

Analysis of Variance for Hardness (N) (component proportions)

Source	DF	Seq SS	Adj SS	Adj MS	F-Value	P-Value
Regression	5	256,595	256,595	51,3191	45,96	0,000
Linear	2	206,248	32,644	16,3220	14,62	0,000
Quadratic	3	50,348	50,348	16,7826	15,03	0,000
cpf*cf	1	25,216	20,645	20,6454	18,49	0,000
cpf*hf	1	19,132	17,895	17,8952	16,03	0,000
cf*hf	1	6,000	6,000	6,0003	5,37	0,023
Residual Error	91	101,606	101,606	1,1165		
Lack-of-Fit	1	14,782	14,782	14,7822	15,32	0,000
Pure Error	90	86,823	86,823	0,9647		
Total	96	358,201				

Estimated Regression Coefficients for Hardness (N) (component amounts)

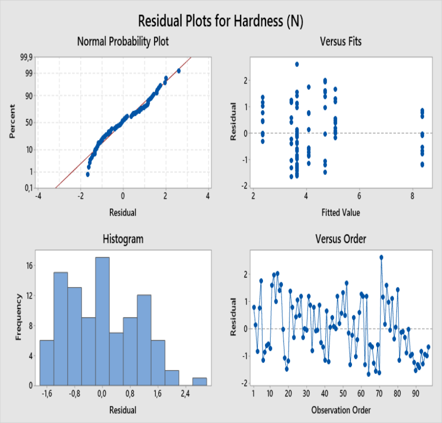
Term	Coef
cpf	0,100230
cf	0,178093
hf	0,064153
cpf*cf	-0,003028
cpf*hf	-0,002766
cf*hf	-0,001589

Fits and Diagnostics for All Observations

Obs	StdOrder	Hardness (N)	Fit	SE Fit	Resid	Std Resid
1	1	4,846	4,075	0,332	0,771	0,77
2	2	4,196	4,075	0,332	0,121	0,12
3	3	3,234	4,075	0,332	-0,841	-0,84
4	4	4,823	4,075	0,332	0,748	0,75
5	5	5,821	4,075	0,332	1,746	1,74
6	6	2,906	4,075	0,332	-1,169	-1,17
7	7	3,194	4,075	0,332	-0,881	-0,88
8	8	3,458	4,075	0,332	-0,617	-0,62
9	9	3,505	4,075	0,332	-0,570	-0,57
10	10	3,342	4,075	0,332	-0,733	-0,73
11	11	6,263	4,691	0,295	1,572	1,55
12	12	6,642	4,691	0,295	1,951	1,92
13	13	5,673	4,691	0,295	0,982	0,97
14	14	6,707	4,691	0,295	2,016	1,99
15	15	6,082	4,691	0,295	1,391	1,37
16	16	6,303	4,691	0,295	1,612	1,59
17	17	4,652	4,691	0,295	-0,039	-0,04
18	18	3,615	4,691	0,295	-1,076	-1,06
19	19	3,200	4,691	0,295	-1,491	-1,47
20	20	3,489	4,691	0,295	-1,202	-1,18
21	21	3,718	2,349	0,285	1,369	1,35
22	22	3,114	2,349	0,285	0,765	0,75
23	23	2,020	2,349	0,285	-0,329	-0,32

24	24	2,781	2,349	0,285	0,432	0,42	
25	25	3,387	2,349	0,285	1,038	1,02	
26	26	2,827	2,349	0,285	0,478	0,47	
27	27	3,524	2,349	0,285	1,175	1,15	
28	28	2,017	2,349	0,285	-0,332	-0,33	
29	29	2,347	2,349	0,285	-0,002	-0,00	
30	30	2,296	2,349	0,285	-0,053	-0,05	
31	31	3,524	2,349	0,285	1,175	1,15	
32	32	9,222	8,373	0,317	0,849	0,84	
33	33	7,565	8,373	0,317	-0,808	-0,80	
34	34	9,157	8,373	0,317	0,784	0,78	
35	35	8,277	8,373	0,317	-0,096	-0,10	
36	36	8,323	8,373	0,317	-0,050	-0,05	
37	37	9,222	8,373	0,317	0,849	0,84	
38	38	7,842	8,373	0,317	-0,531	-0,53	
39	39	7,696	8,373	0,317	-0,677	-0,67	
40	40	7,199	8,373	0,317	-1,174	-1,16	
41	41	9,016	8,373	0,317	0,643	0,64	
42	42	7,160	8,373	0,317	-1,213	-1,20	
43	43	5,145	5,094	0,285	0,051	0,05	
44	44	5,479	5,094	0,285	0,385	0,38	
45	45	5,163	5,094	0,285	0,069	0,07	
46	46	5,094	5,094	0,285	0,000	0,00	
47	47	6,277	5,094	0,285	1,183	1,16	
48	48	5,282	5,094	0,285	0,188	0,18	
49	49	5,653	5,094	0,285	0,559	0,55	
50	50	6,397	5,094	0,285	1,303	1,28	
51	51	5,575	5,094	0,285	0,481	0,47	
52	52	6,762	5,094	0,285	1,668	1,64	
53	53	4,920	5,094	0,285	-0,174	-0,17	
54	54	2,099	3,423	0,317	-1,324	-1,31	
55	55	3,182	3,423	0,317	-0,241	-0,24	
56	56	3,824	3,423	0,317	0,401	0,40	
57	57	2,388	3,423	0,317	-1,035	-1,03	
58	58	3,020	3,423	0,317	-0,403	-0,40	
59	59	3,998	3,423	0,317	0,575	0,57	
60	60	4,683	3,423	0,317	1,260	1,25	
61	61	4,590	3,423	0,317	1,167	1,16	
62	62	2,099	3,423	0,317	-1,324	-1,31	
63	63	4,596	3,423	0,317	1,173	1,16	
64	64	1,750	3,423	0,317	-1,673	-1,66	
65	65	3,033	3,630	0,150	-0,597	-0,57	
66	66	2,948	3,630	0,150	-0,682	-0,65	
67	67	2,364	3,630	0,150	-1,266	-1,21	
68	68	2,061	3,630	0,150	-1,569	-1,50	
69	69	3,016	3,630	0,150	-0,614	-0,59	
70	70	2,006	3,630	0,150	-1,624	-1,55	
71	71	6,252	3,630	0,150	2,622	2,51	R
72	72	4,783	3,630	0,150	1,153	1,10	
73	73	3,771	3,630	0,150	0,141	0,14	
74	74	5,202	3,630	0,150	1,572	1,50	
75	75	4,596	3,630	0,150	0,966	0,92	
76	76	3,557	3,630	0,150	-0,073	-0,07	
77	77	4,735	3,630	0,150	1,105	1,06	
78	78	3,231	3,630	0,150	-0,399	-0,38	
79	79	3,687	3,630	0,150	0,057	0,05	
80	80	5,054	3,630	0,150	1,424	1,36	
81	81	2,455	3,630	0,150	-1,175	-1,12	
82	82	3,481	3,630	0,150	-0,149	-0,14	
83	83	3,503	3,630	0,150	-0,127	-0,12	
84	84	3,295	3,630	0,150	-0,335	-0,32	
85	85	2,727	3,630	0,150	-0,903	-0,86	
86	86	3,595	3,630	0,150	-0,035	-0,03	
87	87	2,628	3,630	0,150	-1,002	-0,96	
88	88	2,666	3,630	0,150	-0,964	-0,92	
89	89	2,386	3,630	0,150	-1,244	-1,19	
90	90	2,071	3,630	0,150	-1,559	-1,49	
91	91	2,286	3,630	0,150	-1,344	-1,28	
92	92	2,188	3,630	0,150	-1,442	-1,38	
93	93	2,786	3,630	0,150	-0,844	-0,81	
94	94	2,318	3,630	0,150	-1,312	-1,25	
95	95	2,671	3,630	0,150	-0,959	-0,92	
96	96	2,626	3,630	0,150	-1,004	-0,96	
97	97	2,941	3,630	0,150	-0,689	-0,66	

R Large residual



Regression for Mixtures: BWL versus cpf; cf; hf

Estimated Regression Coefficients for BWL (component proportions)

Term	Coef	SE Coef	T-Value	P-Value	VIF
cpf	17,864	0,802	*	*	14,63
cf	9,482	0,784	*	*	14,46
hf	19,602	0,980	*	*	22,83
cpf*hf	-37,60	3,94	-9,53	0,000	30,97
cf*hf	13,07	3,91	3,34	0,001	30,73

Model Summary

S	R-sq	R-sq(adj)	PRESS	R-sq(pred)
0,746012	64,20%	62,65%	55,5514	61,16%

Analysis of Variance for BWL (component proportions)

Source	DF	Seq SS	Adj SS	Adj MS	F-Value	P-Value
Regression	4	91,829	91,829	22,9572	41,25	0,000
Linear	2	36,987	54,527	27,2633	48,99	0,000
Quadratic	2	54,842	54,842	27,4210	49,27	0,000
cpf*hf	1	48,621	50,565	50,5653	90,86	0,000
cf*hf	1	6,221	6,221	6,2211	11,18	0,001
Residual Error	92	51,201	51,201	0,5565		
Lack-of-Fit	2	10,163	10,163	5,0815	11,14	0,000
Pure Error	90	41,038	41,038	0,4560		
Total	96	143,030				

Estimated Regression Coefficients for BWL (component amounts)

Term	Coef
cpf	0,198492
cf	0,105352
hf	0,217800
cpf*hf	-0,004641
cf*hf	0,001613

Fits and Diagnostics for All Observations

Obs	StdOrder	BWL	Fit	SE Fit	Resid	Std Resid
1	1	13,330	12,943	0,214	0,387	0,54
2	2	13,970	12,943	0,214	1,027	1,44
3	3	13,260	12,943	0,214	0,317	0,44
4	4	13,640	12,943	0,214	0,697	0,98
5	5	12,640	12,943	0,214	-0,303	-0,42
6	6	12,600	12,943	0,214	-0,343	-0,48
7	7	12,700	12,943	0,214	-0,243	-0,34
8	8	12,400	12,943	0,214	-0,543	-0,76
9	9	12,600	12,943	0,214	-0,343	-0,48
10	10	12,000	12,943	0,214	-0,943	-1,32
11	11	13,220	12,958	0,133	0,262	0,36
12	12	13,790	12,958	0,133	0,832	1,13
13	13	13,890	12,958	0,133	0,932	1,27
14	14	13,300	12,958	0,133	0,342	0,47
15	15	12,100	12,958	0,133	-0,858	-1,17
16	16	11,800	12,958	0,133	-1,158	-1,58
17	17	11,800	12,958	0,133	-1,158	-1,58
18	18	14,120	12,958	0,133	1,162	1,58
19	19	14,360	12,958	0,133	1,402	1,91
20	20	14,360	12,958	0,133	1,402	1,91
21	21	12,100	11,572	0,193	0,528	0,73
22	22	12,700	11,572	0,193	1,128	1,57
23	23	11,800	11,572	0,193	0,228	0,32
24	24	11,500	11,572	0,193	-0,072	-0,10
25	25	11,700	11,572	0,193	0,128	0,18
26	26	11,900	11,572	0,193	0,328	0,46
27	27	11,620	11,572	0,193	0,048	0,07
28	28	12,150	11,572	0,193	0,578	0,80
29	29	12,100	11,572	0,193	0,528	0,73
30	30	12,500	11,572	0,193	0,928	1,29
31	31	12,400	11,572	0,193	0,828	1,15
32	32	13,660	12,973	0,206	0,687	0,96
33	33	13,660	12,973	0,206	0,687	0,96
34	34	13,500	12,973	0,206	0,527	0,73
35	35	12,800	12,973	0,206	-0,173	-0,24

36	36	12,600	12,973	0,206	-0,373	-0,52
37	37	12,800	12,973	0,206	-0,173	-0,24
38	38	12,500	12,973	0,206	-0,473	-0,66
39	39	13,000	12,973	0,206	0,027	0,04
40	40	12,800	12,973	0,206	-0,173	-0,24
41	41	12,600	12,973	0,206	-0,373	-0,52
42	42	12,500	12,973	0,206	-0,473	-0,66
43	43	14,940	14,754	0,193	0,186	0,26
44	44	14,750	14,754	0,193	-0,004	-0,01
45	45	15,340	14,754	0,193	0,586	0,81
46	46	14,940	14,754	0,193	0,186	0,26
47	47	15,000	14,754	0,193	0,246	0,34
48	48	15,500	14,754	0,193	0,746	1,04
49	49	15,700	14,754	0,193	0,946	1,31
50	50	15,300	14,754	0,193	0,546	0,76
51	51	15,400	14,754	0,193	0,646	0,90
52	52	15,100	14,754	0,193	0,346	0,48
53	53	15,500	14,754	0,193	0,746	1,04
54	54	15,640	14,900	0,223	0,740	1,04
55	55	15,670	14,900	0,223	0,770	1,08
56	56	15,700	14,900	0,223	0,800	1,12
57	57	14,600	14,900	0,223	-0,300	-0,42
58	58	14,400	14,900	0,223	-0,500	-0,70
59	59	14,500	14,900	0,223	-0,400	-0,56
60	60	14,300	14,900	0,223	-0,600	-0,84
61	61	14,600	14,900	0,223	-0,300	-0,42
62	62	14,500	14,900	0,223	-0,400	-0,56
63	63	14,100	14,900	0,223	-0,800	-1,12
64	64	14,600	14,900	0,223	-0,300	-0,42
65	65	12,020	12,924	0,097	-0,904	-1,22
66	66	11,670	12,924	0,097	-1,254	-1,70
67	67	12,360	12,924	0,097	-0,564	-0,76
68	68	12,220	12,924	0,097	-0,704	-0,95
69	69	11,540	12,924	0,097	-1,384	-1,87
70	70	12,780	12,924	0,097	-0,144	-0,19
71	71	12,500	12,924	0,097	-0,424	-0,57
72	72	11,600	12,924	0,097	-1,324	-1,79
73	73	12,500	12,924	0,097	-0,424	-0,57
74	74	12,360	12,924	0,097	-0,564	-0,76
75	75	11,540	12,924	0,097	-1,384	-1,87
76	76	13,660	12,924	0,097	0,736	0,99
77	77	12,090	12,924	0,097	-0,834	-1,13
78	78	14,290	12,924	0,097	1,366	1,85
79	79	13,810	12,924	0,097	0,886	1,20
80	80	13,410	12,924	0,097	0,486	0,66
81	81	13,590	12,924	0,097	0,666	0,90
82	82	12,780	12,924	0,097	-0,144	-0,19
83	83	12,850	12,924	0,097	-0,074	-0,10
84	84	13,330	12,924	0,097	0,406	0,55
85	85	13,330	12,924	0,097	0,406	0,55
86	86	14,360	12,924	0,097	1,436	1,94
87	87	11,500	12,924	0,097	-1,424	-1,93
88	88	11,460	12,924	0,097	-1,464	-1,98
89	89	11,860	12,924	0,097	-1,064	-1,44
90	90	12,240	12,924	0,097	-0,684	-0,92
91	91	11,860	12,924	0,097	-1,064	-1,44
92	92	12,710	12,924	0,097	-0,214	-0,29
93	93	12,570	12,924	0,097	-0,354	-0,48
94	94	12,430	12,924	0,097	-0,494	-0,67
95	95	12,150	12,924	0,097	-0,774	-1,05
96	96	12,900	12,924	0,097	-0,024	-0,03
97	97	12,570	12,924	0,097	-0,354	-0,48

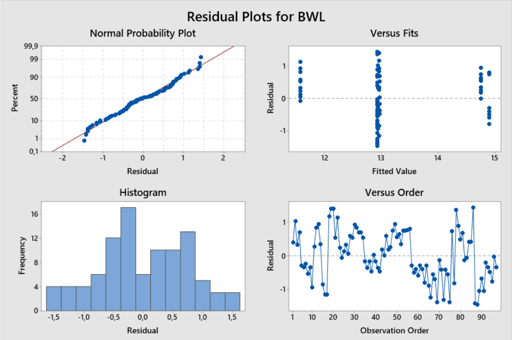


Figure B.1. Minitab outputs of mixture design