RHEOLOGICAL PROPERTIES OF SPAGHETTI ENRICHED WITH RESISTANT STARCH

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ABSTRACT

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Spaghetti samples were produced with control, 5 % and 15 % as resistant starch type III (RS_3) in the formulation. Since RS_3 containing spaghetti was planned to be an alternative for bran containing spaghetti, a commercial bran containing spaghetti was included into the research. Main quality parameters of interest were viscoelasticity, texture and thermal properties of spaghetti besides some well-defined criteria like colour, cooking loss and water absorption. Viscoelasticity was tested by both stress relaxation and creep. The results were modelled by Maxwell, Burger and Peleg models. In general Peleg model was determined to be the best model for both creep and stress relaxation data. Texture profile analysis was done to better understand textural attributes and the results were compared with a panel test. Firmness and adhesiveness, which are the most important textural parameters for spaghetti cooking quality, were found to increase with increasing RS_3 amount in the formulation. Thermal properties of cooked and uncooked samples were also investigated. The onset and peak temperatures of gelatinisation were found 58 and 64 ^{o}C, respectively. Enthalpy values of all spaghetti samples decreased with increase in cooking time. In vitro RS_3 determinations showed that the amount of RS_3 (g/100 g dry sample) in 5 % RS_3 formulated spaghetti is 4.90 and in 15 % RS_3, 7.57. This showed that amount of RS_3 in the end product was increased from low levels to intermediate and high levels successfully. During cooking the amount of RS_3 can be increased to higher values.

Cooking loss values which is an indicator of amount of dry matter lost into the cooking water increased as cooking time increased. It was a also found that spaghetti with 15 % RS_3 in the formulation gave the highest cooking loss values. However, water absorption values were highest for spaghetti produced with 5 % RS_3 in the formulation also there was an increase in water absorption values with increase in cooking time. Enrichment of spaghetti with RS_3 in the formulation made the color of spaghetti a little pale.

Key words: Spaghetti, Resistant starch, Rheology, Viscoelasticity, Texture

ÖZET

DİRENÇLİ NİŞASTA KATKILI SPAGETTİNİN REOLOJİK ÖZELLİKLERİ

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Spagetti numuneleri kontrol, % 5 ve % 15 tip III dirençli nişasta (DN_3) katkılı olarak üretildi. Dirençli nişasta katkılı spagetti, kepekli spagettiye alternatif bir ürün olarak düşünüldüğünden, ticari kepekli spagetti de çalışmaya dahil edilmiştir. Renk, pişme kaybı ve su absorplanması gibi yaygın olarak kullanılan kalite parametrelerinin yanı sıra bu çalışmada temel olarak spagetti numunelerinin viskoelastik, dokusal ve termal özelliklerine değinilmiştir. Viskoelastik özellikler, gerilim-gevşeme ve sürünme testleriyle incelendi. Sonuçlar, Maxwell, Burger ve Peleg denklemleriyle modellendi. Genel olarak Peleg modeli hem gerilim-gevşeme hem de sürünme verileri için en uygun modeldi. Doku profil analizi, pişirilmiş spagettinin dokusal özelliklerini daha iyi anlamak amacıyla yapıldı, verileri duyusal panelle karşılaştırıldı. Spagettinin dokusal özellikleri açısından en önemli iki parametre olan sertlik ve yapışkanlık formülasyonda DN_3 miktarı arttıkça arttı. Pişirilmemiş ve pişirilmiş spagettinin termal özellikleri incelendi. Jelatinizasyonun başlangıç ve bitiş sıcaklığı sırasıyla 58 ve 64 ^{o}C bulundu. Pişme zamanı arttıkça bütün numunelerin entalpi değerleri düştü. Dirençli nişasta miktarı, % 5 ve 15 DN_3 katkılı spagettide % kuru madde cinsinden 4,90 ve 7,57 olarak bulundu. Bu sonuçlar göstermiştir ki son üründe DN_3 miktarı düşük seviyelerden daha yüksek seviyelere çıkarılabilir.

Pişme kaybı değerleri pişme suyuna geçen madde miktarını göstermektedir. Pişme zamanı ve formülasyondaki DN_3 miktarı arttıkça pişme kaybını arttığı bulundu. Bununla beraber, su absorplama değerleri % 5 DN_3 katkılı spagetti için en fazlaydı ve pişme zamanıyla birlikte su absorplama değerleri de arttı.

Spagettinin DN_3 katkısıyla üretilmesi sonucunda kontrol spagettiye kıyasla rengin biraz daha açık olduğu bulundu.

Anahtar kelimeler: Spagetti, Dirençli nişasta, Reoloji, Viskoelastik, Tekstür

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Dedicated to my mother Hanife….

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LIST OF ABBREVIATIONS

a^*	Redness
ANOVA	Analysis of variance
λ_n	Relaxation time (s)
λ_{ret}	Retardation time (s)
b^*	Yellowness
C^*	Chromacity
D_b	Deborah number
D_n	Compliance (kPa^{-1})
db	Dry basis
DSC	Differential scanning calorimeter
E	Modulus of elasticity (Pa)
ΔE	Absorbance read against blank
F	Force (N)
F_c	Conversion from absorbance to micrograms
G	Modulus of rigidity (Pa)
GI	Glycemic index
HT	High temperature
ΔH_t	Gelatinization enthalpy at various cooking times (J/g)
ΔHs	Gelatinization enthalpy of semolina (J/g)
K	Bulk modulus (Pa)
k_1, k_2	Peleg constants
L^*	Brightness
LT	Low temperature
μ_o	Newtonian viscosity (Pa.s)
SCCs	Short chain carbohydrates
SCFA	Short chain fatty acids
RDS	Rapidly digestible starch
RS	Resistant starch
RMS	Root mean square

SDS	Slowly digestible starch
σ_n	Stress
TPA	Texture profile analysis
t	Time (min)
T_o	Onset temperature (^oC)
T_c	Conclusion temperature (^oC)
T_m	Melting temperature (^oC)
VHT	Very high temperature
W	Dry weight of sample analyzed (g)
Wb	Wet basis
YI	Yellowness index

CHAPTER I

INTRODUCTION

The very first story of pasta begins with the Greek myth. The 'Greek God, Vulcan,' invented a device that made "strings of dough." History is very unclear as to whether pasta originated in the Arabic countries or in China. There are also some evidences that Arabs invented the noodles cooked by boiling which was called as itriyah. As a wrong belief it was not Marco Polo who introduced spaghetti to the Italians. Sicilians and Neapolitians were eating macaroni for two thousand years before Marco Polo was born. It is more probable that the ancient Arabic mariner, Sinbad the Sailor, in trading with China discovered their use of dies or presses for extruding their egg cereal grain mixture to make drying easier (www.sreweb.com).

It is undisputable that pasta is a staple in the Italian diet, but this has not always been so. As recent as the 1500's macaroni (the term for any dried pasta) was considered an exotic food, reserved only for the upper class. This was because pasta was an expensive food to produce due to the high costs of importing the proper wheat; the time-intensive labor required for making pasta; and the precise weather requirements necessary for drying and preserving pasta (www.barillaus.com).

Some historians think the Sicilian word "maccaruni" which translates as "made into a dough by force" is the origin of our word, macaroni. Anyone who has kneaded durum wheat knows that force is necessary. Pasta became more popular in Italy because the climate was perfect for growing durum wheat which is the main source of dried pasta.

By the 1300's dried pasta was very popular for its nutrition and long shelf life, making it ideal for long ship voyages. By that time different shapes of pasta have appeared and new technology made pasta easier to make (www.lifeinitaly.com).

A characteristic common to all pasta is the initial preparation of dough that can be extruded or drawn to obtain the desired shapes (Kruger et al., 1996). The components of the dough are normally semolina (flour) and water, or semolina (flour), water and eggs.

The aim of the pasta-making process is to transform semolina into a mixture with a homogeneous structure that is able to maintain a particular shape, which is than stabilized by drying (Kruger et al., 1996). Semolina and water not only make up pasta, but also make the difference between one pasta and another. Semolina and flour are obtained by milling wheat. It is known that the principal classification for grain distinguishes between the "soft" ones and the "durum" ones. And finally it is known that flour is obtained from soft grain and semolina is obtained from hard grain by milling. Flour, by classic standards, is good for making leavened products (bread, biscuits, baked desserts, etc.). On the other hand, semolina, are destined to the pasta factories.

1.1 Wheat grain and semolina

1.1.1 The kernel of wheat

For millers, the caryopsis is a small masterpiece of nature made up of external layers and an internal kernel. From the wheat caryopsis, the mill must obtain flour (or semolina), trying to reconcile the yield from milling with the quality of the product obtained. "Yield" simply means that more flour (or semolina) is obtained from the grain; gain is greater from both a productive and economic standpoint. On the other hand, "quality" refers to the fact that the flour (or semolina) must be as well suited as possible for its intended use (bread, pasta, etc.). It is obvious that the "quality" does not only depend on the "yield", but mainly on the chemical-physical and original intrinsic characteristics of the milled wheat in addition to the technology and the machines used for this purpose.

The external layers and the internal kernel of the grain have their own specific chemical and morphological characteristics. In the external layers of the caryopsis, the chemical characteristics are given by the concentration of cellulose (fiber), minerals, and protein. In the internal kernel, the presence of starches is dominant. There is a third, distinct part of the caryopsis, the "germ". It is the embryo destined to

create a new plant. The wheat germ is rich in fats that can easily go rancid. For this reason, during milling, it must be removed from each grain so that its fats are not lost in the flour (or in the semolina) making preservation precarious. The "strategic" objective of modern wheat milling (for both soft and durum wheat) is the internal kernel of the grain, a concentration of starches that, in addition to another basic chemical component, protein, make up the nutritional (and technological) nucleus of the wheat and the products obtained from milling wheat.

1.1.2 Chemical composition of soft wheat and durum wheat

Table 1.1 indicates reconcentration of the chemical elements that most interest the flour and semolina intended for use in making pasta (Milatovic and Mondelli, 1991). The external part of the grain (pericarp and perisperm) is formed by different layers of intercrossing cellulose.

Table 1.1 Chemical components of the wheat (%)

Components	Minimum	Maximum
Protein (Nx5.7)	7.0	18.0
Ash	1.5	2.0
Fats	1.5	2.0
Water (moisture)	8.0	18.0
Starch	60.0	68.0
Pentosans	6.2	8.0
Saccharose	0.2	0.6
Maltose	0.6	4.3
Cellulose	1.9	5.0

The chemical composition of the grain is made up of cellulose, minerals (bran) and protein with a high biological value. However, due to the low sifting rates of the flour (and the semolina), the protein is practically lost. The external part of the wheat caryopsis is largely made up of indigestible and irritating parts (cellulose and lignin) as well as minerals (ashes) that can interact, creating undesirable compositions during the technological production processes of both dried and fresh pasta. From a technological standpoint, the low sifting of the flour and the semolina determines a

"rational" sacrifice of the biodynamic components present in the external layers of the caryopsis (the protein in the aleuronic layer). A good percentage of these components are, however, present in more highly sifted flour (and semolina).

In modern mills (high milling) the sifting rate determines the type of flour and semolina. The relationship between the principal chemical characteristics of the flour and the sifting rate are very close, even if these characteristics always depend on the intrinsic characteristics of the grains that are milled. Durum wheat is a major stable in pasta production. In fact, the quality requirements of pasta are wholly satisfied by durum wheat only.

1.1.2.1 Starch

Starch, which is the major dietary source of carbohydrates, is the most abundant storage polysaccharide in plants, and occurs as granules in the chloroplast of green leaves and the amyloplast of seeds, pulses and tubers. It is found in cereals in the form of granules act as an energy reservoir during growing of seeds. It is composed of polymers of only one monosaccharide: glucose, from this point it can be concluded that its simple in composition but on the other hand complicated in structure and function. In almost all cereal food products, the native starch granule structure is destroyed as in starch gelatinization.

On an industrial scale starch is produced by separating it from other plant materials, such as fiber, proteins, sugars and salts. The most common sources from which starch is isolated are potato tubers, wheat kernels and corn. Each type of starch is unique. Potato starch granules are largest (15-100 µm diameter), ellipsoidal in shape, and asymmetric with respect to the position of the hilum. Corn starch granules have a more polyhedral shape, varying in size from 5 to 25 µm. In wheat starch two types of granules occur; lenticular A granules with a diameter of 10-45 µm and polyhedral B granules with a diameter up to 10 µm.

1.1.2.1.1 Composition and structure of starch

Starch granules are composed of mainly of a mixture of two large polysaccharide molecules, amylose and amylopectin. In most native starches amylose content is in the range 25 % to 29 %, but waxy and high amylose varieties also exist. Amylose is

an essentially linear molecule consisting of α-D-glucopyranose residues linked together by (1-4) bonds (Figure 1.1). The length of amylose chains among different plant species is variable but usually ranges between 10^2 to 10^4 glucose units (Eliasson and Tatham, 2001; Ponstein, 1990). Amylose has a degree of polymerization (DP) up to 6000 and has a molecular mass of 105 to 106 g/mol (Sajilata et al., 2006). Amylose molecules tend to retrograde from aqueous solutions. This results for instance in the formation of skins on hot pastes. The rate of retrogradation depends on the amount of amylose, the degree of polymerization (the higher, the lower the rate of retrogradation) and the lipid content (the higher, the higher the rate of retrogradation) (Ponstein, 1990).

Amylopectin is the highly branched component (Figure 1.1) of starch with a molecular weight of 10^7 to 10^9. On average, 4-5 % of the glucose residues carry, besides the (1-4) bond, a (1-6) bond to an adjacent residue (Tester et al., 2004). Amylopectin (107 to 109 g/mol) has an average DP of 2 million, making it one of the largest molecules in the nature (Sajilata et al., 2006). Amylopectin is structurally similar to glycogen, the only storage polysaccharide found in bacteria and mammals. Amylopectin contains fewer branch points than glycogen. Moreover, the fine structure of glycogen is different from the fine structure of amylopectin (Ponstein, 1990).

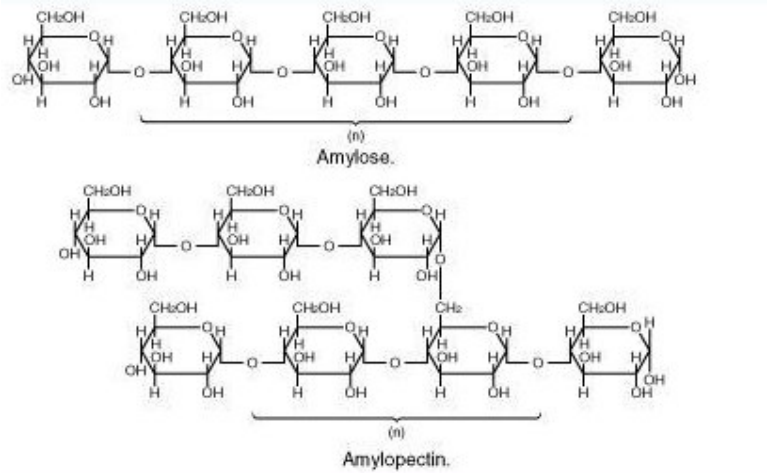

Figure 1.1 Amylose and amylopectin chains

Amylose and amylopectin are deposited in starch granules together with small amounts of lipid, protein, and phosphorus. The minor components in starch may

affect the behavior of starch in various applications such as amylose-lipid complexes reduce the swelling capacity of cereal starches.

Starch can be grouped in two different categories; according to X-ray diffraction and regarding to action of enzymes. Three types of starches, designated as type A, type B, type C, have been identified based on X-ray diffraction patterns. These depend partly on the chain lengths making up the amylopectin lattice, the density of packing within the granules, and the presence of water. Three types of chains, namely A, B and C are distinguished in the highly branched amylopectin (Figure 1.2). The most peripheral chains are A-chains, which are connected to B-chains. Type A structure consists of 23 to 29 glucose units, which is very common in cereals. The type B structure consists of amylopectin of chain lengths of 30 to 44 glucose molecules with water inter-spread. This is the usual pattern of starches found in raw potato and banana. The backbone of the amylopectin molecule is the C-chain, where the B- and A- chains are bound. Additionally, the C-chain has the reducing end- group. The C pattern is typical of peas and beans (Sajilata et al., 2006; Zweifel, 2001).

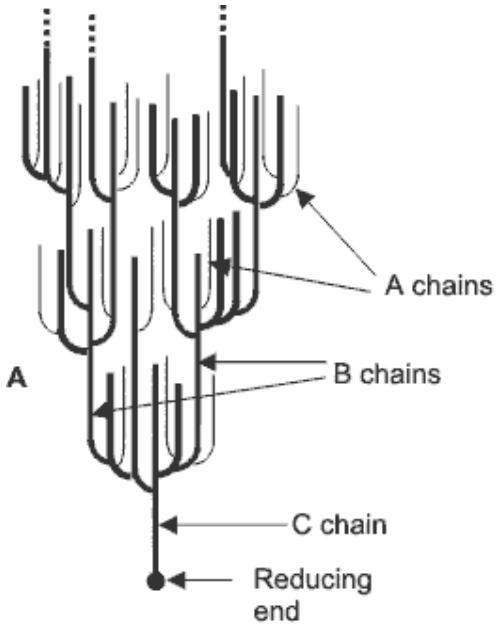

Figure 1.2 Cluster structure of amylopectin

Starches can be classified regarding to their behavior when incubated with enzymes without prior exposure to dispersing agents as follows:

Rapidly digestible starch (RDS): RDS consists mainly of amorphous and dispersed starch and is found in high amounts in starchy foods cooked by moist heat, such as bread and potatoes.

Slowly digestible starch (SDS): Like RDS, SDS is expected to be completely digested in the small intestine, but it is digested more slowly. This category consists of physically inaccessible amorphous starch and raw starch with a type A and type C crystalline structure, such as cereals and type B starch, either in the granule form or retrograded form in cooked foods (Sajilata et al., 2006).

Resistant starch: Resistant starch (RS) was first recognized as a complicating factor in the determination of total dietary fiber levels by the Prosky Method. Since the definition of dietary fiber specifies 'non-starch polysaccharides', it is clear that any form of starch, which interferes with the assay, is not a traditional fiber, and others are unique to starch (Haralampu, 2000). By definition, RS is that portion of starch that is not broken down by human enzymes in the small intestine. It enters the large intestine where it is partially or wholly fermented (Sajilata et al., 2006; Brown, 2004; McCleary and Monaghan, 2002; Haralampu, 2000; Brighenti et al., 1998). RS is considered by many to be a part of dietary fiber. The characteristics of RS are similar to those of insoluble fibers, since it does not affect postprandial insulin, glucose and free fatty acid response after a glucose load and, once in the colon, it moderately increases stool weight. However, like soluble fiber, RS is a substrate for microbial fermentation, giving origin to end products, mainly short chain fatty acids, and influencing lipid and N metabolism in human and animal studies (Brighenti et al., 1998). RS is divided into four subcategories: RS_1, RS_2, RS_3, and RS_4 or type I, II, III, and IV starches.

RS_1 represents starch that is resistant because it is in a physically inaccessible form such as partially milled grains and seeds and in some very dense types of processed starchy foods. It is measured chemically as the difference between the glucose released by the enzyme digestion of a homogenized food sample and that released

from a nonhomogenized sample. RS_1 is heat stable in most normal cooking operations and enables its use as an ingredient in a wide variety of conventional foods.

RS_2 represents starch that is in a certain granular form and resistant to enzyme digestion. It is measured chemically as the difference between the glucose released by the enzyme digestion of a boiled homogenized food sample and that from an unboiled, nonhomogenized food sample. In raw starch granules, starch is tightly packed in a radial pattern and is relatively dehydrated. This compact structure limits the accessibility of digestive enzymes, various amylases, and accounts for the resistant nature of RS_2 such as, ungelatinized starch. In the diet, raw starch is consumed in foods like banana. RS_1 and RS_2 represent residues of starch forms, which are digested very slowly and incompletely in the small intestine.

RS_3 represents the most resistant starch fraction and is mainly retrograded amylose formed during cooling of gelatinized starch. Most moist-heated foods therefore contain some RS_3. It is measured chemically as the fraction, which resists both dispersion by boiling and enzyme digestion. It can only be dispersed by KOH or dimethyl sulphoxide. RS_3 is entirely resistant to digestion by pancreatic amylases. Among the resistant starches RS_3 seems to be more interesting. As mentioned above it contains mainly retrograded amylose with a melting temperature of 150 ^{o}C. This property makes RS_3 an appropriate candidate as a heat-stable pre-biotic food additive, which may be used in cooked or baked goods (Shamai et al., 2003).

RS_4 is the RS where novel chemical bonds other than α- (1-4) or α-(1-6) are formed. Modified starches obtained by various types of chemical treatments are included in this category (Sajilata et al., 2006).

1.1.2.1.2 Factors influencing the formation of resistant starch

The following factors have an influence on the formation of RS.

1. Crystallinity of starch: Any treatment that eliminates starch crystallinity like gelatinization or the integrity of the plant cell or tissue structure increases enzyme availability and reduces the content of RS, whereas recrystallinization and chemical modifications tend to increase.

2. Granular structure: A large variability in susceptibility to amylases shown by raw starch granules has an influence on RS formation. For example, potato starch and high amylose maize starch are known to be very resistant in vitro and incompletely absorbed in vivo. The smaller surface-to-volume ratio of the large potato granules is probably important. The nature of the granule surface also needs to be considered; an adsorbed layer of non-starch material would effectively impede the action of the enzyme.
3. Amylose to amylopectin ratio: A higher content of amylose lowers the digestibility of starch due to positive correlation between amylose content and formation of RS.
4. Retrogradation of amylose: When heated to about 50 ^{o}C, in the presence of water, the amylose in the granule swells, the crystalline structure of the amylopectin disintegrates and the granule ruptures. The polysaccharide chains take up a random configuration, causing swelling of the starch and thickening of the surrounding matrix such as, gelatinization. On cooling/drying, recrystallinization (retrogradation) occurs. The rate and extent to which a starch may retrograde after gelatinization essentially depends on the amount of amylose present. Repeated autoclaving of wheat starch may generate up to 10 % RS. The level obtained appeared to be strongly related to the amylose content, and the retrogradation of amylose was identified as the main mechanism for formation of RS that can be generated in larger amounts by repeated autoclaving.
5. Heat and moisture: Water content is an important factor that affects formation of RS. Repeated heat/moisture treatment is associated with a decrease in the hydrolysis limit of pancreatic α-amylase and increased formation of RS.

1.1.2.1.3 Physiological benefits of resistant starch

In modern societies, great emphasis is frequently placed on the relationship between health, lifestyle and diet. As a result, today's consumers are more aware of what they eat. But, it is still a fact that many individuals do not get the fiber their bodies need to work efficiently and feel comfortable. The significance of fiber and resistant starch for the prevention of civilization related diseases causes us to pay more attention to materials rich in these components. The relatively recent recognition of incomplete digestion and absorption of starch in the small intestine as a normal phenomenon has

raised interest in nondigestible starch fractions. These are called “resistant starches”, and extensive studies have shown them to have physiological functions similar to those of dietary fiber (Brighenti et a., 1998; Haralampu, 2000; McCleary and Monaghan, 2002; Sajilata et al., 2006; Thompson, 2000). RS is highly resistant to mammalian enzymes. In cereal products, the RS fraction is not digestible both in vitro and vivo. Four different RS fractions have been identified in cereal products: native starch, retrograded amylose, the amylo-lipid complex, and encapsulated gelatinized starch. After reaching the large intestine, the RS fractions are fermented by the colonic flora, resulting in short chain fatty acids (SCFA). SCFA profiles derived from RS are lower in acetate and higher in butyrate (Sajilata et al., 2006).

The amount of butyrate produced during colonic fermentation, is highest in resistant starch as compared to other dietary fibers like oat-wheat bran, cellulose, guar gum and pectin (Eliasson, 2004). Butyrate is an important substrate for the colonocyte, and appears to be special relevance in relation to the welfare of the epithelium of the colon (Brighenti et al., 1998). The produced butyrate inhibits division of cancer cells and proliferation if colonic mucosal cells and inhibits potential mutagens, such as nitrosamide and hydrogen peroxide in human colon cells (Kim et al., 2005). Probiotics are food ingredients that stimulate selectively the growth and activity of specific species of bacteria in the gut, usually bifidobacteria and lactobacilli, with benefits to health. In practice, they are short-chain carbohydrates (SCCs) that are nondigestible by human enzymes and that have been called resistant SCCs (Shamai et al., 2003; Cummings et al., 2001).

The major products of prebiotic metabolism are SCFA, the gases hydrogen and carbondioxide, and bacterial cell mass (Cummings et al., 2001). The presence of increased amounts of RS in the colon causes increased fecal bulk, increased levels of SCFA in the colon, and reduced pH of the colon which all contribute to improvement in colon health. Consumption of RS, alters lipid metabolism, improves cholesterol metabolism, and reduce the risk of ulcerative colitis and colon cancer (Giczewska and Borowska, 2003; Shamai et al., 2003). Foods containing RS moderate the rate of digestion. The slow digestion of RS has a control mechanism on glucose release. The metabolism of RS occurs 5 to 7 h after consumption, in contrast to normally cooked starch, which is digested almost immediately (Sajilata et al., 2006). Digestion over a

5 to 7 h period reduces postprandial glycemia and insulinemia and has the potential for increasing the period of satiety. Replacement of 5.4 % of total dietary carbohydrates with RS in a meal could significantly increase postprandial lipid oxidation suggesting reduction in fat accumulation in the long term (Sajilata et al., 2006).

Fibers are thought to be useful food supplements, partly because they lower glycemic index (GI). The GI of a food or meal is defined as the development of the glucose level of the blood in time compared to that of white bread (GI=100). Low GI diet decreases the glucose and insulin response during the day and also the LDL-cholesterol level. Some diets with low GI lead to a bigger feeling of satiety and a delayed feeling of hunger. For RS the opinions are split: some found a clear lowering GI, whereas the others only found an effect on the colon. This difference could be caused by differences in the type of resistant starch.

1.1.2.1.4 Functionality of resistant starch

Resistant starch, which is a natural component that is present in many foods, has a role to play with regard to the nutritional benefits of fiber fortification. Resistant starch offers advantages over cellulosic sources of fiber such as bran. It provides low water holding capacity thereby aiding processing; it enhances the organoleptic qualities of food as a replacement for, or complement to, natural fiber and it can be labeled as ‘dietary fiber’.

The additional benefits of using RS as a food ingredient in place of fiber is in mouth feel, color, flavor, and low water holding ability. These properties make the product more applicable to a wider range of food products than fiber. By contributing to the dietary fiber content of the food, the value of a food ingredient could be increased if fiber claims were made on the product. It has desirable physicochemical properties such as swelling, viscosity increase, gel formation, and water binding capacity, making it useful in a variety of foods. These properties make it possible to use most resistant starches to replace flour on a one for one basis without significantly affecting dough handling and rheology.

1.1.2.1.5 Preparation of resistant starch

RS can be prepared by using heat treatment, enzyme treatment, combined heat treatment and enzyme treatment, and chemical treatment. Heat treatment of starch to various extents, leads to formation of RS. RS can be obtained by cooking the starch above the gelatinization temperature and simultaneously drying. By use of thermally stable α-amylase, a preparation of up to 70 % RS can be obtained. Preparation of RS to be used as a food grade bulking agent, by retrogradation of starch followed by enzymatic or chemical hydrolysis to reduce or remove the amorphous regions of retrograded starch. RS_3 can be prepared from high amylose starch by gelatinization followed by treating the slurry with debranching enzymes like pullulanase and isolating the starch product by drying/extrusion. RS_4 is obtained by modifying the starch by cross-linking with chemical agents. Cross linked starches are obtained by the reaction of starch with bi- or polyfunctional reagents like sodium trimetaphosphate, phosphorus oxychloride or mixed anhydrides of acetic acid and dicarboxylic acids like apidic acid.

1.1.2.1.6 Recommended daily intake of resistant starch

Dietary Recommendations for dietary fiber is 38 and 25 g/day for men and women of age 19-50, respectively (Institute of Medicine, 2002). The alternative recommendation for dietary fiber is 10-13 g/1000 kcal intake. For a non-insulin dependent diabetes mellitus patient, the upper level of recommended intake is 40 g/day. An obese, non-insulin-dependent diabetes mellitus patient is recommended to have 25 g dietary fiber/ 1000 kcal. In families with a history of diet-implicated cancers, they are recommended to have 35-40 g/day of dietary fiber. In the hypercholesterolemic, up to 50g/day would be beneficial in maintaining a normal level of serum cholesterol (Groff and Gropper, 1999). The Food Guide Pyramid recommends 3-5 servings of fruits and vegetables, and 6-11 servings of grains and starches in our daily diet. It is also recommended that fiber-rich legumes are incorporated in the diet; at least 2-3 servings per day of whole grains are consumed regularly as part of the total grains intake. The United States Department of Agriculture provides the public with a tabulation of nutrient contents of each food item. Even though the table offers accurate information on daily dietary fiber intake, it would be inconvenient to constantly refer to it. Therefore the USDA made a generic formula for calculating fiber content in fruits, vegetables, grains and cereals.

The rough estimate of DF intake is within 10 % of the actual results obtained by looking up each individual food's fiber content (Groff and Gropper, 1999). It is also recommended that dietary fiber intake be slowly increased so that our bodies are given time to adjust to the change. Our bodies are not capable of digesting fiber and while fiber is in transit in our gastrointestinal tracts, fermentation occurs. Bloating, cramps, and gas might occur and cause discomfort. Beans and legumes are good sources of fiber, however often they also cause gas to develop due to fermentation of the oligosaccharides. The problem can be easily alleviated over time.

Other ways of increasing fiber intake include taking fiber supplements, and also selecting high-fiber foods. Fiber supplementation may be an option, however it is not recommended by most nutritionists. It is unknown whether fiber supplements are safe and the FDA had banned methylcellulose in 1991 as a result. Fiber supplements were advertised as weight-loss aids; claims were made saying that fiber would expand in the stomach and the consumer would feel full and actually eat less. Researchers are also skeptical about fiber supplements because research indicates that it may not be fiber that has the healthful benefits, but the vitamins and antioxidants that are present in high-fiber fruits and vegetables. Fiber supplements are virtually devoid of the vitamins and antioxidants present in fruits and vegetables (Papazian, 1997).

Approximately 20 g/day is recommended to obtain the beneficial health benefits of RS. RS consumption varies significantly within countries. In developing countries with high starch consumption rates the range is between 30-40 g/day. However this ratio drops to 3-6 g/day in EU countries.

1.1.2.2 Proteins (gluten)

Protein composition of durum wheat varies in quantity and quality, depending on cultivar and environmental factors. Semolina protein is considered to be the most significant factor related to pasta cooking quality (Dexter and Matsuo, 1978; Matsuo et al., 1972) Protein content of durum wheat is higher than common wheat. The average percentage is anyway approximately 13 %, more or less, with concentrations that grow in the surface layers of the kernel and in the layers immediately adjacent to the germ.

Wheat protein can be classified into albumin (extractable in water), globulin (extractable in dilute salt solution), gliadin (extractable in aqueous ethanol solutions) and glutenin (extractable in dilute acid and alkali) (Pomeranz, 1988). Albumins and globulins are cytoplasmic proteins with enzymatic activities, foaming and emulsifying properties. Gliadin and glutenin are storage proteins and represent about 80 % of the total protein wheat flour.

Gliadin and glutenin are commonly considered the star proteins of pasta, at least as regards its features that consumers most highly appreciate (cooking capacity, elasticity, al dente chewability). They perform other technologically fundamental functions, among which water absorption is very important. When water is added to the semolina and the dough is mixed mechanically, glutenin and gliadin form gluten**,** a protein compound that forms a kind of mesh in the structure of the dough, trapping the starch grains and basically preventing the pasta during cooking from turning into polenta (Matsuo and Irvine, 1970). For example, the mechanism of gluten formation and its way of behaving with water is fundamental knowledge also to be able to dry pasta well. Gluten absorbs twice its own weight and moreover tends to hold it through complex chemical bonds. Its tendency for water absorption cannot be completely satisfied in dough formation, since for technological reasons the moisture of the dough normally cannot exceed the limit of 35 %, or it may cause problems in extrusion.

In any case, gluten, in relation to water, behaves as an antagonist for starch, since it tends to take up not only a greater amount of it, but also more quickly once its formation has begun. And here it is needed to make a consideration: the percentage of gluten (gliadin and glutenin) and starches in the semolina (or the flour) in some way rebalance the quantities of water absorbed by these two antagonists: gluten absorbs 200 % of its own weight, starch (not damaged) approximately 35-50 %. Since however starch is present in semolina in a quantity of approximately five times greater than that of gluten, the water of the dough is equally divided between them. Since this competition between gluten and starch is particularly obstinate, if the water is not uniformly distributed already at the initial moment of the formation of the dough it is very difficult for it to then be able to be transferred from one to the other antagonist, in particular from the gluten to the starch.

The capacity of gluten to hold water depends on its quality: this is the main reason why durum wheat semolina pasta prevails over that of soft wheat flour pasta in tenacity, cooking capacity and less stickiness. The gluten of soft wheat flour, in fact, even if it is able to absorb more water than that of semolina, it is less able to hold it. The superior capacity of the gluten to hold water compared to starch obviously has to affect the drying of the pasta: it is well known that when semolina very rich in proteins (and so with high quality gluten) is used it becomes hard to dry the pasta properly. But aside from this observation, the practical consequences are also others: for example the tendency of the gluten to follow the moist zones of the product during pre-drying, since its mobility is obviously possible when the pasta is still in the plastic state, so with a high water content, no lower than 25 %. The water absorption of gluten is not linear: it is very slow at the start of processing the dough, but it grows quickly as the development of the gluten is perfected. The last few minutes of dough formation are when the swelling of the gluten is most accentuated (and also its elasticity) (Miller and Hoseney, 1999; Liu et al., 1996).

1.2 Pasta processing

Overall quality of durum wheat pasta is influenced primarily by the properties of the protein and the starch fraction and their transformations during pasta processing. The following sections give an overview of the physicochemical changes of wheat components during milling, extrusion, drying and cooking of pasta.

1.2.1 Wheat milling

The process of durum wheat milling is a complex procedure of repetitive grinding and sieving. The objective of grinding is to break up wheat kernels and to separate the endosperm from the bran. Granulation or particle size distribution is important since it has an effect on the water absorption of the pasta dough (Dexter et al., 1994; Pomeranz, 1988).

1.2.2 Cleaning

In modern mills cleaning is carried out with a dry method, using specialized systems. Cleaning removes large impurities (rocks or their fragments, iron residues, other foreign bodies, straw, etc.) and the smaller or very small and light weight impurities, such as fine dust, insect fragments and eggs, various types of dirt particles, etc. as

well as removing specific parts of the caryopsis (for example the beards). The techniques used are especially sophisticated and are based on the exploiting the characteristics of the wheat in ratio to those of the impurities and foreign bodies (dimensions, particular shapes, differences in specific weight, magnetism, etc.). Cleaning (followed by a filth test, i.e. checking for the presence of residual dirt) is of fundamental importance to the final characteristics of the product as regards ashes and the presence of microorganisms.

1.2.3 Milling

The process of durum wheat milling is a complex procedure of repetitive grinding and sieving. The very hard durum grain must be tempered to rather high moisture content before grinding on a series of corrugated break rolls (Pomeranz, 1988). The objective of grinding is to break up wheat kernels and to separate the endosperm from the bran.

There exists an abundant literature on the effect of milling conditions on wheat components and pasta quality. Granulation or particle size distribution is important since it has an effect on the water absorption of the pasta dough. However, there is no agreement on the optimum particle size distribution of semolina for pasta production. Traditionally, semolina particle size is selected within a fairly narrow range of 200 - 315 μm with less than 10 % outside this range. A narrow granule size distribution favors uniform hydration during pasta production and reduces the risk of white spots, which results from coarse particles (>500 μm) with low hydration level (Antognelli, 1980). One of the important technological qualities required in semolina and in flour intended for use in making pasta (both dried and fresh pasta) is the low level of damage to the starches. It is evident that such brutal treatment of the grain as occurs in grinding cannot help but cause undesired damage to the crystalline structure of the starches. Furthermore, mechanically damaged starch during milling provides a suitable substrate for amylolytic enzymes during the drying process (Lintas and D'Appolonia, 1973).

1.2.4 The mixer

It is very important that the solid (flours, powders) and the liquid (water, emulsions) are mixed thoroughly even before the dough making process. This operation is

particularly critic for the flour particles (durum wheat semolina or soft wheat flour). If all the single particles do not absorb the liquids in the same way or do not reach the same degree of absorption all at the same time, it will hardly be possible to obtain a thoroughly homogeneous dough and the dry pasta will easily show more or less marked faults (white spots, for instance).

1.2.5 The dough-making unit

In order to obtain an even and homogeneous absorption of the liquids (water and/or egg emulsion) by the flour particles (semolina and/or flour), at least two basic conditions have to be guaranteed: the particles must have the same size or average size ranging between not too distant minimum and maximum values; the time needed for the liquid to be absorbed by the particles has to be evaluated while taking into account their average size and the temperature of both flour and liquid (Kruger et al., 1996). The lower the flour temperature (semolina and flour), the higher has to be that of the liquids used in the dough (water and/or egg emulsion). A very short dough making time increases considerably the line production speed, since it can better match the speed of the following steps (pre-drying, drying, stabilization), speed that has been dramatically increased in the modern pasta production technology. For this very same reason, at present, fine granulometry flours (semolina and/or flour) are preferred, since it is optimum for short dough making times and at the same time it is more likely to give a final product which doesn't show faults due to flour/water mixing and dough making anomalies. Quick dough making also allows reduction in the press size (output capacity being equal), and consequent better plant compactness and smaller dimensions. During the dough forming, the contact with atmospheric oxygen would increase the enzymatic activities and therefore alterations, especially in the product color (greyish shade and lost of the yellow color due to oxidation of natural pigments in semolina). In order to avoid this, the kneading phases, and, for some manufacturers, also the mixing, are carried out in vacuum. The vacuum is obtained throughout systems that may differ from a manufacturer to another.

The water used for the production of the pasta must obviously be drinkable (Kruger et al., 1996). Drinking water normally contains salts of calcium, sodium and magnesium, present in the form of carbonates and bicarbonates. The presence of these salts in the dough water increases its absorption by the gluten, however with

some limits: if there are too many, the gluten stretches to lose elasticity and become fragile. The addition of sodium chloride to the dough water, up to a maximum of 4 %, creates problems during the drying of the pasta because of the hygroscopic nature of salt. Water with foreign bodies in suspension (for example sand) or hygienically not perfect must be avoided or suitably treated before use, since an excessive presence of organic substances aids fermentation and even helps mould form on the pasta. Of course, bacteriologic control is fundamental: the coli, for example, must be totally absent, but in any case the total microbe content must not exceed a few colonies per milliliter.

The microbiological purity of water is normally obtained with treatments based on bactericidal agents. By far the most common treatment is the addition of sodium hypochlorite, or adding chlorine in its gaseous state to the water. Chlorine reacts with water generating oxygen, which kills the bacteria. However after this function, the residual chlorine must be removed. Its reactions with water and with its components normally neutralize it (for instance the hydrochloric acid that is generated is neutralized by its combination with calcium bicarbonates dissolved in water). A residue of chlorine in the treated water is, anyhow, almost unavoidable and that is not helpful for pasta. It acts as an oxidant during the preparation of the dough, negatively affecting the final color of the product. Verifying its residual presence in the drinking water used for the preparation of the dough is therefore important. If the residual chlorine exceeds a level of 1.2 ppm per liter of water the formation of chlorophenol, whose unpleasant smell is easily detected in cooked pasta, is also possible.

1.2.6 The extruder

Pasta dough contains around 31 g water/100 g (wb), which renders it rather dry and crumbly in texture. Water allows the plasticization of proteins, which, in turn, induce changes in the aggregation state of the storage proteins. The latter transformations are promoted by the mechanical energy input during the mixing and the extrusion step.

The final dough is extruded in the extrusion unit, consisting of a cylinder inside which a special extrusion screw turns. The screw rotation pushes the dough towards the head press on which a die is set. The pressure on the dough makes it go through

the openings in the die and get the required product shape. The dough extrusion is a complicated process that causes risk situations for both the product and the extrusion unit. The protein matrix can be partially ruptured during extrusion, resulting in more rapid disintegration of pasta during cooking (Kruger et al., 1996). Barrel temperatures above 55 ^{o}C have been reported to denaturate gluten and adversely affect pasta quality. The denaturation of wheat storage proteins involves complex disaggregation and repolymerization phenomena. These changes of wheat storage protein fractions are manifested by a decreased solubility and thus decreased extractability from pasta. This occurs because:

-The pressure values are necessarily high bar, and this can cause a mechanical stress to the dough, damaging its texture,

-The friction caused by the turning screw and the compression values produce dough heating that, if not kept under safety limits (usually < 40 °C), can cause thermal stress to the dough itself,

-The heavy mechanical stress under which the extrusion unit is kept (cylinder, screw, head and their respective supports) requires control and safety devices to be accurate and timely.

Gluten is less developed in pasta dough than in bread dough due to the low water content of the dough, the short mixing time and the low mechanical energy input .On the other hand, little transformation occurs in the starch fraction if the extrusion temperature does not exceed 45 ^{o}C. Otherwise, considerable changes in the starch fraction, i.e. crystal melting and swelling take place during extrusion (Debbouz and Doetkott, 1996; Abecassis et al., 1994)

Many investigations have been carried out to prevent bleaching of the carotenoids during pasta manufacturing. The most common physical approach is to remove molecular oxygen by applying a vacuum during extrusion. This limits the oxidation catalyzed by lipoxygenase. At the same time it prevents the inclusion of air bubbles in the dough that impair the appearance and cooking performance of the product (Kruger et al., 1996).

1.2.7 The die

The die function is to give the product the chosen shape. The great variety of pasta kinds and sizes is due to the possibility of making specific dies. The long cut pasta, for instance, is produced in many different shapes that can be summarized, according to their section, as follows: long round pasta without hole (e.g. spaghetti); long round pasta with hole (e.g. bucati, ziti, zitoni); long oval pasta (e.g. linguine); flat straight pasta with rectangular section (e.g. fettuccine); flat straight pasta with simple (on one side) or double (on both sides) festoons (e.g. mafalde, curly lasagna) (Milatovic and Mondelli, 1991). The dimensions of these shapes (section, diameter, length, width, thickness) can vary from a producer to another, even if many shapes have standard commercial values. The die is made of a bronze support with a shape, which is usually rectangular for long cut pasta and round for the short one. In the bronze support (that must have the right thickness to give it the necessary strength for the high and continuous pressure it is subjected to), there are holes in which inserts are placed. The inserts are designed and patterned so as to give shape to the product. Both the die and the inserts have to be built with extreme precision and made of special materials (e.g. Teflon) able to assure not only the die life but also its efficiency, with concern to both the product quality (even surface, color, etc.) and the press output capacity. The dies made entirely in bronze, directly holed by profiles suitable for the required shapes, are still used for rough surface pasta. Their average life is though considerably shorter than those of Teflon insert dies and are therefore used mainly for small special productions.

1.2.8 Drying

On leaving the die, pasta normally has moisture content of approximately 31-32 % (depending on the type of dough and the shapes made). It is considered dry when its internal moisture content is equal to or less than 12.5 % and balanced with the surrounding environment. This means that, to keep well, besides being dry, pasta needs to be stable. It must keep its remaining internal moisture content uniform. On leaving the die, pasta is in a plastic state. This condition has specific physical properties: a body in a plastic state can deform under the action of external forces without any particular tension forming inside it and, moreover, it can permanently keep the shape acquired as a result of these forces. The dough in its plastic state is deformed by the action of the die and the shape obtained will not be altered at all

after the pressure of the die has stopped. Pasta in its plastic state can then undergo even powerful drying without this causing any internal tension and the risk of damage. Also the deformation (contraction) suffered due to extraction of the water will be maintained. In the plastic state the contraction of the pasta is generally in proportion to the amount of water subtracted from it. When, proceeding with drying, the product's moisture content falls further (22-18 %), the state of the pasta changes from plastic to elastic. In this new state the product's behavior is totally different: an elastic body subjected to stress deforms, but tends to recover its original shape as soon as the stress stops. Besides causing deformation, stresses can then bring about tension inside the product. If the tension comes within the product's specific limit of elasticity, it can be absorbed precisely by its own elasticity. If it exceeds this limit product will inevitably be damaged. When the moisture inside the product falls to approximately 20 % its physical state passes from being plastic to elastic. Clearly, the moisture level marking the change in state is not fixed; it can change according to the temperature of the product and be for example 18 % (the higher the temperature of the pasta, the lower the level of moisture its state changes at). Close to the above-mentioned moisture level, both states, plastic and elastic, initially coexist in proportions continually varying until the change of state is complete. In practice, the change in the state of the pasta from plastic to elastic, starting from 22-18 % moisture, has the following consequences:

-From this point of the process onwards, drying generates tension inside the product.

-The pasta tends to recover the even minimal deformation caused by eliminating the water inside it.

-The water extracted from the pasta produces a contraction that however can no longer be recovered from the product except by reabsorbing water, which is precisely what must not happen, since the goal is that of drying.

-The water must therefore be extracted so that the tension generated does not exceed the product's limit of elasticity. If this occurs, the pasta will be damaged to a greater or lesser extent (cracks, splits, veining, etc.). Since water is extracted from the surface, during the drying process the internal part close to the surface will inevitably have lower moisture content than the central portion. This unbalance also generates tension that needs to be able to be reabsorbed to prevent damaging the product.

Currently, there are three technologies being used in the production of pasta;
(i) Low Temperature (LT) drying technology based on drying at low temperatures (<60 ^{o}C).
(ii) High Temperature (HT) drying technology based on drying at high temperatures (<80 ^{o}C).
(iii) Very high temperature (VHT) drying technology based on drying at very high temperatures (>80 ^{o}C).

The main advantages of HT drying are (i) a considerably reduced drying time compared to conventional drying cycles, (ii) very low levels of bacterial charge in the end product, (iii) improved colour of the dried product (Dexter et al., 1981), and (iv) improved cooking quality of the final product especially when durum wheat with low protein content is used. The application of HT drying during the first hour of drying reduces process costs and improves the textural and microbiological quality of the product. The disadvantage of HT drying is a moderate loss of nutritive value, i.e. a loss of the essential amino acid, lysine, because of the formation of furosine as the main stable Amadori compound in the Maillard reaction. The loss of lysine depends on the time-temperature conditions during HT drying (Dexter et al., 1984). However, the loss of lysine is not a serious defect, because pasta products are not consumed as a source of essential amino acids. Therefore, the improvement in overall quality resulting from the application of HT drying outweighs these slight nutritional disadvantages.

Starch, which was isolated from HT dried pasta, showed an increased gelatinization temperature, increased viscosity and lower swelling power and solubility compared to LT dried pasta (Vansteelandt and Delcour, 1998). Starch isolated from differently HT dried pasta showed a significantly narrower gelatinization range, but did not detect changes in onset and peak gelatinization temperatures, nor in gelatinization enthalpy compared to unprocessed semolina. The melting enthalpy of the amylose-lipid complexes was not affected by the drying cycles. Nevertheless, there still is a lack of information on the effect of HT drying on the properties of starch, as most investigations did not follow the changes of the physicochemical properties of starch at the different stages of drying. There are indications that the gelatinization

behaviour does not change steadily in the course of drying (Vansteelandt and Delcour, 1998).

In the protein fraction, extensive transformations take place during drying. The transformations are primarily dependent on the temperature-moisture-time conditions because they are controlled by the glass transition temperature (T_g). Above T_g the protein behaves as a rubber like material, whereas below T_g, the protein behaves as a glass. At temperature-moisture conditions below T_g the molecular mobility is decreased and the free volume, which is the volume not occupied by the macromolecules, is at its lowest thermodynamically possible value. Above T_g, the mobility of the protein molecules increases as the free volume increases and chain segments of the polymer have sufficient room to move fully. As a result, the extractability of gluten from pasta is reduced, since protein aggregation upon HT drying leads to a decreased solubility of wheat storage proteins (gliadin and glutenin) in dilute acetic solutions (Dexter and Matsuo, 1979). Albumin, globulin and glutenin are more sensitive to heat treatment than gliadin (Dexter and Matsuo, 1977). Temperatures above 80 ^{o}C lead to complete inactivation of lipoxygenase during drying of pasta. If the lipoxygenase is not inactivated, this enzyme catalyzes the oxidation of polyunsaturated fatty acids and by coupled oxidation reaction mechanisms degrades carotenoid pigments. The reaction has a negative effect on the color of the dried product.

1.2.8.1 Drying phases

The most significant physical states for pasta drying technology are the moisture and temperature of the air and the humidity and temperature of the product. The laws governing the phenomenon of these physical states must therefore be applied for all drying operations. Briefly, drying pasta means modulating and appropriately controlling the evaporation of water from the product, using heat and ventilation. The surfaces of liquids or moist bodies give off water molecules into the surrounding air if it is not saturated. In order to evaporate, water needs heat, i.e. the energy necessary for the molecules to break away from its surface. Evaporation is much greater the larger the surface and the more agitated the air moving over this surface. The air close to the surface, as saturation point is approached, slows down evaporation, which is then facilitated by the air continually being changed. In drying pasta, ventilation plays a fundamental role since, besides removing the water given off by

the product due to evaporation; it is used as a vehicle to convey heat. The heat energy conveyed by the ventilation air is used to heat the product and the water it contains, making it evaporate. Therefore, knowing the volume of air required for a certain phase of the drying process and controlling its intensity and flow is then an essential condition for drying pasta correctly. Since drying pasta brings about a reduction in its moisture content from 30 % to 12 %, it is done technologically in two distinct phases that correspond to the plastic and elastic states of the product. During pre-drying (first phase) the moisture content of the product falls from 30-32 % to 18-17 %. In practice, this means that it is necessary to eliminate approximately 22 kg of water for every 100 kg of final dry product. The time interval this phase takes depends on a few variables, the main one of which is temperature. Using temperatures that enable moist product to reach and/or exceed 75 ^{o}C speeds up this phase of the process and at the same time determines a number of advantages.

Rapidly heating the product causes drastic evaporation of the water on the surface of the pasta and therefore an equally drastic migration of water particles from the inside towards the surface. The first transfer of water takes place at the cost of the starch, which during preparation of the dough has absorbed approximately 1/5 as much of it as the gluten. Afterwards, by osmosis, the water moves from the gluten to the starch. Since gluten is elastic it tends to follow the water particles, moving from the inner most parts of the product, where it is more highly concentrated because there is more moisture there, towards the outside. This redistribution of gluten can take place at up to approximately 26 % moisture of the pasta. If the pre-drier chamber is very hot and damp, the conditions are ideal for this complex phase of migration and redistribution, this being decisive for the end result of the entire drying process. In short, then, this pre-drying technology makes it possible to accomplish:

-Partial blockage of some enzyme activity and virtually total blockage of any product fermentation, helping to sanitize it, since there are relatively few micro-organisms that at 75 °C are capable of surviving, and also any insect eggs are easily destroyed.

-Uniform gluten distribution making full use of the capacity of gluten to hold back the starch particles (so better cooking capacity and less stickiness of the product).

-A decrease in oxidation of the yellow pigments contained in the semolina and therefore a brighter color of the dried product.

-Better shape stability.

Maintenance of the product's capillarity, essential to redistribute the particles of water during the following phases of the process. The following phase of drying must envisage alternating phases of water evaporation from the surface and redistribution inside. In this phase ambient temperature and humidity normally decrease, clearly complying with the current temperature and moisture of the product. The speed of this phase is inevitably less than that of pre-drying because the structure of the product (passed on to the elastic state) has become more rigid, capillary action has decreased and so the migration of the remaining particles of water from the inside to the outside of the product is slower. The drying phase is a delicate one because on the one hand it is necessary to prevent drying that is too fast from completely blocking the capillary action of the pasta, on the other hand it is always a good rule for drying to be completed relatively quickly, compatibly with the technology used. Drying normally takes approximately 6-8 times longer than the time required for pre-drying, including the phases of the internal redistribution of water particles. This figure changes in relation to the formats: longer ones take much longer to dry than short ones, especially if they are of medium-high thickness.

1.2.9 Pasta cooking

In dried pasta, starch is almost in its native state so that the product requires cooking prior to consumption. During cooking of pasta, the temperature rises close to 100 ^{o}C, and hydration of the product occurs by a diffusion-controlled process. Water is an exceptionally good plasticizer for starch and protein and, thus, has a strong glass transition depressing effect. Furthermore, the melting of starch crystallites is Tg dependent, since a previous softening the amorphous zones facilitates crystal melting.

Cooking of pasta induces major changes in the starch fraction since the temperature-moisture conditions induce the gelatinization of starch. During the first stage of gelatinization, long-range molecular order and crystallinity are lost as detected by the lost of birefrigence and by enthalpy changes, respectively. Birefringence refers to the characteristic maltese cross appearing on the native granules under polarized light and its disappearance indicates the irreversible loss of molecular order and orientation. Simultaneously, the starch granules begin to swell at the initial gelatinization temperature. Gelatinization starts at the hilum of the granule and

rapidly attains the periphery. Water initially penetrates the amorphous growth rings of native starch followed by hydration of the intercrystalline amorphous phase as heating proceeds. As a consequence, the water binding capacity of the starch granules increases and water becomes more bound to starch (Chinachoti et al., 1991). Gelatinization of starch is accompanied by an increase of viscoelasticity and starch solubilization. Regarding the changes at the macroscopic level, starch gelatinization progresses towards the center of the pasta strand as the cooking time increases. Thus, the morphological changes of starch range from strong swelling and partial disintegration in the outer layer of the strand to slight swelling in the center.

Similarly to starch, changes in the protein fraction occur during cooking of pasta. At the molecular level, the secondary structure of the protein is transformed but their primary structure remains unchanged. As a result of the protein unfolding a rapid decrease of the solubility of the cytoplasmic proteins (albumin and globulin) and storage proteins (gliadin and glutenin) occurs. At the supramolecular level, the unfolded proteins tend to cross-link with each other, which results in a firming, known as coagulation (Wrigley and Bekes, 1999; Dexter and Matsuo, 1979). The protein matrix gradually disintegrates during cooking of pasta, which determines the loss of solids into the cooking water and the stickiness of pasta (Kruger et al., 1996).

1.3 Theoretical background for some rheological measurements

As the eating habits of consumers have become more complex day by day, much attention has given to the quality of foods, which is greatly affected by process and storage conditions.

During pasta production as drying proceeds the structure changes from a more plastic to elastic state. However, when it has been cooked the structural change is the other way around. The main plasticizer ‘water’ has a great influence on these changes so it is of great importance to understand the relationship between water mobility and mechanical properties of food materials. Textural attributes are usually correlated to rheological parameters obtained by mechanical measurements, which are very important in understanding the structure of food and biological materials.

Rheology, the science of deformation and flow of matter, has its specific objective on the investigation of the properties of materials that govern their flow and deformation under external forces. In order to accomplish this objective, rheologists study the load-deformation behavior of materials under controlled experimental conditions. The most important and basic concepts of rheology are stress, strain and strain rate. The rheological response of any material is physically expressed by stress, which is a measure of force concentration on material (Faridi and Faubion, 1990).

Rheological principles and theory can be used as an aid in process control and design, and as a tool in the simulation and prediction of the material's response to the complex flows and deformation conditions often found in practical processing situations which can be inaccessible to normal rheological measurement. There are three ways to deform a substance: shear, extension, and bulk compression. It is possible to conduct tests in all three modes of deformation, under steady state or dynamic conditions, and compare the resulting moduli and compliances (Dobraszczyk and Morgenstern, 2003; Steffe, 1996). Rheological parameters such as maximum stress, maximum strain, elastic modulus, compliance, and measure of stiffness contain useful information for the textural characteristics of solid food. A small test piece of the material is usually deformed in a controlled way, normally on a motor driven machine, and the force is measured as well as the distance moved or displacement of the object. The force is then usually plotted against the displacement to give a force-displacement curve. Rheological properties should be independent of size, shape and how they are measured; shortly they must be universal (Shimonovich and Shimoni, 2003).

1.3.1 Viscoelasticity

As its name implies, viscoelasticity combines elasticity and viscosity (viscous flow). The overall behavior of pasta as a macromolecular material under stress can be described as viscoelastic so that from the material point of view on one hand pasta behaves in a viscous way, as a liquid, on the other hand elastically, as a solid. Mainly starch and gluten are responsible of the viscoelastic characteristic of pasta.

In process engineering, data on viscoelasticity can be collected either in the linear or non-linear region. When materials are tested in the linear range, material functions

do not depend on the magnitude of stress, the magnitude of the deforming strain, or the rate of application of the strain. If linear, an applied stress will produce a proportional strain response. The linear range of testing is determined from experimental data. Testing can easily enter the non-linear range by applying excessive strain (usually greater than 1 %) or high deformation rates to the sample.

For a large deformation compression test prior to the initiation of relaxation testing, the strain or stress level is always at a few folds higher than its linear viscoelastic range, and, hence, shows a typical non-linear decay trend. Non-linear viscoelasticity is experimentally and theoretically much more complex than linear viscoelasticity.

An ideal viscous body cannot maintain any force/stress in the absence of motion, and, thus, reaches the lowest datum level. On the contrary, an ideal elastic solid is able to attain instantly the force/stress that is equal to the same magnitude that it possessed at the beginning of the relaxation testing. It is obvious that a viscoelastic material such as food dough will show an intermediate effect between these two extreme cases.

In Figure 1.3, force curve of a nonlinear compression test is shown. At a constant strain, force depends on time alone with usually three zones; the initial portion shows a high slope, whereas the third zone has the lowest slope and appears to approach a residual (or an equilibrium) value whereas the second zone is an intermediate of these two zones. The slope of the initial portion of the curve is independent of the rate of the strain when the sample is compressed to a small strain level (Yadav et al., 2006). The importance of large deformation (non-linear) in food rheology must not be overestimated. Many processes, such as mastication and swallowing, are only accomplished with very large deformations. Collecting viscoelastic data relevant to this type of problem involves testing in the non-linear range of behavior. Practically these data can be quite useful but from a fundamental stand point, they can only be used for comparative purposes because the theoretical complexity of non-linear viscoelasticity makes it impractical for most applications (Steffe, 1996).

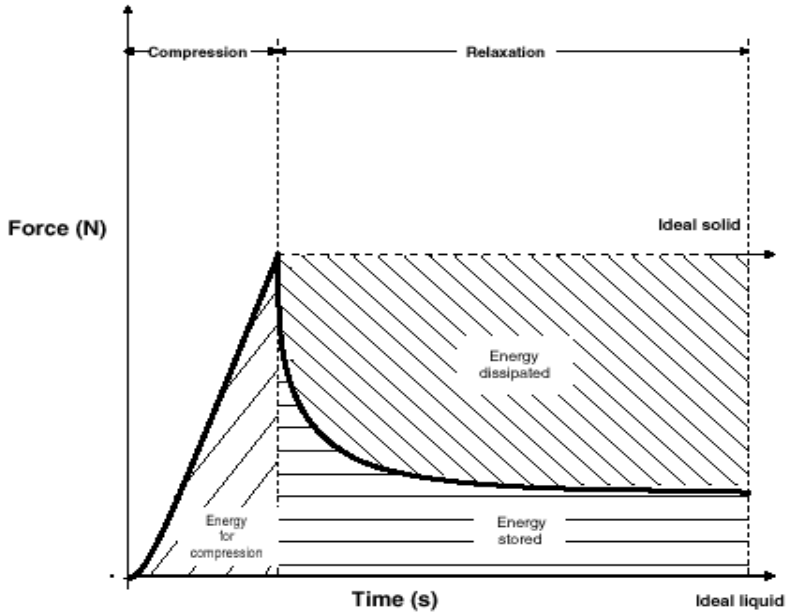

Figure 1.3 Nonlinear compression-relaxation diagram of a viscoelastic body

Pure elastic behavior is defined such that when a force is applied to a material, it will instantaneously and finitely deform; and when the force is released, the material will instantaneously return to its original form. Such a material is called a Hookean solid. The amount of deformation is proportional to the magnitude of the force. The rheological representation of this type of solid is a spring. The modulus calculated by applying a force perpendicular to the area defined by the stress is called the modulus of elasticity (E), the modulus calculated by applying a force parallel to the area defined by the stress, or a shearing force, is called the shear modulus or modulus of rigidity (G). If the force is applied from all directions and the change in volume per original volume is obtained, then one can calculate the bulk modulus (K).

A pure viscous flow of a liquid means that the liquid begins to flow with the slightest force, and that the rate of flow is proportional to the magnitude of the force applied. This liquid flows infinitely until the force is removed, and upon removal of the force, has no ability to regain its original state. Such a material is called a Newtonian liquid. The rheological representation for this type of liquid is a dashpot, which can be thought of a piston inside a cylinder. When a force is applied to the piston, it moves in or out of the cylinder at constant velocity, the rate depending upon the magnitude of the force. When the force is removed, the piston remains fixed and cannot return

to its original position. A material of this nature has a rheological constant called the coefficient of viscosity. If foods were either Hookean solids or Newtonian liquids, determination of their rheological constants would be simple. However, foodstuffs possess rheological properties associated with both elastic solid and the viscous fluid. The rheological representation of this type of material is a body incorporating at least one spring (representing the solid character) and at least one dashpot (representing the viscous character). The number of springs and dashpots in the body and the manner in which they are connected can be manipulated to represent different types of viscoelastic materials and to demonstrate how they will behave under a stress or strain (Rao and Skinner, 1986).

1.3.1.1 Models of viscoelasticity

The most common mechanical analogs of rheological behavior are the Kelvin (sometimes called Kelvin-Voigt) and Maxwell models shown in Figures 1.4 and 1.5.

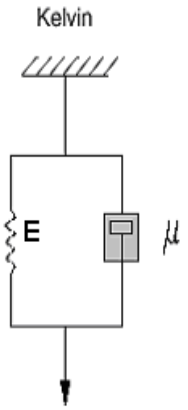

Figure 1.4 Kelvin model

Mechanical analogs are quite useful in means of investigating creep and strain data (Steffe, 1996).

1.3.1.1.1 Stress relaxation

In a stress relaxation test an instantaneous strain is applied and the force required to maintain the deformation is observed as a function of time. Frequently used mathematical models for stress relaxation are simple Maxwell, generalized Maxwell and Peleg & Normand models. The Maxwell model, which is the simplest viscoelastic material representation, consists of an elastic (spring) and a viscous

(dashpot) element in series. Regardless of whether a particular model contains or does not contain a parallel spring, its relaxation curve will be determined by the initial force and the fixed deformation. In other words if any particular Maxwellian model or even conventional nonlinear models is let to relax from initial conditions of higher deformation and force, the relaxation curve will always be above the curves which started at initial conditions of which both the deformation and the force had smaller values. In Maxwell model applied force (F) can be used instead of stress. The instantenous force can be replaced by any other decaying parameter such as stress or modulus of elasticity (Khazaei and Mann, 2004).

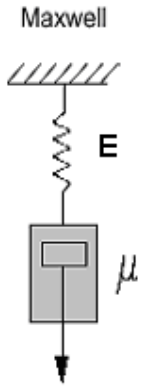

Figure 1.5 Maxwell model

For a simple Maxwell model, at constant strain, the applied force (F) decays from F_1 to F (t), after time t

$$F(t) = F_1 \exp(-t/\lambda_1) \qquad (1.1)$$

where F_1 is the decay force and λ_1 is the relaxation time. Although an exact definition of relaxation time is difficult, it can be thought of as the time it takes a macromolecule to be stretched out when deformed (Cheng et al., 2005).

The simple Maxwell model is not sufficiently general to describe the behavior of a linear viscoelastic material. For example, if a constant stress is applied to a Maxwell model, the model exhibits only Newtonian flow and not a retarded elastic deformation, which is experimentally observed in a creep or constant stress test. To

avoid this problem, an infinite number of Maxwell models are used in parallel and the resulting model is called a generalized Maxwell model (Rao and Rizvi, 1986; Peleg and Normand, 1982).

Most viscoelastic foods do not follow the simple Maxwell model (eqn.1.1) and it is necessary more complex models to describe their stress relaxation curves. The generalized Maxwell model, consisting of a small number of parallel simple elements, can be described by the following equation:

$$F(t) = F_1 \exp(-t/\lambda_1) + F_2 \exp(-t/\lambda_2) + ... + F_n \exp(-t/\lambda_n) \qquad (1.2)$$

where λ_1 and λ_n are the relaxation times, F_1 to F_n are the decay forces, and F(t) is the instantaneous force in a stress relaxation test. The instantaneous force could be replaced by any other decaying parameter such as stress or modulus of elasticity (Khazaei and Mann, 2004). For most of the foods a Maxwell model with three terms involving six constants is sufficient enough to represent stress relaxation data.

It is difficult to express biological materials with a fixed number of elements. The general case of deformation mainly consists of three progressive stages in which different kinds of mechanical phenomena may play the dominant role;

a) A stage in which no permanent physical change occurs and the deformation is dominantly elastic and rate independent.
b) A stage in which some irreversible changes progressively occurs. This stage is characterized by viscoelastic behavior and history dependent phenomena.
c) Failure and post failure stages. These are characterized by an apparent physical rupture of the material and should be discussed in terms of failure phenomena. From a rheological point of view the material is still viscoelastic but shows considerably different viscoelastic behavior if compared to its pre-failure stages (Peleg and Calzada, 1976).

In many materials of biological origin difficulty of rheological data analysis arises because of heterogenous and nonuniform internal structure that does not allow many of the simplifying assumptions in existing theories. Furthermore, most biological materials tend to exchange moisture with the environment, a factor that has a

significant effect on their rheological properties. In such cases, long term rheological characteristics in the conventional sense, e.g., equilibrium stress in relaxation or strain in creep, either does not exist or must be extremely difficult to determine. Conventional models and methods of rheological characterization, therefore, have only limited applicability when applied to these kinds of materials.

Another common factor that restricts the accuracy of any rheological analysis of biological material is the technical limitation in obtaining a desirable kind of specimen. Frequently, small shape variations among specimens are inevitable, and in many materials textural nonuniformity within the tissue is an inherent property. In such cases rheological properties can only be estimated and the application of sophisticated methods rendered pointless.

Under these circumstances an empirical approach to rheological analysis seems to have clear advantage. In selecting a procedure, however, one should not only consider the mathematical convenience, but also whether the method is internally consistent and sensitive enough to account for structural changes that do occur during the deformation course (Peleg, 1980).

To overcome these difficulties, they suggest stress relaxation data can be calculated as a normalized stress (or force) and fit to the following linear equation:

$$\sigma_o t/(\sigma_o - \sigma) = k_1 + k_2 t \qquad (1.3)$$

where σ_o is the initial stress, σ is the decreasing stress at time t, and k_1 and k_2 are constants. Fitting experimental data to equation (eqn. 1.3) is a quick and effective way to handle stress relaxation data (Steffe, 1996).

The best adjustment of the selected models to the stress relaxation data can be determined by calculation of root mean square (RMS) between the model-predicted values and the experimentally measured values. The model with the number of terms corresponding to a RMS value of $\leq 10\%$ was chosen as the best-fit model.

$$RMS = 100 * \sqrt{\frac{\sum\left(\frac{\text{exp.} - \text{pred.}}{\text{exp.}}\right)^2}{N}} \qquad (1.4)$$

where exp and pred refers to experimental and predicted values respectively. N represents the number of data. R^2 values were also calculated for each model.

1.3.1.1.2 Creep compliance

One of the manifestations of viscoelastic materials is that they undergo creep, i.e. continue to deform under constant stress or load. The distinction between constant stress and constant load (force) is necessary, especially for highly deformable foods, because of the progressive change the specimen's cross-sectional area. Thus, a constant load (i.e. dead weight) produces a progressively increasing stress in uniaxial tension and decreasing stress in compression (Purkayastha, 1985). The typical creep curve is shown in Figure 1.6.

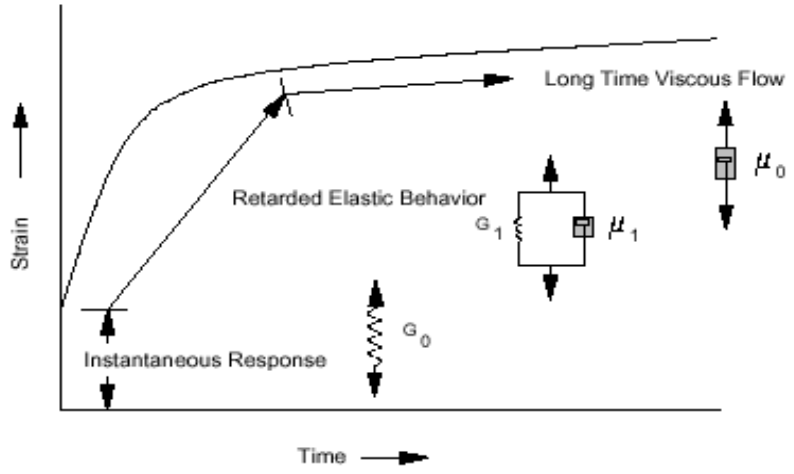

Figure 1.6 Typical creep curve showing where various elements of the Burgers model describe flow behaviour

The output of creep tests is normally in three forms:

a) The strain-time curves under various selected constant loads,
b) The recovery curves after removal of the loads;
c) The time to failure (if within reasonable experimental duration) under various loads (Peleg, 1979).

Creep data may be described in terms of a creep compliance function, given by equation 1.5 in terms of shear deformation.

$$D(t) = \gamma(t)/\sigma \qquad (1.5)$$

To develop a mechanical analogue for creep behavior the starting point is Kelvin model which contains a spring connected in parallel with a hydraulic dashpot. In creep where the material is allowed to flow after being subjected to a constant shear stress (σ_o), the change in stress with time is zero resulting the following equation:

$$\gamma = f(t) = \sigma_o (1 - \exp(-t/\lambda_{ret}))/E \qquad (1.6)$$

The Kelvin model shows excellent elastic retardation but is not general enough to model creep in many biological materials. The solution to this problem is to use a Burgers model which is a Kelvin and a Maxwell model placed in series.

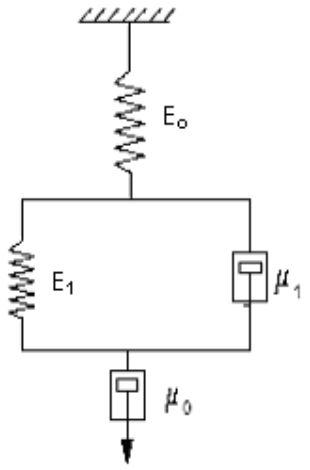

Figure 1.7 Burgers model

Data following Burgers model (Figure 1.7) show an initial elastic response due to the free spring, retarded elastic behavior related to the parallel spring-dashpot combination, and Newtonian type of flow after long periods of time due to the free dashpot

$$\gamma = f(t) = (\sigma_o / E_o) + (\sigma_o / E_1)(1 - \exp(-t/\lambda_{ret_1})) + (\sigma_o / E_2)(1 - \exp(-t/\lambda_{ret_2})) + (\sigma_o t/\mu_o) \quad (1.7)$$

$\lambda_{ret} = \mu / E$, the retardation time of the Kelvin portion of the model. The Burgers model can also be expressed in terms of creep compliance by dividing eqn. (1.7) by the constant stress:

$$\gamma/\sigma_o = f(t) = (1/E_o) + (1/E_1)(1 - \exp(-t/\lambda_{ret_1})) + (1/E_2)(1 - \exp(-t/\lambda_{ret_2})) + (t/\mu_o) \quad (1.8)$$

which will give;

$$D = f(t) = D_o + D_1(1 - \exp(-t/\lambda_{ret_1}) + D_2(1 - \exp(-t/\lambda_{ret_2}) + (t/\mu_o) \quad (1.9)$$

where D_o is the instantaneous compliance, D_1 and D_2 are retarded compliances, λ_{ret1} and λ_{ret2} are retardation times of the Kelvin component, and μ_o is the Newtonian viscosity of the free dashpot. At the beginning of creep there is an instantaneous change in compliance due to the spring in the Maxwell portion of the model. Then, the Kelvin component produces an exponential change in compliance related to the retardation time. After sufficient time has passed, the independent dashpot generates a purely viscous response. Data from the linear portion of the creep curve are related to two parameters: the slope is equal to $1/\mu_0$; and the intercept, sometimes called the steady state compliance is equal to $D_0 + D_1$ (Figure 1.8).

At $t = t_1$ the load is removed and there is an instantaneous change in compliance equal to D_0. the free dashpot causes permanent deformation in the material related to a compliance of t_1/μ_0. If a substance obeying Burgers model is tested in the linear viscoelastic region of material behavior, then the values of D_0 and D_1 determined from the creep curve will be equal to the values from recovery curve (Steffe, 1996).

Peleg has also suggested that creep data could be modelled with the following linear equation (Peleg, 1980):

$$t/D = k_1 + k_2 t \quad (1.10)$$

Burgers model is more precise than Pelegs model.

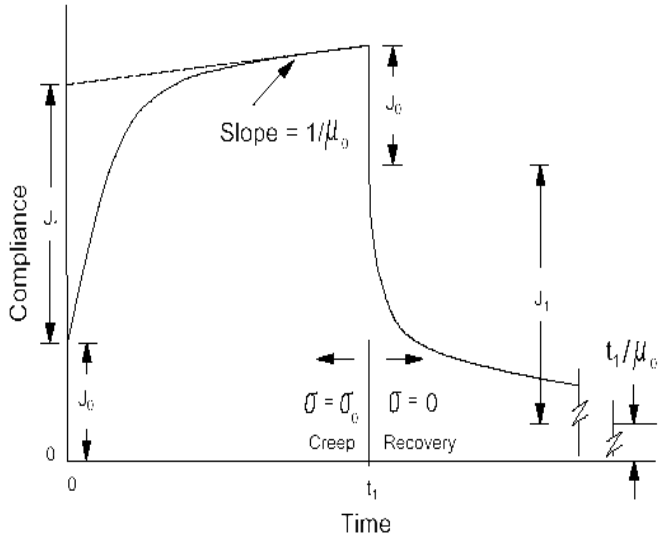

Figure 1.8 Compliance and recovery curves showing compliance

1.4 Texture profile analysis (TPA)

Texture has been referred to as the 'forgotten attribute', because for many years it commanded little attention, especially compared with flavor. It is now agreed that texture and mouthfeel are major determinants of consumer acceptance and preference for foods and beverages. Food preference and acceptance, in turn, have a great impact on the nutritional status of consumers and on the profits of food manufacturers (Guinard and Mazzucchelli, 1996).

Texture is defined as the attributes of a substance resulting from a combination of physical properties and perceived as the senses of touch, sight and hearing and the evaluation of the foods texture is driven in the cause of mastication (Chuang and Yeh, 2006). The term texture first came about to describe the visual and tactile characteristics of fabrics. Later, the term was applied to other materials including foods. Food texture was first defined as the "mingled experience deriving from the sensations of skin in the mouth after ingestion of a food or beverage, as it relates to density, viscosity, surface tension and other physical stimuli that result from contact between some part of the body and the food". A more recent definition, by Szczesniak, is "the sensory manifestation of the structure of the food and the manner in which this structure reacts to the applied forces, the specific senses involved being vision, kinesthesia, and hearing" (kinesthesia is the sensation of presence, position or

movement, resulting chiefly from stimulation of sensory nerve endings in muscles, tendons and joints). Whereas texture is used mostly in reference to solid and semi-solid foods, mouthfeel includes all of the tactile (feel) properties perceived from the time at which solid, semi-solid or liquid foods or beverages are placed in the mouth until they are swallowed (Guinard and Mazzucchelli, 1996). A main goal in many texture studies is to devise one or more mechanical tests with the capacity to replace human sensory evaluation as a tool to evaluate food texture. The TPA procedure was developed by a group at the General Foods Corporation Technical Center. Most researchers now use a universal testing machine to perform TPA, and many use a digitizer interfaced to a computer or a direct computer readout of the data (Faridi and Faubion, 1989). Texture profile analysis is one of the first empirical tests that have been developed. It is very similar to a fundamental compression test, with the difference that in TPA the sample is subjected to two consecutive compression cycles, simulating a two-bite process by teeth. This procedure results in a typical TPA curve (Figure 1.9) where one can extract information about primary parameters of hardness, cohesiveness, springness and adhesiveness, and into the second (or derived) parameters of fracturability, chewiness and gumminess.

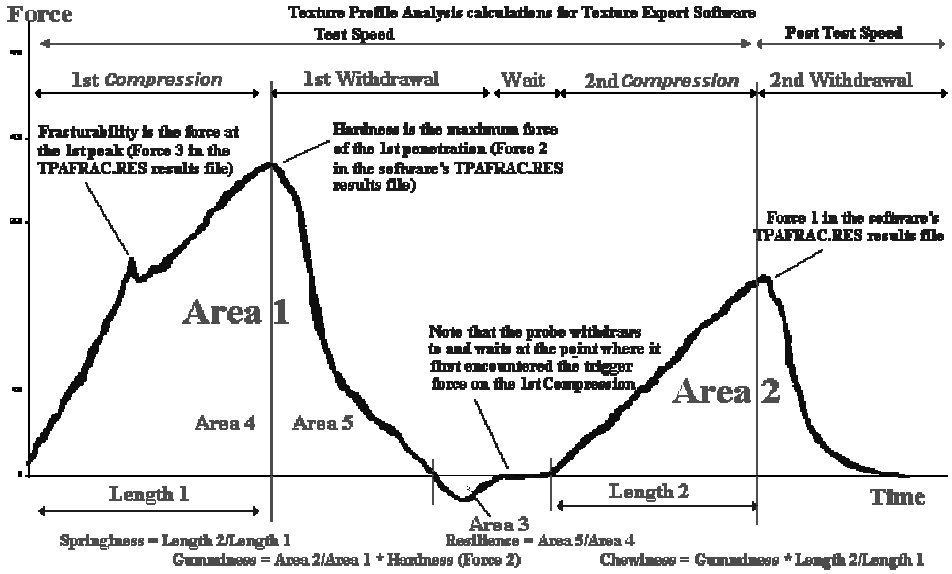

Figure 1.9 Typical TPA curve

The definitions of the TPA parameters in Figure 1.9:

Hardness: The hardness value is the peak force of the first compression of the product. The hardness need not occur at the point of deepest compression, although it typically does for most products.

Fracturability: Not all products fracture; but when they do fracture the Fracturability point occurs where the plot has its first significant peak (where the force falls off) during the probe's first compression of the product.

Cohesiveness: Cohesiveness is how well the product withstands a second deformation relative to how it behaved under the first deformation. It is measured as the area of work during the second compression divided by the area of work during the first compression. (Refer to Area 2/Area 1 in the above graph).

Springiness: Springiness is how well a product physically springs back after it has been deformed during the first compression. The springback is measured at the downstroke of the second compression, so the wait time between two strokes can be relatively important. In some cases an excessively long wait time will allow a product to springback more than it might under the conditions being researched (eg you would not wait 60 seconds between chews). Springiness is measured several ways, but most typically, by the distance of the detected height of the product on the second compression (Length 2 on the below graph), as divided by the original compression distance (Length 1). The original definition of springiness used the Length 2 only, and the units were in mm or other units of distance. We do not subscribe to that original description of springiness since the springiness value can only be compared among products, which are identical in their original shape & height. Many TPA users compress their products a % strain, and for those applications a pure distance value (rather than a ratio) is too heavily influenced by the height of the sample. By expressing springiness as a ratio of its original height, comparisons can be made between a more broad set of samples and products.

Chewiness: Chewiness only applies for solid products and is calculated as Gumminess*Springiness (which is Length 1/Length 2). Chewiness is mutually exclusive with Gumminess since a product would not be both a solid and a semi-solid at the same time.

Gumminess: Gumminess only applies to semi-solid products and is Hardness *Cohesiveness (which is Area 2/Area 1).

Resilience: Resilience is how well a product "fights to regain its original position". You can think of it as instant springiness, since resilience is measured on the withdrawal of the first penetration, before the waiting period is started. The calculation is the area during the withdrawal of the first compression, divided by the area of the first compression. (Area 5/Area 4 on the above graph) Resilience is not

always measured with TPA calculations, and was not a direct part of the original TPA work. Resilience can be measured with a single compression; however, the withdrawal speed must be the same as the compression speed.

1.5 The aim of the present study

Pasta and its products are the main subgroup of many diets. In fact there are bran containing pasta products in the market; consumers still do not like to include these products into their diet because of many organoleptic and textural reasons such as colour, odour, cohesiveness, hardness, etc. Nowadays most of the diseases result from inadequate feeding and some of them may be related to insufficient fiber intake. As a result consumers are in need of good-tasting, high fiber foods. From this point of view RS sources can be included in to diet, since they do not cause pronounced organoleptic alterations, as do traditional fiber sources like bran. This study was focused on production of spaghetti enriched with resistant starch. The objectives of this research were:

1. Production of spaghetti enriched with resistant starch.
2. To determine the rheological and textural properties of uncooked and cooked spaghetti.
3. Cooking kinetics of enriched spaghetti samples (degree of cooking, water absorption and cooking loss).
4. Image and thermal analysis of spaghetti samples.
5. To determine the amount of resistant starch formation in uncooked and cooked spaghetti.
6. Consumer acceptance of the enriched spaghetti samples.

CHAPTER II
MATERIALS AND METHODS

2.1 Materials

2.1.1 Raw materials

Resistant starch (RS) was supplied from National Starch & Chemical Co. (Manchester, UK). The properties of RS are listed in Table 2.1 (the values are from the National starch data sheet except RS_3 content). Durum wheat semolina was supplied from Beslen pasta factory (Gaziantep, Turkey).

Table 2.1 Properties of resistant starch

RS_3 (% db)	45*
Moisture content (%)	8
Water holding capacity (% wb)	200
pH	5.5
Color	White
Flavor	Neutral

* refers to amount of RS_3 determined experimentally for this study

2.1.2 Chemicals

All chemicals used in this work were supplied from Merck Chemical Co., (Germany) except the ones supplied in the Resistant Starch Assay Kit (Megazyme, Ireland).

2.1.3 Sample preparation

Control, spaghetti samples enriched with 5 %, 10 % and 15 % resistant starch were prepared in Beslen pasta factory (Gaziantep, Turkey) with the following process outline (Figure 2.1). Bran containing spaghetti was purchased from a local supermarket.

All cooking tests were performed in duplicate. Cooking procedure was carried out for 10 g of spaghetti samples, which were cooked in 250 ml boiling deionized water (Dexter et al., 1983). Boiling was kept at this level for the entire cooking period.

Cooking properties of samples were measured in 2 min intervals starting from 6 min to 18 min except for differential scanning calorimeter analysis. Samples were cooled by soaking in cold water for 10 sec and excess water was removed by lightly patting between paper towels. The samples were immediately used for analytical and instrumental measurements. For DSC analysis samples were cooked starting from 2 min to 12 min and samples were taken every 2 min after they were cooled by soaking in cold water and were cut into 1 mm pieces and freeze-dried (Eyela Model FD-1, Tokyo Rikakikai Co., Tokyo, Japan) before evaluating the residual ungelatinized starch fraction, which was done after rehydrating the freeze-dried sample to a known moisture content (Riva et al., 2000).

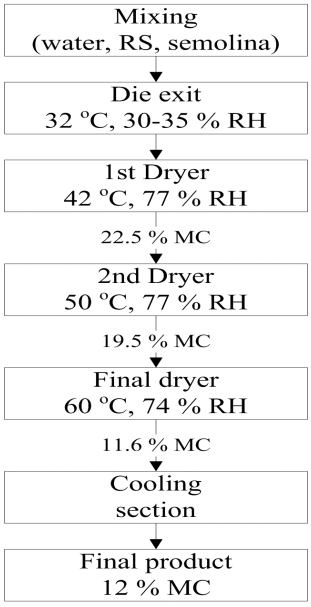

Figure 2.1 Process outline

2.2 Methods

2.2.1 Instrumental measurements

2.2.1.1 Rheological measurements

All rheological measurements of dry and cooked spaghetti were evaluated using a TA-XT2i Texture Analyzer (Stable Micro Systems Ltd., Godalming, Surrey, UK) fitted with a 25 kg load cell. Each experiment except breaking strength test was performed in triplicate. Breaking strength test consisted of 10 replicates.

2.2.1.1.1 Breaking strength

The breaking strength of dry pasta was determined by a three-point-bend test. Samples were measured two months after production. The samples were prepared by breaking spaghetti strands into 10 cm. One spaghetti strand was placed between two vertical and aluminum bars with 4 cm gap between them (Figure 2.2). The upper probe was lowered towards the base plate with a speed of 1 mm/s. The maximum resistance force at breaking was recorded. The results were expressed as mean of 10 measurements.

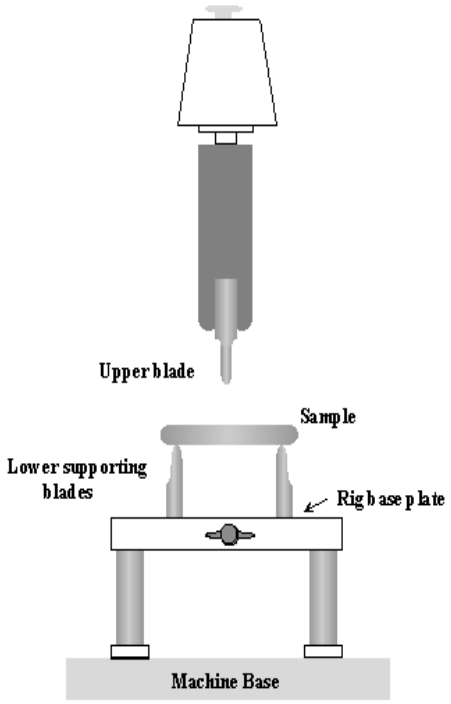

Figure 2.2 Experimental set up of three point bending test

2.2.1.1.2 Stress relaxation test

Cooked spaghetti strands were replaced beside each other and cut for the size in such a way to fit under the probe area. Samples were deformed at a constant strain of 20 % with residual force being continuously recorded as a function of time. The stress was calculated as force/area. The results were analyzed with Maxwell and Peleg & Normand models.

2.2.1.1.3 Creep test

Creep measurement for each cooked spaghetti sample used a constant stress of 42 kPa for 8 min, and data were calculated as creep compliance (D) versus time (t). Creep behavior was characterized using Peleg and Burgers models (Dobraszczyk and Morgenstern, 2003; Steffe, 1996).

2.2.1.1.4 Texture profile analysis of cooked spaghetti

Texture profile analysis (TPA) of cooked spaghetti samples was measured as a function of cooking time by using pasta stickiness rig. Test samples were compressed with a speed of 1 mm/s. The test is a simulation of the action of jaw by compressing the bite size of food two times. The resulting force-time curve is used to extract textural parameter values. These are primary parameters (hardness, cohesiveness, springness and adhesiveness) and secondary parameters (brittleness, chewiness, gumminess and resilience).

2.2.1.2 Thermal analysis

DSC measurements were done to semolina, uncooked spaghetti and freeze-dried cooked spaghetti after gently grinding with a mortar and pastle to pass through a 0.25 mm mesh screen and packed into culture tubes. The moisture content of the samples were immediately determined after milling by an Infrared Dryer (Sartorious Thermo-Control YTC, Göttingen, Germany). Ground samples were weighed (10 mg) into DSC pans and moistened with distilled deionized water with a ratio of dry sample to water around 1:3.33. The DSC pans were sealed and let to reach equilibrium conditions in a refrigerator at 4 ^{o}C for overnight. The measurements were carried out in a Perkin-Elmer DSC 6 equipped with a Pyris software (Perkin Elmer Inc., Wellesley, USA) calibrated with indium and empty pan as a reference. The samples were heated at a rate of 5 ^{o}C/min from 20 to 140 ^{o}C with nitrogen flushing (40 cm^3/min). Each experiment was carried out in duplicate. For each endotherm, onset (T_o), melting (T_m), and conclusion (T_c) temperatures were determined using the Pyris DSC software programme. The melting ranges ($\Delta T_r = T_c - T_o$) were calculated. The heat flow signals were recorded in an ASCII format and analyzed with SPSS Inc. SigmaPlot for Windows version 6.0. Degree of gelatinization (%) was determined as follows (Ndife et al., 1998):

Gelatinization degree (%) = (1- (ΔH_t / ΔH_s))*100 (2.1)

ΔH_t : gelatinization enthalpy at various cooking times (J/g db)

ΔH_s : gelatinization enthalpy of semolina (J/g db)

2.2.1.3 Image analysis

Swelling of product and degree of cooking was monitored by examining digital cross-sectioned images of cooked and drained spaghetti (Riva et al., 2000). Samples cooked for 6 min – 18 min within 2 min intervals were cut into 1 mm thickness and replaced on glass slides, which were covered immediately with lamels. They were pressed for 1 min under a force of 200 g to better observe the ungelatinized parts. All the samples were monitored under microscope (Olympus BX51, Olympus Co. Ltd., Japan) and photographed (20X objective) with a camera attached to the microscope. Degree of cooking can be observed either by eye or image analysis. In this study it was determined by the disappearance of the black core in the center of images. The pictures were analyzed with IMAQ vision builder (v.5.0, National Instruments Corp., Austin, Texas, USA) digital analyzing programme by determining the maximum and minimum areas. Degrees of cooking of samples were evaluated by the ratio of cooked area to total area.

2.2.2 Analytical measurements

2.2.2.1 Moisture content

Moisture content of uncooked samples was determined by drying 2 g of sample for 2hr at 105^{o}C (AOAC, 1995).

2.2.2.2 Protein content

Protein content for uncooked spaghetti was determined as described by the standard Kjehdahl method (Malcolmson et al., 1993). Percent protein content was expressed in dry basis.

2.2.2.3 Ash content

2 g of sample was ground and put into crucibles. Ashing was carried out at 900 ^{o}C in a furnace and was completed when the cool residue is white or nearly white (ICC No, 104).

2.2.2.4 Cooking loss

Cooking loss, which is the amount of material leached out of pasta strands during cooking, was determined by weighing the residue (cooking water) after drying in an oven at 105 ^{o}C for 2 hours and the result is expressed as % cooking loss.

% cooking loss = 100(dry weight/wet weight) * (ml cooking water remaining/ weight of spaghetti cooked) (2.2)

2.2.2.5 Water absorption

Cooked samples were weighed soon after removing the excess water and dried in an oven at 105 ^{o}C for 2 hours. Water absorption was expressed as % water absorption.

2.2.2.6 Resistant starch determination

The presence of a starch fraction resistant to enzymic hydrolysis was first recognized by Englyst et al. during their research on the measurement of non-starch polysaccharides (Englyst et al., 1982). This work was extended by Berry (Berry, 1986) who developed a procedure for the measurement of RS incorporating the α-amylase/pullulanase treatment employed by Englyst et al. (1982), but omitting the initial heating step at 100 ^{o}C, so as to more closely mimic physiological conditions. By the early 1990s the physiological significance of RS was fully realized. There were several authors who made modifications on RS determination techniques (Akerberg et al., 1998; Goni et al., 1996; Faisant, et al., 1995; Champ, 1992) The method used in this study is an approved by AOAC (Method 2002.02) and AACC (Method 32-40).

Samples were incubated in a shaking water bath with pancreatic α-amylase and amyloglucosidase (AMG) for 16 hr at 37 ^{o}C, during which non-resistant starch solubilised and hydrolyzed to glucose by the combined action of the two enzymes. The reaction was terminated by the addition of an equal volume of ethanol, and the RS was recovered as a pellet on centrifugation. Free liquid was removed by decantation. RS in the pellet is dissolved in 2 M KOH by vigorously stirring in an ice-water bath over a magnetic stirrer. This solution was neutralized with acetate buffer and the starch is quantitatively hydrolyzed to glucose with AMG. Glucose was measured with glucose oxidase/peroxidase reagent (GOPOD), and this was a measure of the RS content of the sample. Absorbance was measured using a

spectrophotometer (Pharmacia Biotech, Novaspec II, UK) at 510 nm. Sodium acetate buffer (0.1 M, pH 4.5) and glucose (1 mg/ml in 0.2 % benzoic acid) were used as a blank and glucose standard, respectively. Figure 2.3 shows the steps in RS determination in detail.

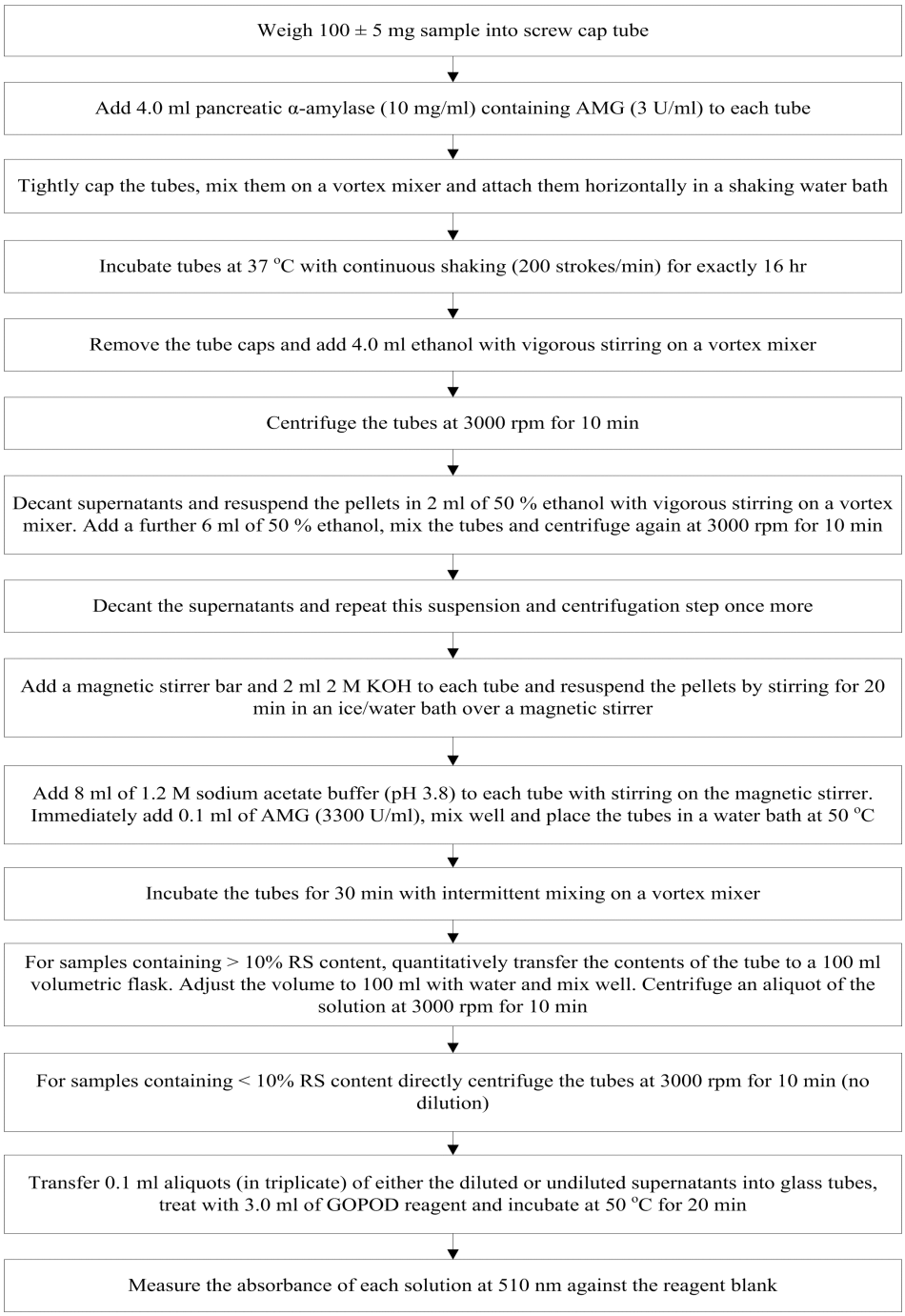

Figure 2.3 Resistant starch determination outline

RS (g/ 100 g dry sample) (samples containing > 10% RS):

$= \Delta E \times F_c \times 100/0.1 \times 1/1000 \times 100/W \times 162/180$

$= \Delta E \times F_c/W \times 90$ (2.3)

RS (g/100 g dry sample) (samples containing < 10% RS):

$= \Delta E \times F_c \times 10.3/0.1 \times 1/1000 \times 100/W \times 162/180$

$= \Delta E \times F_c/W \times 9.27$ (2.4)

where:

ΔE : absorbance read against the reagent blank

F_c : conversion from absorbance to micrograms (the absorbance obtained for 100 μg of glucose in the GOPOD reaction is determined and F_c = 100 (μg of glucose) divided by the GOPOD absorbance for this 100 μg of glucose)

100/0.1 : volume correction (0.1 ml taken from 100 ml)

1/1000 :conversion from micrograms to milligrams

W : dry weight of sample analyzed

100/W : factor to present RS as a percentage of sample weight

162/180 : factor to convert from free glucose, as determined, to anhydro-glucose as occurs in starch

10.3/0.1 : volume correction (0.1 ml taken from 10.3 ml)

2.2.2.7 Color measurements

Spaghetti color was determined with a HunterLAB ColorFlex (Model A60- 1010-615) (Hunter Associates Lab. Inc. Reston VA, USA) color difference meter according to method of Zweifel (Zweifel, 2001). The results were presented on the CIE 1976 L*a*b*-space. Dry spaghetti samples were cut into pieces of approximately 1-2 cm before each reading. Four readings were taken for each filling. The effect of sample alignment was minimized by rotating the beaker by 90^o between each reading. Four measurements were taken with filling with new sample. Results express the mean and standard deviation of readings.

Chromacity was defined as follows:

$C^* = (a^{*2} + b^{*2})^{1/2}$ (2.5)

2.2.3 Sensory panel

Sensory analysis was carried out to find the relationship between sensory and instrumental measurements of spaghetti. Spaghetti samples were cooked in distilled water to optimum cooking time. The sensory test panel consisted of 7 panellists (4 female and 3 male, 23-40 years old) selected from previously trained academic staff. Panelists received training to define texture terms for the spaghetti one month before test and they were asked to do a pre-panel. The following textural parameters were evaluated: hardness, the resistance of cooked pasta to compression by the teeth, was measured by compressing the spaghetti strand against the palate with the tongue. Adhesiveness was evaluated by placing the spaghetti in the mouth, pressing it against the palate and determining the force required to remove it with the tongue. Chewiness was measured as the number of chews to masticate a known amount of sample at a constant rate of force application to reduce it to a consistency ready for swallowing. Cohesiveness was meaured as the rate at which the spaghetti strands disintegrate under mechanical action. Springness was measured as the degree to which the product returns to its original shape after partial compression (without failure) between the tongue and palate or teeth. Each of these five parameters was evaluated on a scale ranging from 0 to 9 (Szczesniak et al., 1963). The panelists were asked to define which product they liked the best and explain the reason.

2.2.4 Data analysis

Analysis of variance (ANOVA) for cooking and texture properties were carried out using Statgraphics Plus for Windows. Pearson's correlation matrix was used for comparison of instrumental and sensory variables by SPSS software. All the modelings were done by SigmaPlot 2000 for Windows (v 6.0).

CHAPTER III
RESULTS AND DISCUSSION

In this chapter some physical and thermal characteristics of both uncooked and cooked spaghetti samples are given. The result of experimental studies and the treatment of the resultant data are presented in graphical and tabular forms and discussed separately regarding to differences in formulation and cooking times.

3.1 Preliminary work

A preliminary work was carried out before the actual research. The aim of such a work was to face with the problems that may occur during production and to get prepared for the actual production. From this point of view an intermediate formulation of 10 % RS was chosen. Table 3.1 presents the initial quality parameters of spaghetti samples, which are RS 10 % and its control used for the preliminary work.

Table 3.1 Initial quality parameters of spaghetti samples used in preliminary work

Parameters	Control	RS 10 %
Protein (%db)	12.52±0.08	12.21±0.05
Moisture content (%)	9.98±0.03	8.97±0.07
Ash (%db)	0.81±0.01	0.86±0.01

3.1.1 Instrumental measurements

3.1.1.1 Breaking strength

Good quality pasta must be strong and flexible enough to withstand stresses especially during packaging and transportation. However, it does not relate directly to textural properties of pasta during or after cooking. But the gluten strength and quality in semolina can be judged from the breaking strength data. Table 3.2 showed that addition of RS did not change the breaking strength values dramatically. The slightly increase in force value can be explained by the compactness and dense

internal structure that was attained by the addition of RS. It is also clear from the results of elastic modulus that RS 10 % spaghetti is more flexible.

Table 3.2 Three point bending test parameters of uncooked spaghetti samples

Spaghetti type	Force (N)	Deflection point (m)	Flexure strain	Flexure stress (kPa)	Elastic modulus (kPa)
Control	1.41 ± 0.12^{a}	$1.50*10^{-3}\pm0.00^{a}$	0.009 ± 0.001^{a}	$2.14*10^{4}\pm0.1^{a}$	$2.46*10^{6}\pm0.1^{a}$
RS 10 %	1.62 ± 0.16^{b}	$1.55*10^{-3}\pm0.00^{a}$	0.009 ± 0.001^{a}	$2.35*10^{4}\pm0.1^{b}$	$2.54*10^{6}\pm0.1^{b}$

Different letters indicate statistically significant differences exist at $\alpha=0.05$ based on multiple range test

3.1.1.2 Stress relaxation test

Relaxation force curves for control and RS 10 % spaghetti cooked for 12 min were shown in Figure 3.1. Initially, there was an increase in curve with the introduction of constant deformation, which decreased with time as in all viscoelastic materials. Simple Maxwell, generalized Maxwell and Peleg & Normand models with values of root mean square (RMS) and determination coefficient (R^2) were applied to spaghetti samples. Results were represented in Table 3.3. The RMS values decreased with an increase in number of terms. For the two termed model RMS values varied between 0.14–1.55 % and for the three termed model it varied between 0.02–1.18 %. Three-termed Maxwell model were found to fit better than the two termed model values by looking both R^2 and RMS values. The regression coefficients were highest in three-termed Maxwell model.

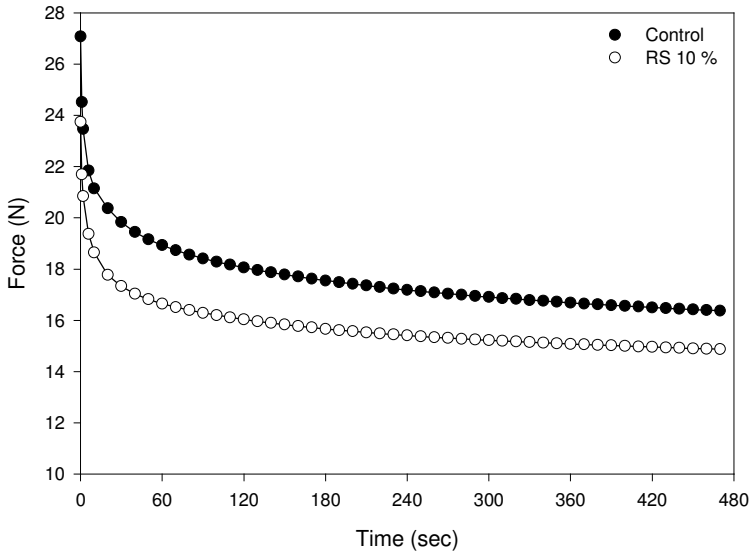

Figure 3.1 Relaxation curves of spaghetti samples cooked for 12 min

Table 3.3 Parameters of two-termed Maxwell model for cooked spaghetti samples

Spaghetti type	Cooking time (min)	F_1 (N)	F_2 (N)	λ_1 (s)	λ_2 (s)	RMS (%)	R^2
Control	6	34.76	6.70	4042	66.34	0.67	0.9990
	8	29.81	5.50	4103	69.55	0.14	0.9992
	10	22.02	7.27	2629	11.23	1.27	0.9659
	12	18.66	5.05	3269	22.10	1.06	0.9687
	14	16.43	4.59	3397	20.46	1.02	0.9702
	16	13.87	4.49	3599	12.98	1.08	0.9630
	18	13.89	4.17	3443	14.42	1.12	0.9613
RS 10 %	6	28.60	10.40	1665	17.65	1.55	0.9765
	8	23.09	7.71	2880	9.05	0.86	0.9799
	10	19.98	5.58	3432	16.90	1.18	0.9600
	12	16.47	4.89	4211	16.99	1.54	0.9165
	14	14.81	5.23	4120	12.03	1.04	0.9640
	16	14.18	4.89	3255	13.11	1.09	0.9684
	18	12.18	4.32	3288	11.51	1.15	0.9625

Tables 3.3 and 3.4 show the elements of two and three termed Maxwell models, respectively. The first term of the three-termed Maxwell model (F_1) made a major contribution of 80.20 %, 68.35 % for optimum cooked control and RS 10 % spaghetti samples, respectively (Table 3.4). The elastic components of the Maxwell element can be represented by decay forces F_1, F_2 and F_3, which indirectly measure elasticity of the material being tested. Relaxation times and force values decreased as cooking time proceeded in spaghetti samples, which is associated with product softening.

Table 3.4 Parameters of three termed Maxwell model for cooked spaghetti samples

Spaghetti type	Cooking time (min)	F_1 (N)	F_2 (N)	F_3 (N)	λ_1 (s)	λ_2 (s)	λ_3 (s)	RMS (%)	R^2
Control	6	33.36	5.95	2.55	6239	120.1	25.42	0.02	0.9999
	8	28.56	5.03	2.02	6440	126.3	26.66	0.02	0.9999
	10	20.91	3.25	3.45	4213	69.82	7.41	0.25	0.9980
	12	18.15	3.39	5.20	4359	51.88	2.51	0.30	0.9979
	14	15.99	2.93	4.44	4583	50.54	2.89	0.30	0.9977
	16	13.51	2.19	4.42	4954	43.91	2.79	0.32	0.9968
	18	13.41	2.17	2.80	4945	51.02	2.79	0.32	0.9969
RS 10 %	6	26.48	6.14	10.68	2539	79.15	4.06	0.46	0.9977
	8	22.62	2.59	7.25	3478	41.84	3.54	0.38	0.9961
	10	19.32	3.10	5.69	5056	57.30	3.23	0.59	0.9911
	12	15.79	2.54	4.77	6507	68.50	4.41	1.18	0.9482
	14	14.43	2.30	4.94	5930	43.56	3.36	0.29	0.9968
	16	13.83	2.39	4.67	4291	42.45	3.03	0.34	0.9972
	18	11.85	1.98	4.31	4443	42.43	2.68	0.35	0.9965

The reciprocal of k_1 value in Peleg & Normand model represents the initial decay rate (Table 3.5). A high k_1 value was associated with a low decay rate indicating pronounced elastic behaviour. The k_1 values were in the range of 38-60. The k_2

values increased after 10 min of cooking and did not change so much after that. The k_2 value was related with liquid like, viscous behaviour.

The parameters of the models three termed generalized Maxwell and Peleg & Normand showed that control spaghetti had more pronounced elastic behaviour than control spaghetti. But it was also a fact that there was not such a great difference between the samples, which was expected and looked for. Because it was aimed to produce a product that is texturally and physically more close to the original product.

Table 3.5 Parameters of Peleg & Normand model for cooked spaghetti

Spaghetti type	Cooking time (min)	F_0 (N)	k_1	k_2	RMS (%)	R^2
Control	6	41.00	54.16	1.95	4.09	0.9975
	8	35.64	49.22	2.19	3.72	0.9978
	10	32.29	54.67	2.31	1.23	0.9980
	12	27.08	57.84	2.45	2.78	0.9985
	14	23.75	56.65	2.49	2.63	0.9986
	16	20.46	44.60	2.46	2.88	0.9990
	18	20.35	45.85	2.46	2.82	0.9988
RS 10 %	6	44.59	60.06	1.90	4.28	0.9969
	8	33.17	58.15	2.43	3.65	0.9974
	10	28.63	55.37	2.53	2.75	0.9971
	12	23.74	42.81	2.65	2.31	0.9608
	14	22.11	38.72	2.48	2.60	0.9993
	16	21.22	45.94	2.35	3.05	0.9988
	18	18.47	41.72	2.32	4.45	0.9989

3.1.1.3 Creep test

Figure 3.2 shows creep curves of control and RS 10 % spaghetti samples cooked for 12 min. From the creep data for each cooking time (results not shown) it was found that creep compliance which is an indicator of softness increased with time. This behaviour is manifested by the different values of Burgers equation used to model creep data (Table 3.6).

D_o and D_1 shear compliance values for control spaghetti were in general higher than RS 10 % spaghetti. This meant that RS 10 % spaghetti was firmer than control spaghetti. As cooking time proceeded it was easier to deform the spaghetti samples because of possible softening of the structure with starch gelatinization.

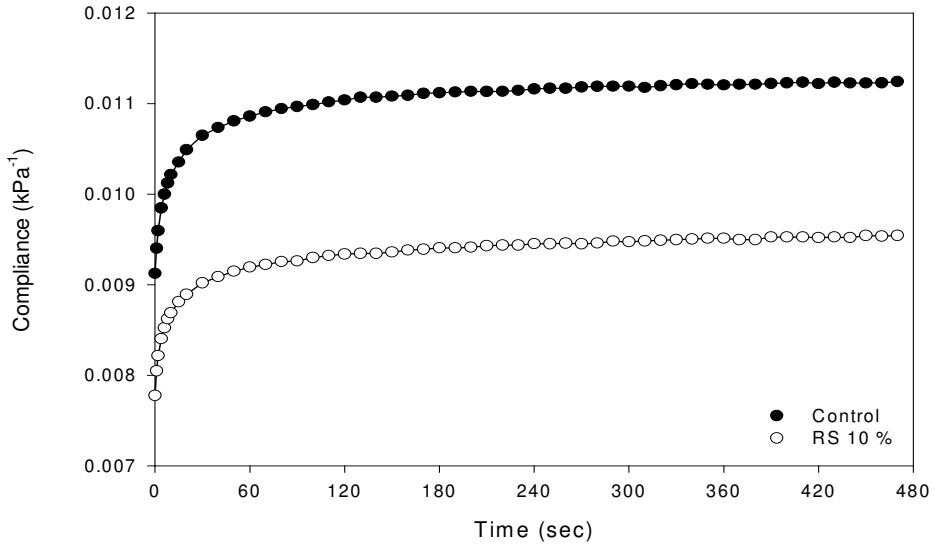

Figure 3.2 Creep behaviour of 12 min cooked control and RS 10 % spaghetti

Table 3.6 Parameters of Burgers model for cooked spaghetti samples

Spaghetti type	Cooking time (min)	D_o*10^{-3} (kPa^{-1})	D_1*10^{-4} (kPa^{-1})	D_2*10^{-4} (kPa^{-1})	μ_o*10^6 (kPa.s)	λ_{ret1} (s)	λ_{ret2} (s)	RMS (%)	R^2
Control	6	5.13	12.03	8.78	7.26	279.2	6.84	0.38	0.9952
	8	6.38	7.00	7.69	6.19	147.5	10.67	0.79	0.9541
	10	7.40	6.06	10.08	5.68	129.2	9.54	0.22	0.9946
	12	8.42	7.64	15.25	4.98	83.48	5.74	0.32	0.9887
	14	9.08	5.81	11.31	3.58	67.97	7.15	0.16	0.9953
	16	9.35	7.41	10.29	3.25	51.01	5.88	0.13	0.9978
	18	9.69	7.98	12.16	2.69	47.82	5.45	0.11	0.9980
RS 10 %	6	5.65	9.99	5.98	6.80	367.3	10.30	0.26	0.9961
	8	6.12	6.92	6.88	6.99	210.4	13.25	0.21	0.9964
	10	7.05	5.46	8.35	6.97	116.3	9.21	0.21	0.9941
	12	7.91	5.92	9.40	5.99	78.68	7.10	0.57	0.9916
	14	8.87	6.68	11.22	4.99	67.08	6.76	0.14	0.9964
	16	8.95	6.85	11.27	3.75	55.87	5.89	0.15	0.9955
	18	10.06	6.92	8.72	2.68	32.56	4.02	0.45	0.9425

From Table 3.7, k_1 values of Peleg model were lower for over cooked spaghetti resulting in a less stiff product. However k_2 values which is more associated with plastic material properties decreased as cooking time increased.

Creep test is more related with surface properties than stress relaxation test. During cooking on the surface of spaghetti there is always a kind of starchy layer, which is probably responsible of the measured plasticity. As cooking time proceeded due to breakdown of the gluten network starch can more easily escape on the cooking water and its concentration on the surface of spaghetti strand relatively decreases.

Table 3.7 Parameters of Peleg model for cooked spaghetti samples

Spaghetti type	Cooking time (min)	k_1	k_2	RMS (%)	R^2
Control	6	1511	140.1	11.56	0.9992
	8	648.4	125.7	8.70	0.9992
	10	431.0	109.4	7.89	0.9999
	12	292.0	92.03	7.22	0.9999
	14	184.4	91.69	6.30	0.9990
	16	191.7	88.41	6.40	0.9999
	18	183.3	83.90	6.37	0.9999
RS 10 %	6	1205	140.9	10.82	0.9995
	8	795.0	132.5	9.34	0.9998
	10	411.1	117.1	7.61	0.9999
	12	258.2	104.6	6.70	0.9996
	14	216.4	92.59	6.50	0.9999
	16	197.5	90.72	6.35	0.9999
	18	110.6	84.73	5.59	0.9997

3.1.1.4 Texture profile analysis (TPA)

Hardness and adhesiveness are the most important textural parameters. The hardness values of RS 10 % spaghetti were higher than the control (Table 3.8). On the other hand adhesiveness values were lower. The difference between either hardness values or adhesiveness values can be related to the difference in particle size of added resistant starch and semolina. Resistant starch was in fine powder form limiting water diffusion inside spaghetti strand. It can be hypothesized that it had a kind of filling effect, which limited water migration. The fact that there is not much difference between the protein content of control and RS 10 % spaghetti strengthens this hypothesis. The protein (% d.b.) and moisture content of control and RS 10 % spaghetti were 12.52 (% protein), 9.98 (% M.C.) and 12.21 (% protein), 8.97 (% M.C.), respectively.

Adhesiveness is basically related to starch that escapes during cooking. As cooking time proceeds there was a decrease in hardness and adhesiveness values since starch granules leach into cooking water and more protein stays in spaghetti structure.

Cohesiveness can be a good indicator of how the sample holds together upon cooking. There were not so much difference between cohesiveness values of control and RS containing spaghetti (Table 3.9).

Table 3.8 Mean values and standard deviations of TPA results of cooked spaghetti samples

Spaghetti type	Cooking time (min)	Hardness (N)	Adhesiveness (N.s)	Cohesiveness	Chewiness
Control	6	66.27±1.79^{a}	0.77±0.03^{a}	0.74±0.01^{a}	44.32±3.28^{a}
	8	55.49±7.23^{b}	0.54±0.04^{bc}	0.78±0.00^{ab}	40.12±5.65^{a}
	10	55.65±7.45^{c}	0.44±0.09^{bc}	0.81±0.01^{ab}	35.33±5.15^{ab}
	12	35.79±1.62^{d}	0.40±0.01^{b}	0.83±0.01^{ab}	27.87±1.22^{bc}
	14	28.24±2.19^{de}	0.55±0.07^{bc}	0.84±0.00^{b}	22.54±1.37^{c}
	16	26.00±2.48^{ef}	0.45±0.01^{bc}	0.84±0.00^{ab}	20.58±2.43^{c}
	18	23.52±3.01^{f}	0.55±0.05^{c}	0.83±0.02^{ab}	18.39±3.40^{c}
RS 10 %	6	68.94±0.88^{a}	0.56±0.10^{ab}	0.75±0.03^{a}	47.98±1.73^{a}
	8	50.07±1.02^{b}	0.45±0.03^{bc}	0.79±0.01^{ab}	37.04±2.48^{b}
	10	40.24±2.48^{c}	0.34±0.01^{c}	0.84±0.02^{bc}	31.70±3.51^{bc}
	12	33.74±3.12^{cd}	0.40±0.03^{c}	0.85±0.01^{bc}	27.22±2.17^{cd}
	14	32.53±4.39^{cde}	0.48±0.06^{c}	0.84±0.03^{bc}	26.15±2.73^{cde}
	16	28.42±4.78^{de}	0.41±0.01^{c}	0.83±0.04^{bc}	21.96±2.14^{de}
	18	25.00±2.83^{f}	0.38±0.01^{c}	0.90±0.01^{c}	20.50±2.12^{e}

Different letters indicate statistically significant differences exist at α=0.05 based on multiple range test

Table 3.9 LSD multiple range analysis of TPA parameters for cooked spaghetti samples

Effect		LS Mean±standard error[1] Hardness (N)	Adhesiveness (N.s)	Cohesiveness	Chewiness
Spaghetti type	Control	40.22±1.06^{a}	0.53±0.02^{a}	0.81±0.01^{a}	29.67±0.89^{a}
	RS 10 %	39.86±1.06^{a}	0.46±0.02^{b}	0.81±0.01^{a}	30.23±0.89^{a}
Cooking time (min)	6	67.60±1.99^{a}	0.66±0.03^{a}	0.76±0.01^{a}	45.43±1.66^{a}
	8	52.78±1.99^{b}	0.49±0.03^{b}	0.78±0.01^{b}	38.58±1.66^{b}
	10	43.24±1.99^{c}	0.39±0.03^{c}	0.82±0.01^{c}	33.51±1.66^{c}
	12	34.76±1.99^{d}	0.40±0.03^{c}	0.83±0.01^{c}	27.53±1.66^{d}
	14	30.37±1.99^{de}	0.42±0.03^{d}	0.83±0.01^{c}	24.34±1.66^{de}
	16	27.21±1.99^{ef}	0.51±0.03^{cd}	0.83±0.01^{c}	21.26±1.66^{ef}
	18	24.31±1.99^{f}	0.58±0.03^{a}	0.82±0.01^{c}	18.99±1.66^{f}

[1]Means within a column followed by different levels are significantly different (P<0.05)

Chewiness which is related to the elastic strength of the protein matrix was higher for RS 10 % spaghetti. As cooking time proceeded chewiness of both control and RS 10 % spaghetti decreased dramatically (Table 3.8) due to possible break down of gluten network and leaching of starch to cooking water.

3.1.1.5 Thermal analysis

Table 3.10 shows the mean values for DSC gelatinization of starch from semolina, uncooked and cooked spaghetti samples. The analysis of the peak temperatures did not make so much difference between the different spaghetti samples (Table 3.10). However, the range for gelatinization temperatures made some difference. Uncooked spaghetti enriched with RS had the lowest gelatinization temperature. For all the

spaghetti samples when water migration increased, as cooking time proceeded, ΔH values decreased regardless of spaghetti type. Figure 3.3 shows the gelatinization (%) with respect to cooking time (min). Spaghetti with RS found to gelatinize at a faster rate than control spaghetti.

Table 3.10 Thermal characteristics of spaghetti samples: onset (T_o), peak (T_p), and completion (T_c) temperatures, gelatinization enthalpies (ΔH), and gelatinization ranges ($\Delta T_r = T_c - T_o$)

Spaghetti type	Cooking time (min)	T_o (°C)	T_p (°C)	T_c (°C)	ΔT_r (°C)	ΔH (J/g)
Control	0	57.42±0.04	63.00±0.56[a]	68.64±0.78	11.22±0.83	3.19±0.08[a]
	2	57.85±0.52	62.73±0.34[a]	68.42±0.63	10.57±0.11	2.93±0.24[a]
	4	58.50±0.17	62.46±0.15[a]	67.87±0.25	9.37±0.42	1.71±0.32[b]
	6	58.91±0.16	62.57±0.75[a]	68.16±0.55	9.25±0.72	1.47±0.02[b]
	8	58.94±0.42	63.23±0.45[a]	67.76±0.15	8.82±0.26	0.62±0.01[c]
	10	62.12±0.04	65.56±0.17[a]	67.97±0.84	5.85±0.83	0.47±0.03[c]
RS 10 %	0	57.79±1.30	63.15±0.37[a]	68.36±0.84	10.57±1.14	2.17±0.34[a]
	2	58.63±1.58	63.54±1.05[a]	68.68±1.11	10.05±0.46	1.62±0.02[b]
	4	58.53±0.73	63.23±0.01[a]	68.41±1.81	9.88±1.55	1.28±0.02[c]
	6	58.73±0.61	63.29±0.36[a]	67.34±1.58	9.61±1.19	0.82±0.02[d]
	8	60.05±0.73	65.06±0.16[b]	68.39±0.66	8.34±0.06	0.25±0.01[e]
	10	60.85±0.71	65.36±1.50[b]	68.44±0.70	7.59±0.01	0.12±0.01[f]

Different letters indicate statistically significant differences exist at α=0.05 based on multiple range test

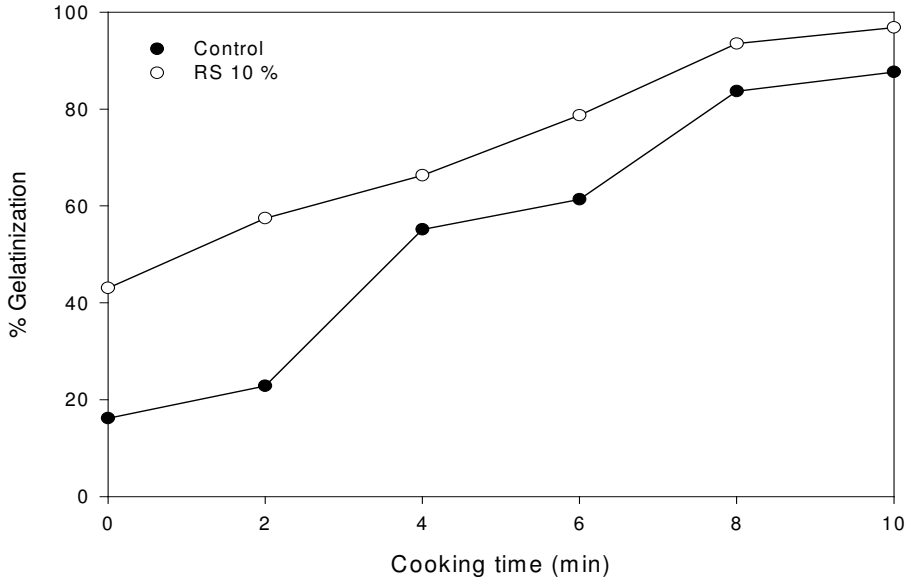

Figure 3.3 % Gelatinization of control and RS 10 % spaghetti

3.1.1.6 Image analysis

Image analysis enabled to calculate uncooked and cooked areas much more easily and correctly. From the ratio of cooked area to total area, optimum-cooking times were determined. As cooking time proceeded both the cooked area and total area increased (Table 3.11).

Table 3.11 Percent gelatinization by image analysis

Cooking time (min)	Gelatinization %	
	Control	RS 10 %
6	87.56	86.35
8	92.25	93.61
10	98.38	98.32
12	98.73	99.59

3.1.2 Analytical measurements

3.1.2.1 Cooking loss and water absorption

Cooking loss is the amount of dry matter lost into the cooking water of optimally cooked spaghetti. Cooking loss was higher in control spaghetti (Table 3.12). The decrease in cooking loss with RS containing spaghetti can be explained by the compactness given to the structure with the addition of RS in fine powder form. This finding encompasses with the results of breaking strength test.

Table 3.12 Percent cooking loss of spaghetti samples

Cooking time (min)	Control	RS 10%
6	6.37±0.78	4.80±0.19
8	6.71±0.65	5.30±0.23
10	8.17±0.25	6.00±0.23
12	8.03±0.35	7.40±0.37
14	8.97±0.49	7.50±0.48
16	10.36±0.55	7.00±0.45
18	10.11±0.27	8.20±0.45

Swelling of spaghetti strands occurs during cooking of spaghetti. Water uptake shows how well spaghetti responds to cooking. Spaghetti enriched with 10 % RS had slightly higher water absorption results as compared to control spaghetti (Table 3.13).

Table 3.13 Percent water absorption of spaghetti samples

Cooking time (min)	Control	RS 10 %
6	136.84±0.42	133.21±2.09
8	152.15±3.35	152.67±2.83
10	175.36±1.09	180.61±0.76
12	191.70±1.10	201.91±1.37
14	199.49±0.33	214.17±4.05
16	228.69±3.35	222.94±4.13
18	233.05±1.70	247.70±1.04

3.2 Main work

In this section the quality of RS 5 %, RS 15 %, their control and bran containing spaghetti samples were compared for physical, thermal and sensorial attributes. Different from the preliminary work in this part bran spaghetti was included into the research since RS was chosen to be a good alternative for traditional fiber sources. As a result, it is of great importance to see the extremes in this type of spaghetti. In the Table 3.14 some initial quality parameters like moisture, protein, ash and RS_3 content of samples are given. RS_3 content of bran containing spaghetti was not determined since the assay procedure was not suitable for determining insoluble fiber content. There was a decrease in protein content of samples as some portion of semolina was replaced by RS. The amount of RS_3 in the commercial RS, which was used for enrichment, was 45 (g/100 g dry sample). So a 5 and 15 % of RS enrichment in the spaghetti formulation caused 4.05 and 7.57 RS_3 formation. If the amount of RS formed during processing is taken into account there was a little difference than expected RS_3 amount of RS 15 % spaghetti. The amount of RS_3 formed during processing of control spaghetti was 0.45.

Table 3.14 Initial quality parameters of spaghetti samples

Type of spaghetti	Moisture content (%)	Protein content (%db)	Ash content (%db)	RS_3 content (g/100 g dry sample)
Control	9.92±0.05	12.58±0.02	0.79±0.01	0.45±0.001
RS 5 %	10.24±0.03	12.29±0.02	0.71±0.01	4.05±0.001
RS 15 %	8.92±0.04	11.46±0.03	0.66±0.03	7.57±0.007
Bran	8.03±0.03	15.39±0.05	1.17±0.01	not tested

3.2.1 Instrumental measurements

3.2.1.1 Breaking strength

The gluten strength/quality of the parent semolina may determine the dry strength of the pasta. Breaking strength aids to determine how well the product tolerates shipping and may indicate how well a product holds together upon cooking. Processing conditions however, have a more impact on breaking strength than semolina quality. As a result, testing of breaking strength alone is not sufficient enough to predict the cooking quality of pasta, but it might be useful as a quality control procedure for the pasta industry, as the measurement can be done more rapidly than a cooking test.

Breaking strength of samples was determined by performing three point bending test. The breaking strength of the sample was taken as the maximum values of the curve. Other textural parameters of interest were distance to break, strain and elasticity. The parameters of three point bending test are shown in Table 3.15. According to results, RS 15 % had the highest elasticity value and deflection point. Deflection point values gives an idea about brittleness of the sample as this shows how far a sample can be deformed before fracture. The increase in elasticity values in RS 15 % spaghetti sample can be the result of a more compact and dense structure. Since all the samples were subjected to the same drying process the effect of drying on stress building overestimated.

Table 3.15 Three point bending test parameters of spaghetti samples

Spaghetti type	Force (N)	Deflection point (m)	Flexure strain	Flexure stress (kPa)	Elastic modulus (kPa)
Control	1.49 ± 0.20^{a}	$1.52*10^{-3}\pm0.00^{a}$	0.01 ± 0.001^{a}	$2.40*10^{4}\pm0.20^{a}$	$2.45*10^{6}\pm0.20^{a}$
RS 5 %	1.59 ± 0.11^{b}	$1.78*10^{-3}\pm0.00^{bc}$	0.01 ± 0.001^{a}	$2.56*10^{4}\pm0.17^{b}$	$2.39*10^{6}\pm0.20^{b}$
RS 15 %	1.56 ± 0.12^{b}	$1.90*10^{-3}\pm0.00^{c}$	0.01 ± 0.001^{a}	$2.77*10^{4}\pm0.15^{c}$	$2.53*10^{6}\pm0.20^{c}$
Bran	1.62 ± 0.11^{b}	$1.72*10^{-3}\pm0.00^{b}$	0.01 ± 0.001^{a}	$2.37*10^{4}\pm0.12^{d}$	$2.30*10^{6}\pm0.09^{d}$

Different letters indicate statistically significant differences exist at $\alpha=0.05$ based on multiple range test

At low temperatures and low moisture contents many cereal-based foods are brittle. Brittle fracture is distinguished by the ability to put the pieces of the broken object back into its original size and dimensions. As temperature or moisture increases, the food system begins to yield before fracture occurs, it becomes ductile.

3.2.1.2 Rheological measurements for cooked spaghetti samples

During drying the mechanical properties of pasta change significantly, the soft product (i.e., fresh pasta) transforms into a rigid product (i.e. dry pasta). The changes in mechanical properties of pasta change from plastic behavior (above 39 % water db) to elastic behavior (below 23 % water db), with an intermediate plasto-elastic behavior (Cuq et al., 2003). However, during cooking the elastic pasta passes to a more plastic state by the action of water. Whole durum wheat is employed in traditional pasta manufacture because of the unique rheological properties of gluten. Cooking quality of pasta and pasta products influenced by the quality of semolina. Cooking quality is determined by two independent parameters: viscoelastic behavior (particularly firmness after cooking) and the surface condition of cooked pasta (Liu et al, 1996). Gluten is mainly responsible of the elastic nature of spaghetti. The replacement of durum wheat semolina with RS in the formulation can change the viscoelastic properties. So it was important to see the extent of this change. Stress relaxation and creep tests are good examples of rheological tests that allow an insight into the structure of the material, because the physical manifestation of a material is due to its chemical makeup. Tests like texture profile analysis correlate consumer acceptance with some rheological aspect of solid foods – for example, hardness or adhesiveness of cooked spaghetti – with consumer acceptance (Rao and Skinner, 1986).

3.2.1.2.1 Stress relaxation test

A viscoelastic material consist of several dashpots and springs with several rheological constants. There is no simple constant for viscoelastic materials such as modulus, because the modulus will change over time. Stress relaxation under constant strain can be used to map out viscoelastic characteristics. The mechanical properties of cooked spaghetti were characterized by measuring the corresponding force values under constant deformation rate. Relaxation force curves for all spaghetti types cooked for 12 min were shown in Figure 3.4. Initially, there was an increase in curve with the introduction of constant deformation. Afterwards the force necessary for the maintenance of the deformation decreased with time as in all viscoelastic materials. During cooking of pasta, water migrates from outside to inner parts causing starch gelatinization and protein denaturation. This is also evident from

the water uptake results. The increase in water content of spaghetti caused a decrease in force values. Increase in cooking time is related with an increase in water absorption in time. It should be noted that when spaghetti is dry, it behaves as a rigid, elastic material (Shimonovich and Shimoni, 2003).

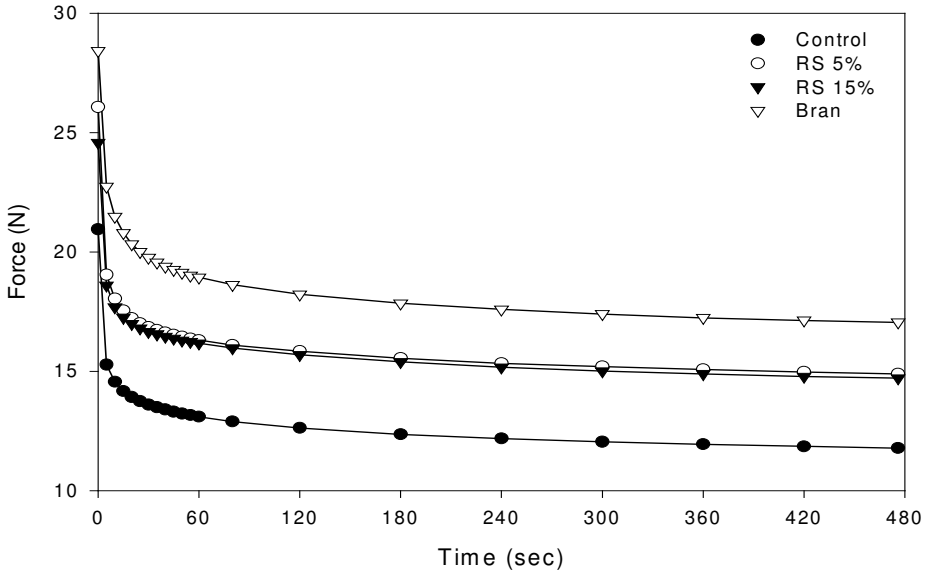

Figure 3.4 Relaxation curves of spaghetti samples cooked for 12 min

With the water migration and structural changes such as starch gelatinization and protein denaturation it behaves like a viscoelastic material. As cooking time proceeds especially after 14 min in the overcooked region it starts to behave as a soft material.

Iterative calculations using SigmaPlot 2000 (for Windows version 6.0) software based on a least square algorithm, gave the relaxation parameters. Simple Maxwell, generalized Maxwell and Peleg & Normand models with values of root mean square (RMS) and determination coefficient (R^2) were applied to spaghetti samples. The number of Maxwell elements required to represent the sample efficiently can be determined by the method of successive residuals or by comparing R^2 (percent explained variation) values for relaxation data fit to individual model equations. Results were represented in Tables 3.16-3.17. The RMS values decreased with an increase in number of terms. For the two termed model RMS values varied between 1.14–2.86 % and for the three termed model it varied between 0.25–0.84 %. Goodness of fit (or an increase in R^2 values) of the relaxation model to the relaxation

data can, in fact, be increased by adding one or more Maxwell elements. Three-termed Maxwell model were found to fit better than two termed Maxwell and Peleg & Normand values by looking both R^2 and RMS values. The regression coefficients were highest in three-termed Maxwell model.

Tables 3.16 and 3.17 show the elements of two and three termed Maxwell model, respectively. The first term of the three termed Maxwell model (F_1) made a major contribution of 61.48 %, 62.26 %, 65.37 %, 65.89 % for optimum cooked control, RS 5 %, RS 15 % and bran spaghetti, respectively (Table 3.17). The initial force dissipated at a very slow rate for all spaghetti samples. The elastic components of the Maxwell element can be represented by decay forces F_1, F_2 and F_3, which indirectly measure elasticity of the material being tested. Force values associated with stress relaxation behaviour more affected than the relaxation time. As force values decreases the samples are not hard and it needs a lower force to reach a given deformation. Spaghetti can be thought as a polymer system that consists of both starch and gluten. Spaghetti cooking can be analysed in three different regions; early stages of cooking, optimum cooking and over cooking. Rheological properties of spaghetti samples changed dramatically with increasing cooking time. The optimum cooking time was approximately 12 min for each spaghetti type.

It was hypothesized that spaghetti samples structurally come to equilibrium in the optimum cooked region with the plasticizing action of water. In fact bran spaghetti seems to be more elastic by looking at the force values, it had lower relaxation time than spaghetti samples enriched with RS. In general relaxation time of spaghetti samples decreased with increasing cooking time. Spaghetti is a composite material in which gluten forms the continuous matrix and starch granules act as filler particles within that matrix. The rheological properties of the composite depend on the material properties of the protein matrix and starch filler, and degree of adhesion and interaction between the starch granules and protein matrix (Edwards et al., 2002).

Table 3.16 Parameters of two-termed Maxwell model for cooked spaghetti samples

Spaghetti type	Cooking time (min)	F_1 (N)	F_2 (N)	λ_1 (s)	λ_2 (s)	RMS (%)	R^2
Control	6	21.66	11.43	1729	7.54	2.04	0.9519
	8	18.05	8.70	2948	7.72	1.51	0.9413
	10	14.56	6.11	3513	8.54	1.49	0.9342
	12	13.12	5.15	3826	8.72	1.40	0.9318
	14	11.41	5.15	3892	6.80	1.57	0.9151
	16	10.30	4.74	3336	6.18	1.39	0.9396
	18	9.78	4.73	3213	5.93	1.57	0.9481
RS 5 %	6	29.47	14.23	2509	9.55	1.57	0.9555
	8	23.36	10.03	4074	7.40	1.24	0.9430
	10	20.45	8.76	3463	5.65	1.47	0.9302
	12	16.38	6.95	4280	6.95	1.25	0.9388
	14	14.85	7.01	3888	5.39	1.49	0.9254
	16	11.55	4.93	3397	7.29	1.47	0.9344
	18	11.23	5.57	2974	5.13	1.65	0.9291
RS 15 %	6	32.07	14.28	2512	9.43	1.41	0.9626
	8	24.23	8.67	4292	9.86	1.19	0.9453
	10	21.17	7.83	4278	6.08	1.10	0.9447
	12	16.24	6.05	4146	7.27	1.17	0.9455
	14	14.11	5.04	3730	7.80	1.16	0.9491
	16	12.04	4.86	3746	7.64	1.30	0.9417
	18	10.84	5.63	3438	5.28	1.50	0.9326
Bran	6	24.03	22.85	1910	5.30	2.07	0.9521
	8	23.30	8.20	3801	11.73	2.86	0.9767
	10	19.36	5.86	4153	18.64	2.70	0.9969
	12	18.76	6.56	4329	14.67	1.06	0.9630
	14	16.36	5.43	4701	15.23	0.95	0.9682
	16	15.24	4.88	4829	15.44	0.92	0.9676
	18	13.79	5.10	4106	11.33	1.14	0.9561

The drop in force between first, second and third terms can be related to destruction of internal structure and water migration in time. Relaxation times and force values decreased as cooking time proceeded in spaghetti samples, which is associated with product softening. The relation between the coefficient of viscosity and the modulus of elasticity, in the Maxwell model, is called relaxation time ($\lambda = \mu/E$), which corresponds to the duration of stress to reduce to 1/e of its original value. The knowledge of this time allows the calculation of the number of Deborah ($D_b = \lambda/t_o$), where t_o is the time of experimental observation: $D_b << 1$ is the index of a viscous fluid; $D_b >> 1$ is the index of an elastic solid; and $D_b \sim 1$ is the index of a viscoelastic behaviour (Chandra and Sobral, 2000). Relaxation times decreased as number of terms increased.

Table 3.17 Parameters of three termed Maxwell model for cooked spaghetti samples

Spaghetti type	Cooking time (min)	F_1 (N)	F_2 (N)	F_3 (N)	λ_1 (s)	λ_2 (s)	λ_3 (s)	RMS (%)	R^2
Control	6	20.39	4.58	12.74	2504	51.90	1.80	0.63	0.9955
	8	17.60	3.92	9.22	3788	28.33	1.25	0.50	0.9949
	10	14.06	2.59	6.65	5509	42.10	1.76	0.44	0.9946
	12	12.74	2.29	5.69	5703	37.80	1.53	0.42	0.9945
	14	11.06	2.07	5.77	6105	35.70	1.23	0.48	0.9931
	16	10.05	1.82	4.93	4454	30.33	1.37	0.40	0.9954
	18	9.50	1.72	3.02	3256	28.11	1.20	0.37	0.9918
RS 5 %	6	28.39	6.10	14.64	3465	40.82	2.26	0.50	0.9957
	8	22.89	4.16	10.06	5448	28.65	1.61	0.41	0.9948
	10	19.68	2.97	9.36	5676	47.24	1.60	0.39	0.9948
	12	16.02	2.71	7.00	6026	31.15	1.65	0.44	0.9929
	14	14.33	2.26	7.27	6598	42.64	1.64	0.43	0.9935
	16	11.20	1.99	5.33	4952	37.62	1.51	0.48	0.9936
	18	10.82	1.89	5.91	4482	40.05	1.32	0.46	0.9942
RS 15 %	6	30.95	5.82	14.29	3406	43.13	2.59	0.45	0.9961
	8	23.58	3.76	9.02	6505	41.35	2.23	0.35	0.9952
	10	20.71	2.63	7.96	5939	35.84	1.80	0.40	0.9933
	12	15.80	2.14	6.23	6259	42.93	2.16	0.38	0.9941
	14	13.80	2.04	5.25	4935	34.66	1.75	0.40	0.9947
	16	11.72	1.90	5.11	5380	37.52	1.80	0.40	0.9941
	18	10.55	1.94	5.76	4801	30.41	1.34	0.48	0.9934
Bran	6	23.40	2.59	9.50	2272	11.90	17.65	0.84	0.9946
	8	22.71	2.89	7.89	5282	50.72	4.84	0.28	0.9971
	10	18.95	3.53	9.65	5543	44.90	3.95	0.27	0.9970
	12	18.34	3.53	5.97	6049	39.37	2.92	0.37	0.9957
	14	15.95	2.62	5.26	7105	47.19	4.09	0.26	0.9976
	16	14.88	2.43	4.76	7134	45.51	3.86	0.25	0.9976
	18	13.39	2.13	4.46	6274	46.27	3.75	0.28	0.9969

In the first terms of relaxation time (λ_1), $D_b >> 1$ but on the second and third terms $D_b << 1$ (Table 19). The first term related with elastic properties and the rest with viscous properties. Materials that present a predomince of viscous behaviour (plastic) in detriment of its elastic character have smaller relaxation time, i.e. dissipate faster the applied stress or force (Giczewska and Borowska, 2003). Spaghetti samples behaved as a viscoelastic material showing a dominant elastic behaviour. Unfortunately, there are no works specialized on viscoelastic properties of spaghetti in the literature. For this reason it is impossible to make comparison with other results of viscoelastic properties. Peleg & Normand model is a good alternative to Maxwell models. It is easy to perform and analyse the results.

The only disadvantage is loss of some information in the initial stage of the relaxation process. The determination coeffiecient, R^2 of the generalized Maxwell model was around 0.995 for all spaghetti samples, and root mean squares, RMS, ranged between 0.27-0.84 %. In the Peleg model R^2 was higher than Maxwell model around 0.999 and RMS varied from 2.76-7.25 %. A comparison between the determination coefficient R^2 and root mean squares RMS for the force relaxation curves received on the basis of the generalized Maxwell model and the Peleg model indicated that the generalized Maxwell model predicted experimental data better than the Peleg model. But it should be taken into account that the Peleg model has only two parameters whereas Maxwell model has six parameters, and the Peleg model has more physical meaning. The reciprocal of k_1 value in Peleg & Normand model represents the initial decay rate (Table 3.18).

A high k_1 value was associated with a low decay rate indicating pronounced elastic behaviour. The k_1 values were in the range of 20-42. The k_1 values of optimal cooked spaghetti samples were 27.69, 25.29, 32.29, and 36.25 for control, RS 5 %, RS 15 % and bran containing spaghetti, respectively. By the addition of RS into formulation k_1 values decreased which showed that spaghetti declined from a more elastic structure to a viscous structure. Bran containing spaghetti had the highest k_1 value. The k_2 value was related with liquid like, viscous behaviour. For all spaghetti samples the k_2 values were around 2.5 and increased slightly with cooking time. On the other hand within different spaghetti types it didn't change so much.

Table 3.18 Parameters of Peleg & Normand model for cooked spaghetti

Spaghetti type	Cooking time (min)	F_0 (N)	k_1	k_2	RMS (%)	R^2
Control	6	38.37	34.00	1.75	6.00	0.9986
	8	30.99	26.58	1.99	6.52	0.9993
	10	23.64	27.53	2.18	3.21	0.9996
	12	20.95	27.69	2.25	3.42	0.9996
	14	19.06	21.80	2.14	3.68	0.9997
	16	16.93	21.78	2.13	4.16	0.9993
	18	16.27	20.13	2.16	3.41	0.9996
RS 5 %	6	50.11	31.46	1.95	4.40	0.9951
	8	37.48	26.10	2.26	3.40	0.9995
	10	32.41	29.20	2.24	3.91	0.9994
	12	26.05	25.29	2.30	3.30	0.9996
	14	24.18	23.36	2.21	3.60	0.9996
	16	18.74	28.09	2.17	3.90	0.9994
	18	18.81	26.75	2.05	4.60	0.9994
RS 15 %	6	52.16	36.98	2.04	4.25	0.9988
	8	36.95	31.61	2.43	2.86	0.9995
	10	31.67	32.85	2.50	3.31	0.9994
	12	24.58	32.29	2.45	3.20	0.9994
	14	21.32	36.24	2.41	3.50	0.9991
	16	18.98	29.57	2.28	3.50	0.9994
	18	18.43	22.91	2.06	4.29	0.9995
Bran	6	53.89	17.24	1.54	7.25	0.9994
	8	35.38	38.50	2.38	3.03	0.9991
	10	29.08	41.53	2.45	2.53	0.9992
	12	28.42	36.25	2.44	2.36	0.9995
	14	25.03	33.09	2.43	2.36	0.9996
	16	23.14	33.51	2.47	2.34	0.9995
	18	21.25	32.84	2.37	2.76	0.9995

3.2.1.2.2 Creep test

It has been shown that creep compliance tests can provide more information than tests involving stress relaxation. The main advantage of creep compliance tests over stress relaxation tests is that analysis can be facilitated by using the Burgers model (Alvarez et al., 1998). With this model a larger number of rheological parameters can be estimated and elastic, viscoelastic and viscous flow characteristics can be predicted separately. Model parameters should be associated with discrete components of the product being tested, reflecting microstructural changes. In creep compliance samples are subjected to constant stress. Creep data are time consuming to handle because of the large volume of the data generated during the experiment as a result of this fact a macro was written to compute and select some data points.

Deformation was measured as a function of time and the resulting data was expressed as in Figures 3.5 and 3.6. Figure 3.5 shows creep compliance values of

control spaghetti cooked for 6, 8, 10, 12, 14, 16, and 18 min. From this figure it is quite clear that spaghetti samples became softer with cooking time and creep compliance, which is an indicator of softness increased with time. Viscoelastic compliances (D) of all spaghetti samples were lowest after 6 min of cooking and highest after 18 min of cooking.

Figure 3.6 shows creep curves of all spaghetti samples cooked for 12 min. This behaviour is manifested by the different values of Burgers equation used to model creep data (Table 3.19). Initial shear compliance (D_o) value is the instantaneous compliance in which the linkages between the structural units stretched elastically (Alvarez et al., 1998). D_o values of bran spaghetti were lower than RS and control spaghetti samples. The reason can be related to higher amount of protein in bran spaghetti (Table 3.14). In general, the viscoelastic compliance D_1 values were lower than D_2, reflecting the greater elasticity associated with the second element of the model.

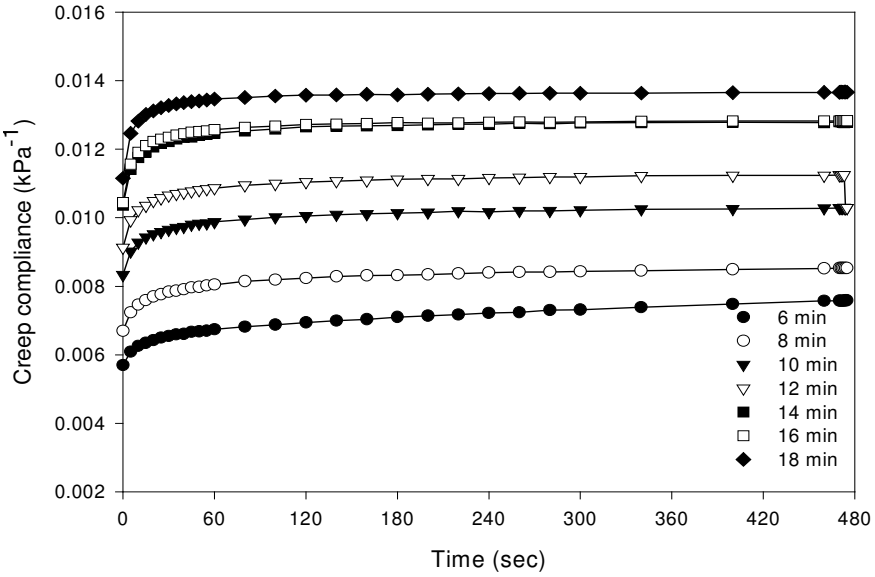

Figure 3.5 Creep recovery curves of control spaghetti cooked for 6-18 min

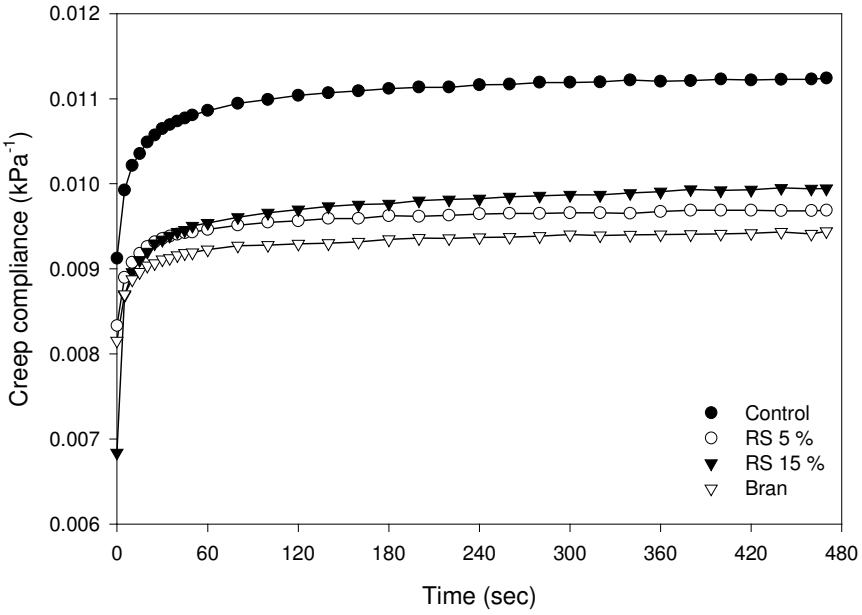

Figure 3.6 Creep recovery curves of 12 min cooked spaghetti samples

Viscoelastic compliance values (D_o and D_1) for control spaghetti were higher than spaghetti enriched with RS. It is known that spaghetti consists of starch embeded in a continuous protein network and as cooking time proceeds there will be an increase in the number of broken linkages. The weaker ones will be broken before the strong ones (Alvarez et al., 1998). In the retarded elastic region the rate of strain decreases from the D_o value because the linkages in the network begin to rupture.

As cooking time proceeded it was easier to deform spaghetti samples than early stages of cooking. In the optimum cooking time (12 min) the viscosity (μ_o) of bran spaghetti was lowest resisting less to flow. It was interesting to see that compliance value in the third term of Burgers model (D_2) was so much different for bran spaghetti than the other two types. The reason was presence of bran particles resulting a decrease in gluten network strength and having a diluting effect on gluten cohesiveness (Manthey et al., 2004; Kordonowy and Youngs, 1985). Viscosity values of bran spaghetti were also lowest in all cooking times. Retardation time of first element (λ_1) was higher than the second element (λ_2) for all spaghetti samples and cooking times. Retardation time reflects viscoelastic behaviour over short

periods (Alvarez et al., 1998) and the structural components in the second term reached equilibrium faster than the components of first term.

One of the drawbacks of the creep compliance test is a high degree of variability, particularly of data relating to early stages of test. Some authors attribute this variability to physiological factors (Pitt, 1992). Food is a complex system where food constituents, such as proteins, carbohydrates, minerals, vitamins, etc, interact in an aqueous environment. The complex chemical and physical interactions arising during processing and before consumption are the main factors determining the heterogeneous structure and texture of foods (Hongsprabhas, 2001). During compression of spaghetti strands some variations may occur in the gluten matrix and starch embedded inside it. The deformations caused by constant stress, caused variability of viscoelastic and viscous flow behaviour. Decrease in viscosity values by cooking time may be the result of more rapid flow of water inside the gluten matrix as compared to early stages of cooking.

In this work two Voigt units were used to describe the viscoelastic behaviour, which suggests that different structural components may be associated with different units (Alvarez, et al., 1998). Second retardation times (λ_2) were lower in all spaghetti samples as compared to the times of first unit. At the same time compliance values of the first unit were lower than the second unit. This shows that greater stability of the structural components is attributed to the first unit.

In the pre-described Burgers model there is a variable number of empirical constants. The appropriate model can be selected either elaborating trial and error procedure or prior knowledge of material's general properties. Another difficulty in proper mathematical treatment of rheological analyses arises from the fact that in real materials, especially where finite or large deformations are of concern, the measured rheological response is strongly affected by both the stress level and the stress history of the specimen (Peleg, 1980).

Table 3.19 Parameters of Burgers model for cooked spaghetti samples

Spaghetti type	Cooking time (min)	D_o $(kPa^{-1})*10^{-3}$	D_1 $(kPa^{-1})*10^{-4}$	D_2 $(kPa^{-1})*10^{-4}$	μ_o $(kPa.s)*10^{6}$	λ_{ret1} (s)	λ_{ret2} (s)	RMS (%)	R^2
Control	6	5.69	13.09	8.07	8.70	321.1	10.91	0.22	0.9982
	8	6.69	7.71	9.90	8.50	102.7	8.33	0.16	0.9959
	10	8.33	7.75	10.90	7.17	74.98	6.46	0.16	0.9963
	12	9.12	8.38	11.86	6.89	61.13	5.55	0.14	0.9462
	14	10.40	9.31	13.74	6.35	48.81	4.55	0.12	0.9969
	16	10.40	8.80	14.66	6.02	39.81	3.74	0.13	0.9962
	18	11.10	9.15	15.57	5.67	30.14	3.01	0.12	0.9960
RS 5 %	6	5.46	6.62	6.16	8.50	199.6	8.64	0.19	0.9968
	8	6.53	5.23	7.33	8.20	99.78	7.32	0.17	0.9955
	10	7.58	4.68	7.87	7.37	60.52	5.22	0.13	0.9951
	12	8.33	4.76	8.08	6.43	55.37	5.09	0.12	0.9952
	14	9.36	5.15	9.39	6.37	50.49	4.49	0.12	0.9945
	16	10.40	6.27	11.32	5.00	50.33	4.44	0.12	0.9953
	18	9.27	6.02	10.14	4.90	34.56	3.40	0.10	0.9957
RS 15 %	6	5.29	7.67	5.66	6.72	295.1	9.29	0.20	0.9969
	8	6.21	3.89	6.47	6.58	85.54	7.01	0.16	0.9943
	10	7.83	4.18	6.73	6.08	58.03	5.70	0.12	0.9944
	12	8.15	4.04	7.65	4.35	50.67	4.87	0.12	0.9939
	14	9.09	4.86	8.20	3.86	32.63	3.99	0.09	0.9958
	16	9.25	5.07	6.24	3.66	31.38	4.53	0.08	0.9962
	18	9.23	5.12	6.35	3.52	30.82	4.52	0.08	0.9986
Bran	6	4.54	7.18	8.79	7.85	290.3	9.82	0.40	0.9919
	8	4.99	7.37	14.18	5.75	132.0	4.87	1.10	0.9000
	10	6.87	7.02	13.60	3.20	80.60	4.30	0.36	0.9883
	12	6.95	9.20	18.56	1.99	40.48	1.67	0.89	0.9999
	14	8.83	8.16	19.96	1.74	32.45	3.29	0.14	0.9961
	16	8.50	13.04	21.97	1.73	28.58	1.66	0.25	0.9932
	18	8.67	11.12	18.47	1.71	29.40	2.25	0.20	0.9946

In Burgers model, one of the problems is that constants can vary independently as a result quantitative comparison of curves is usually an extremely difficult task. Furthermore, equilibrium conditions are of great importance in rheological evaluation of materials. But for foods as mentioned before in the introduction part of this thesis it is quite difficult to attain equilibrium conditions. From this point of view Peleg model is a good alternative. Where applicable, it has an additional benefit over other mathematical expressions (such as series of decaying exponential terms), since its constants are independent of the test duration and the calculation procedure.

Table 3.20 Parameters of Peleg model for cooked spaghetti samples

Spaghetti type	Cooking time (min)	k_1	k_2	R^2
Control	6	1371	130.8	0.9993
	8	494.1	116.7	0.9999
	10	267.5	96.89	0.9999
	12	172.9	88.84	0.9995
	14	128.4	77.98	0.9999
	16	103.4	77.76	0.9999
	18	69.32	73.12	0.9999
RS 5 %	6	906.2	147.9	0.9998
	8	404.8	126.8	0.9999
	10	198.5	112.0	0.9999
	12	162.0	102.9	0.9999
	14	128.7	91.60	0.9999
	16	125.2	81.38	0.9999
	18	112.3	90.89	0.9999
RS 15 %	6	1128	151.9	0.9996
	8	354.1	136.1	0.9999
	10	188.4	110.8	0.9999
	12	177.6	105.8	0.9999
	14	121.8	94.97	0.9999
	16	116.4	95.10	0.9999
	18	100.2	93.80	0.9998
Bran	6	1261	163.8	0.9995
	8	838.9	137.3	0.9987
	10	435.0	109.4	0.9999
	12	353.3	99.84	0.9990
	14	218.1	91.49	0.9999
	16	186.1	81.33	0.9999
	18	185.7	83.90	0.9999

As it is seen from Table 3.20, k_1 and k_2 values of Peleg model were lower for RS spaghetti resulting in a less stiff product. In rheological terminology k_1 from Peleg model roughly represents the solid properties of the samples at the corresponding strain. The higher k_1 value the more solid the sample (Pollak and Peleg, 1980). Spaghetti enriched with 5 % RS had the lowest k_1 values especially for optimum cooked spaghetti (12 min). Values of k_2 can be used to represent hypothetical

equilibrium conditions that pertain to the major short-term properties of the original specimen. Since k_2 is the asymptotic level of D (t), it also represents the portion of the stress that would have remained unrelaxed at equilibrium. The k_2 values related with plastic behaviour was lowest for control spaghetti. However, it did not change so much after 12 min of cooking time for all spaghetti types. The R^2 values of Burgers model ranged between 0.900-0.999 and for Peleg model the rank was around 0.999.

These results show that software systems developed for modelling rheological behaviour of spaghetti strands either under constant stress or strain can express models that give good fit. But still an optimisation needed in data analysis to determine whether the dependence of each deformation component is linear or non-linear. Further morphological research must be carried on spaghetti enriched with resistant starch to understand better how resistant starch addition affects the rheological properties.

3.2.1.2.3 Texture profile analysis (TPA)

Determination of the factors that influence pasta texture after cooking is of vital importance to the foodservice industry. With the increasing popularity of pasta, these products have become a major growth segment of the food industry in the past few years. In part, the growth is due to pasta prepared for consumption in buffet-style restaurants. Under these conditions pasta is kept, or held, in steam trays until consumption. The quality of this type of cooked pasta can be determined by a number of attributes, such as texture, flavor and appearance. Texture plays an essential role in determining the final acceptance by the consumer and it is one of the predominant criteria for assessing pasta quality. Good quality pasta should be *al dente*, that is, it should have high degrees of firmness and elasticity. Furthermore, pasta should also be resistant to overcooking and maintain its shape during swelling (Gonzales et al., 2000).

Pasta texture is often evaluated for a short period after cooking, for instance, immediately after cooking or 15 min after cooking (Kovacs et al., 1995; Edwards et al., 1995). It is generally accepted that the main criterion for cooking quality of pasta is based on evaluation of texture. Cooked pasta is desired to be not sticky when eaten

and exhibit some firmness to the bite. In fact sensory evaluation is the most reliable method in measuring quality of pasta it is time consuming so mechanical tests are preferred (Sözer, 2001).

Moisture distribution and migration are important factors that determine the textural properties of food products. Moisture transfer will occur in the direction of the concentration gradient between the external environment and the surface of the pasta. In addition, moisture gradients within the pasta enhance the possibility of the internal moisture migration, even in the absence of water transport between the sample and the surroundings (Gonzales, et al., 2000).

3.2.1.2.3.1 Hardness and adhesiveness

Hardness and adhesiveness are the most important textural attributes of cooked pasta. Adhesiveness is related to the surface properties, while firmness is linked to the internal structure of cooked pasta. When cooking durum wheat pasta, starch gelatinization and protein coagulation cause major structural changes and hence influence the final texture (Steffe, 1996). During cooking good quality pasta, protein absorbs water and swells more rapidly than does starch. Hydration of the protein fraction of pasta before the beginning of starch gelatinization appears to be important to produce a firm, good quality pasta (Sözer, 2001).

The hardness values of bran spaghetti were higher than the control and RS spaghetti samples (Table 3.21). Increasing the amount of gluten in spaghetti decreases the amount of residue in the cooking water and increases the force required to produce a given extension in cooked spaghetti (Matsuo and Irvine, 1970). In the literature it has been proved that firmness and compressibility are primarily affected by protein level (Nobile et al., 2005). The protein content of spaghetti samples were 12.58, 12.29, 11.46, and 15.39 for control, RS 5 %, RS 15 % and bran containing spaghetti, respectively. The protein content of bran spaghetti was higher than the other spaghetti types resulting in higher hardness values. Cooking time had a strong effect on hardness values. Increasing the cooking time resulted a decrease in hardness values. In a study made by Gonzales et al., (2000) during performing textural measurements a video camera was used to visualize and understand the effect of pasta macrostructure on texture. It was found that the initial slope in the force

deformation curve (Figure 3.7) changed which showed that the surface of the pasta strained due to normal and shear forces.

The center of the pasta strained by normal forces, but to a lower extent than the surface. It can be assumed that the initial slope of the force-deformation curve was determined principally by the pasta structure at the surface region. As soon as the probe penetrated inside the spaghetti strand the forces are more effective on the unhydrated center that has not ruptured (Gonzales et al., 2000). Longer-cooking times resulted in an increased water absorption (which is shown in the analytical measurements section) that led to moisture migration into the core of spaghetti.

The dramatic change in hardness values can be related with the increase in mobility of biopolymer chains by the plasticization action of water. There was a decrease also in the slope value of the first peak of TPA curve for all samples with increasing cooking time. Another reason that the structure inside the uncooked parts is more effective in textural parameters. During cooking spaghetti surface is exposured to heat more severe. This may change the structural conformation of the protein-starch network, which can lead to loss or rigidity in the structure.

Both firmness and adhesiveness values increased by increasing RS content for the optimum cooked region. Since the particle size of RS much more smaller than semolina it refills the empty spaces in the network and had a kind of limiting effect for water migration.

During the spaghetti cooking process the granules imbibe water, swell, and gelatinize. This water penetration and starch gelatinization is dependent on the quality of the surrounding protein network (Grzybowski and Donnelly, 1979). Adhesiveness or stickiness is related with the amount of starch and starch gelatinization. At first, adhesiveness values for both spaghetti types were higher.

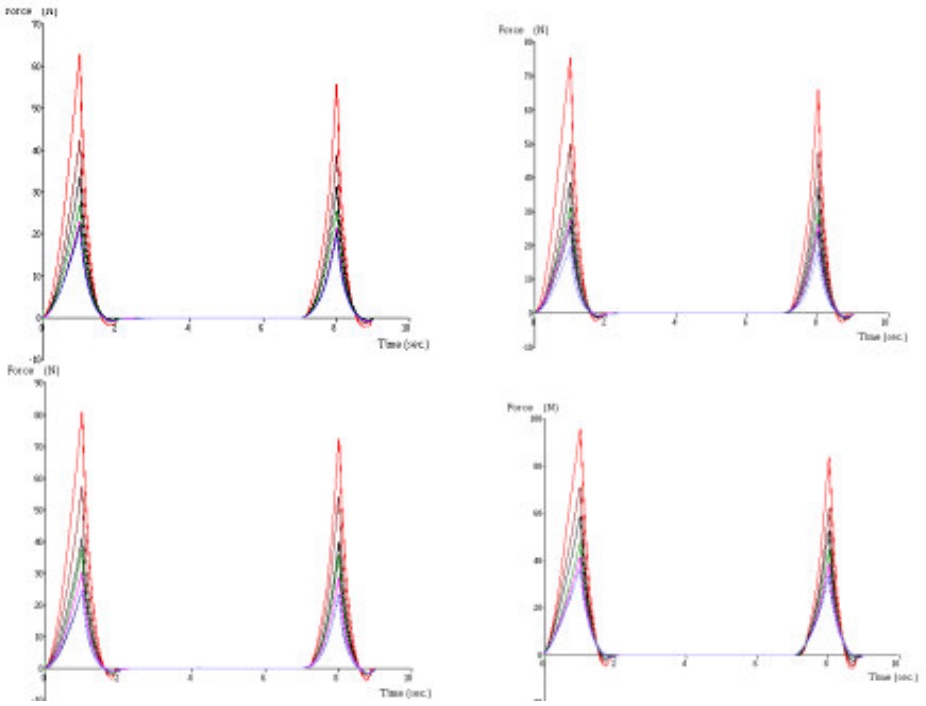

Figure 3.7 TPA curve of control, RS 5 %, RS 15 %, and bran containing spaghetti cooked for 6 (red line), 8 (brown line), 10 (black line), 12 (green line), 14(pink line), 16 (purple line), 18 (blue line) min .

Water migration during cooking starts from outside to inner parts of spaghetti strand making it relatively easier for the starch to leach out from the surface. Resistant starch type 3 consists of retrograded amylose molecules, which is relatively a smaller molecule than amylopectin that can leach out easily during cooking. Up to 10 min of cooking adhesiveness of bran containing spaghetti was higher than 15 % RS containing spaghetti but after this time 15 % of RS enriched spaghetti had higher adhesiveness value.

Multifactor ANOVA results for both hardness and adhesiveness showed that the effect of cooking time and spaghetti type during cooking was significant ($P<0.05$) (Table 3.22). From the LSD analysis it was found that hardness and adhesiveness values of RS 5 % and RS 15 % spaghetti samples were homogenously in the same group (Table 3.23). However, the values for control and bran spaghetti were different.

3.2.1.2.3.2 Cohesiveness

Cohesiveness can be a good indicator of how the sample holds together upon cooking. It is mainly related with tensile strength. Cohesiveness values of control and RS containing spaghetti samples were homogenously in the same group (Table 3.23). Since bran had a kind of diluting effect on gluten network, bran-containing spaghetti had the lowest cohesiveness (Kordonowy & Youngs, 1985). This meant that it was more difficult for the bran containing spaghetti to hold the structure together as cooking time proceeded.

As cooking time increased cohesiveness values of all spaghetti samples increased. Gluten network formed during cooking entrap starch. If gluten network does not develop starch granules swell and disperse during cooking, the structure of pasta becomes weaker leading to a less cohesive material. Gluten can modify the availability of water to the starch with reduction of both granule swelling and starch leaching (Riva et al., 1991). Cohesiveness of spaghetti is mainly dependent on competition between starch and protein molecules to form a continuous network. Cohesiveness values found to change more, up to 12 min cooking. During cooking water can migrate from sites where it is bound more strongly to sites where it is more weakly bound. Riva et al. (2000) claimed that water is more tightly bound to proteins than to the starch. Protein network limits water diffusion to the starch granules, which directly affects cohesiveness.

Multifactor ANOVA results showed that effect of cooking time and spaghetti type on cohesiveness was significant ($P<0.05$) (Table 3.22).

3.2.1.2.3.3 Chewiness

Chewiness which is related to the elastic strength of the protein matrix was highest for bran containing spaghetti. The reason is both presence of bran and high protein content in this type of spaghetti. Chewiness of RS 5 % and RS 15 % spaghetti were homogenously in the same group (Table 3.23).

As cooking time proceeded chewiness of all spaghetti types decreased dramatically (Table 3.21) due to possible break down of gluten network and leaching of starch to cooking water. While raw pasta is relatively uniform, cooked pasta has a structure,

which changes continually from the surface to the core. The changes are greatest at the surface, which has been subjected to the effects of cooking for the longest period. At the center of cooked spaghetti there is some ungelatinized starch, outside the core area the starch granules have been gelatinized and are swollen but still intact. On the other hand the gluten is still elastic enough that it can stretch to accommodate the swollen starch granules resulting in a structure, which is very dense. Closer to the surface of the strand, the granules are no longer intact and the starch is present as strands or amourphous structures surrounded with protein network. Continuous protein matrix seen in central regions start to break down due to denaturation of protein. As overcooking occurs protein filaments become more dense because of higher degrees of denaturation and there is not so much starch present (Voisey et al., 1978).

The cooking time-spaghetti type interactions were not significant for chewiness ($P>0.05$) (Table 3.22). LSD multiple range test was also carried out to determine the effect of cooking time and spaghetti type on TPA parameters (Table 3.23). The effect of cooking time and spaghetti type on chewiness during cooking was significant ($P<0.05$).

3.2.1.2.3.4 Resilience

Resilience is a measurement of how the sample recovers from deformation both in terms of speed and forces derived. Cooked spaghetti resilience is strongly correlated to protein content (Voisey et al., 1978). Resilience values spaghetti samples did not differ from each other.

Resilience values were found to decrease as cooking time changes from optimum to overcooked region. As cooking time passes spaghetti becomes more plastic because of starch retrogradation and plasticization of polymeric chains by the action of water. So the applied force dissipated inside the material and it has less resistance against it.

The cooking time-spaghetti type interactions were significant for resilience ($P<0.05$) (Table 3.22) The effect of cooking time and spaghetti type on resilience during cooking was significant ($P<0.05$) according to LSD analysis (Table 3.23).

Table 3.21 Mean values and standard deviations of TPA results of cooked spaghetti samples

Spaghetti type	Cooking time (min)	Hardness (N)	Adhesiv (N.s)	Cohesiv.	Chew.	Spring.	Gumm.	Resilience
Control	6	61.66±1.45	0.99±0.01	0.72±0.00	41.35±0.98	0.93±0.00	44.34±1.23	0.50±0.00
	8	44.85±3.75	0.76±0.05	0.74±0.01	31.41±1.90	0.94±0.01	33.41±2.27	0.51±0.03
	10	32.61±1.14	0.60±0.05	0.79±0.01	24.18±0.67	0.94±0.01	25.72±0.53	0.57±0.00
	12	26.51±0.31	0.38±0.04	0.79±0.00	19.42±0.74	0.92±0.02	21.04±0.25	0.57±0.01
	14	23.14±0.32	0.83±0.05	0.79±0.00	17.04±0.40	0.94±0.00	18.16±0.36	0.54±0.01
	16	20.67±1.53	0.78±0.20	0.72±0.00	15.01±1.12	0.94±0.00	15.57±1.19	0.54±0.00
	18	19.62±1.33	0.76±0.03	0.77±0.03	14.27±0.42	0.94±0.00	15.14±0.51	0.52±0.02
RS 5 %	6	77.24±2.68	1.19±0.39	0.71±0.02	50.18±3.75	0.92±0.01	54.52±3.66	0.51±0.04
	8	53.14±4.72	0.90±0.07	0.78±0.02	38.64±2.49	0.93±0.00	41.44±2.84	0.55±0.01
	10	38.98±0.68	0.84±0.06	0.82±0.00	30.18±0.95	0.94±0.01	32.00±0.65	0.54±0.01
	12	30.70±0.40	0.89±0.20	0.81±0.01	23.48±0.09	0.95±0.00	24.84±0.09	0.54±0.02
	14	26.57±1.49	0.89±0.20	0.80±0.00	20.11±1.15	0.95±0.00	21.22±1.14	0.50±0.01
	16	23.11±3.55	0.90±0.10	0.78±0.01	16.67±2.43	0.93±0.01	17.95±2.41	0.52±0.00
	18	19.60±0.05	0.93±0.19	0.77±0.01	14.05±0.20	0.94±0.01	15.02±0.10	0.49±0.01
RS 15 %	6	80.34±0.45	1.27±0.19	0.72±0.01	54.25±0.55	0.94±0.00	58.00±0.59	0.54±0.00
	8	57.88±1.06	1.03±0.01	0.76±0.01	41.46±0.64	0.94±0.01	43.98±0.18	0.53±0.01
	10	40.42±0.60	0.76±0.08	0.78±0.01	29.19±0.57	0.92±0.00	31.64±0.74	0.51±0.00
	12	37.59±0.46	0.98±0.00	0.81±0.01	27.79±0.30	0.89±0.06	28.24±2.41	0.62±0.10
	14	29.97±0.06	1.13±0.03	0.78±0.01	22.34±0.17	0.95±0.00	23.51±0.18	0.52±0.01
	16	27.93±4.85	0.80±0.06	0.76±0.01	19.52±2.78	0.92±0.02	21.31±3.45	0.51±0.02
	18	22.35±3.11	0.76±0.06	0.76±0.00	15.66±2.08	0.92±0.00	17.02±2.26	0.50±0.00
Bran	6	92.72±3.95	1.76±0.13	0.63±0.02	52.45±4.54	0.91±0.00	57.76±4.78	0.50±0.03
	8	72.13±1.54	1.14±0.21	0.65±0.01	42.76±2.20	0.91±0.01	46.82±1.87	0.51±0.02
	10	57.46±1.49	0.81±0.10	0.73±0.06	39.18±1.94	0.94±0.00	41.77±1.92	0.54±0.03
	12	47.14±0.23	0.70±0.08	0.76±0.01	33.83±0.83	0.95±0.00	35.79±0.86	0.56±0.01
	14	42.26±1.24	0.65±0.13	0.78±0.01	31.08±0.95	0.95±0.00	32.72±1.00	0.57±0.00
	16	37.48±1.47	0.71±0.01	0.78±0.01	27.55±1.48	0.95±0.00	29.15±1.56	0.57±0.00
	18	34.84±2.16	0.82±0.02	0.77±0.01	25.32±1.51	0.95±0.00	26.65±1.59	0.55±0.01

Table 3.22 Two-way ANOVA for cooked spaghetti samples

TPA parameters	Source	Sum of Squares	Degree of freedom	Mean square	F-ratio	P-value
Hardness	cooking time	20931.60	6	1824.68	166.28	P<0.05
	spaghetti type	3761.06	4	1025.98	93.49	P<0.05
	Interaction cooking time-spaghetti type	674.22	24	28.09	1.53	N. S.
Adhesiveness	cooking time	2.08	6	0.34	8.84	P<0.05
	spaghetti type	2.24	4	0.56	14.25	P<0.05
	Interaction cooking time-spaghetti type	1.46	24	0.06	2.50	P<0.05
Cohesiveness	cooking time	0.08	6	0.01	42.67	P<0.05
	spaghetti type	0.06	4	0.01	48.38	P<0.05
	Interaction cooking time-spaghetti type	0.02	24	0.0003	3.18	P<0.05
Chewiness	cooking time	7068.77	6	1268.12	102.09	P<0.05
	spaghetti type	1208.51	4	302.13	24.32	P<0.05
	Interaction cooking time-spaghetti type	389.41	24	16.22	1.31	N.S.
Springness	cooking time	0.014	6	0.002	1.03	N.S.
	spaghetti type	0.014	4	0.003	1.57	N.S.
	Interaction cooking time-spaghetti type	0.057	24	0.002	1.05	N.S.
Gumminess	cooking time	9051.43	6	1508.57	115.68	P<0.05
	spaghetti type	1401.54	4	350.38	26.87	P<0.05
	Interaction cooking time-spaghetti type	352.54	24	14.69	1.23	N.S.
Resilience	cooking time	0.019	6	0.003	5.52	P<0.05
	spaghetti type	0.029	4	0.007	12.89	P<0.05
	Interaction cooking time-spaghetti type	0.027	24	0.001	1.95	P<0.05

Table 3.23 LSD multiple range analysis of TPA parameters for cooked spaghetti samples

Effect	LS Mean±standard error[1]						
Spaghetti type	Hard.	Adhesiv.	Cohesiv.	Chew.	Spring.	Gumm.	Resilience
Control	32.72±1.15^{a}	0.77±0.04^{a}	0.77±0.01^{a}	23.24±0.94^{a}	0.94±0.01^{ab}	24.83±0.96^{a}	0.53±0.0.01^{ab}
RS 5 %	38.48±1.15^{b}	0.92±0.04^{b}	0.78±0.01^{a}	27.62±0.94^{b}	0.94±0.01^{ab}	29.57±0.96^{b}	0.52±0.0.01^{a}
RS 15 %	40.22±1.15^{b}	0.91±0.04^{b}	0.77±0.01^{a}	28.32±0.94^{b}	0.91±0.01^{a}	30.53±0.96^{b}	0.53±0.0.01^{ab}
Bran	54.86±1.15^{c}	0.94±0.04^{c}	0.73±0.01^{b}	36.02±0.94^{c}	0.93±0.01^{ab}	38.66±0.96^{c}	0.54±0.0.01^{b}
Cooking time (min)							
6	76.18±1.35^{a}	1.15±0.05^{a}	0.70±0.01^{a}	49.24±1.11^{a}	0.93±0.02^{ab}	53.24±1.14^{a}	0.52±0.01^{a}
8	55.62±1.35^{b}	0.86±0.05^{b}	0.74±0.01^{b}	38.26±1.11^{b}	0.93±0.02^{ab}	41.06±1.14^{b}	0.53±0.01^{abc}
10	41.94±1.35^{c}	0.67±0.05^{cd}	0.79±0.01^{cde}	30.87±1.11^{c}	0.94±0.02^{ab}	32.93±1.14^{c}	0.55±0.01^{c}
12	32.14±1.35^{d}	0.57±0.05^{d}	0.80±0.01^{e}	23.94±1.11^{d}	0.90±0.02^{a}	25.69±1.14^{d}	0.58±0.01^{d}
14	30.89±1.35^{de}	0.79±0.05^{de}	0.79±0.01^{cd}	23.34±1.11^{d}	0.95±0.02^{b}	24.56±1.14^{de}	0.54±0.01^{bc}
16	27.52±1.35^{ef}	0.72±0.05^{de}	0.78±0.01^{de}	20.14±1.11^{e}	0.94±0.02^{ab}	21.54±1.14^{ef}	0.54±0.01^{abc}
18	24.30±1.35^{f}	0.84±0.05^{b}	0.78±0.01^{e}	17.78±1.11^{e}	0.94±0.02^{ab}	18.88±1.14^{f}	0.53±0.01^{ab}

[1]Means within a column followed by different levels are significantly different (P<0.05)

3.2.1.3 Color and appearance

Factors that are important for the appearance of the pasta product are its color, uniformity, clarity and surface properties. Excessive crack formation is undesirable and impair the appearance of spaghetti. As a result, visual inspection of spaghetti samples were carried out two months after samples production (Figure 3.8). In Table 3.24 the effect of RS addition on spaghetti colour values regarding to chromacity (C*), brightness (L*), redness (a*), yellowness (b*) and yellowness index (YI) are presented. Bran containing spaghetti showed lower brightness values than the control sample. The brightness of spaghetti enriched with addition of 15 % of RS into formula does not adversely affected. Bran containing spaghetti also showed greater color intensity, as reflected by higher chromacity values. Because of the red-brown color of bran containing spaghetti redness and yellowness values were greater; being 9.04 and 41.06, respectively. The color of pasta is determined primarily by the carotenoid content of the raw material and the extent of caretonoid degradation by endogenous lipoxygenase (Zweifel, 2001).

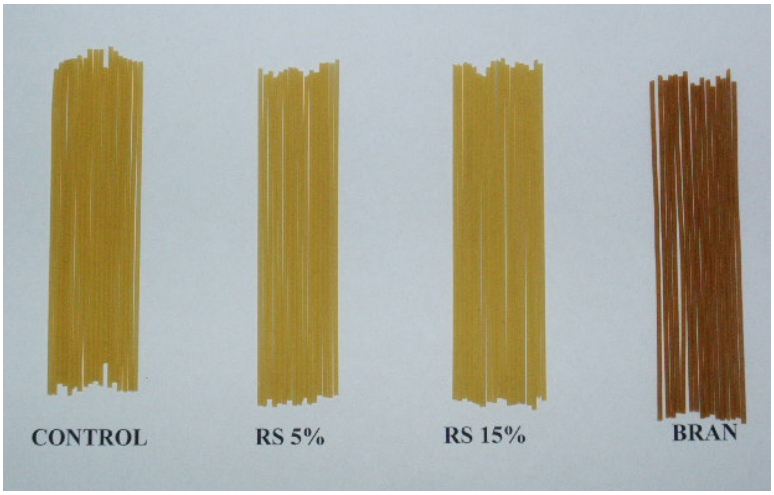

Figure 3.8 Photos of spaghetti samples

Table 3.24 Colour parameters of dry spaghetti samples

Spaghetti type	Chromacity C*	Brightness L*	Redness a*	Yellowness b*	YI
Control	22.97±0.43	46.68±1.11	6.37±0.18	22.07±0.39	93.68±0.90
RS 5 %	22.90±0.38	48.20±1.19	5.79±0.11	22.16±0.36	90.30±1.01
RS 15 %	22.52±0.20	46.73±0.64	5.56±0.07	21.83±0.19	91.42±0.54
Bran	42.04±0.23	32.34±0.66	9.04±0.06	41.06±0.22	98.55±0.85

YI refers to Yellowness Index

3.2.1.4 Thermal analysis

Final texture and quality of cooked pasta depended on starch gelatinization and gluten denaturation. At temperatures above 50 ^{o}C rheologically effective cross-links in gluten occur. Gluten can function as either thermoplastic or a thermosetting amorphous polymer in response to heat/moisture treatment. Above the glass transition temperature gluten undergoes an irreversible structural transformation from viscous polymer with transient disulfide links to an elastic, permanent disulfide cross-linked gel (Cocero and Kokini, 1991). In the literature there are several works done on thermal behavior of gluten. These works especially deal with glass transition of gluten, which showed that wheat gluten is a glassy, amorphous, and plasticizable polymer, with water acting as a plasticizer to depress gluten's glass transition temperature (Hoseney et al., 1986; McMaster and Bushuk, 1983). Although starch represents up to 80 % of semolina dry matter and is the major component of pasta, it has received less attention in research. Firmness of cooked pasta is mainly related to amylose content in starch. Amylose also was thought to affect the surface properties of pasta (Yue et al., 1999).

Starch gelatinization and melting is an important phenomenon occurring in various food processing operations because it provides unique textural and structural characteristics for the products. The knowledge of the kinetics of starch gelatinization and melting is required for food process engineers to design and optimise processes such as extrusion and cooking of pasta (Spigno and De Faveri, 2004). Starch is the major component of semolina, and firmness in cooked spaghetti must, in part, be influenced by gelatinised starch properties (Dexter and Matsuo, 1979). The native starch granule is a partially crystalline polymer system which losses its crystallinity and molecular order during gelatinization. The gelatinization temperature is characteristic of the starch type and depends on the glass transition of the amorphous fraction of the starch (Eerlingen and Delcour, 1995). Figure 3.9 shows the changes in DSC gelatinization endotherms that decreased in magnitude with increasing cooking time. The onset and peak temperatures of gelatinization were found 58 and 64 ^{o}C, respectively. These temperatures were lower than the melting temperatures of amylopectin crystallites. It was reported in the literature that dissociation transition of retrograded starch occurs at 54 ^{o}C, which is lower than the

peak of gelatinization (Chinnaswamy et al., 1989). Transitions observed in this study may be attributed to the dissociation of retrograded amylopectin.

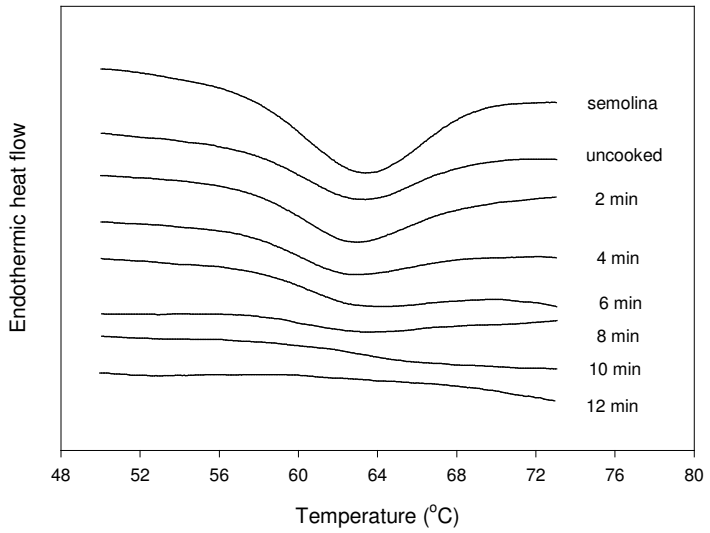

Figure 3.9 DSC thermogram of semolina and partially cooked control spaghetti

Table 3.25 shows the mean values for DSC gelatinization of starch from semolina, uncooked and cooked spaghetti samples. The analysis of the peak temperatures did not make so much difference between the different spaghetti samples. It was found that uncooked bran containing spaghetti had the lowest gelatinization temperature range. The enthalpy values for RS containing spaghetti samples were lower than the control and bran containing spaghetti samples since it losses its crystallinity during processing (Yeo and Seib, 2000). In general peak temperature values for control spaghetti was in good aggrement with literature (Zweifel, 2001; Cunin et al., 1995; Vansteelandt and Delcour, 1998; Yue et al., 1999).

Enthalpy values of all spaghetti samples decreased with increase in cooking time. The percentage of decrease was 13.48, 7.69, 1.85, and 8.69 for control, RS 5 %, RS 15 % and bran containing spaghetti, respectively. Spaghetti enriched with 15 % RS showed the least change. This type of behaviour can be explained in general; with the

beginning of gelatinization starch granules becomes less thermostable and less energy is required to melt its structure (Biliaderis, 1990).

Table 3.25 Thermal characteristics of spaghetti samples: onset (T_o), peak (T_p), and completion (T_c) temperatures, gelatinization enthalpies (ΔH), and gelatinization ranges ($\Delta T_r = T_c - T_o$)

Cooking time (min)	Spaghetti type	T_o (^oC)	T_p (^oC)	T_c (^oC)	ΔT_r (^oC)	ΔH (J/g)
0	Control	57.46±0.04	63.82±0.56^a	70.25±0.78	12.79±0.83	4.30±0.08^a
	RS 5 %	58.23±1.30	64.15±0.37^a	69.61±1.14	11.38±0.84	2.34±0.34^b
	RS 15 %	58.66±1.85	64.31±0.65^a	70.13±1.55	11.47±0.81	2.70±0.05^b
	Bran	58.06±1.33	63.89±0.01^a	69.19±1.38	11.13±2.71	3.45±1.42^c
2	Control	59.34±0.52	63.60±0.34^a	69.45±0.63	10.11±0.11	1.96±0.24^a
	RS 5 %	59.03±1.58	63.65±1.05^a	69.24±0.46	10.22±1.11	1.45±0.02^b
	RS 15 %	58.90±0.73	64.70±1.04^a	69.30±0.91	10.40±1.54	1.58±0.26^b
	Bran	57.53±0.08	63.37±0.01^a	68.65±0.77	11.12±0.69	1.24±0.71^c
4	Control	59.23±0.17	64.05±0.15^a	70.76±0.25	11.53±0.42	1.51±0.32^a
	RS 5 %	58.93±0.73	63.72±0.01^a	68.41±1.55	9.48±1.81	1.05±0.02^b
	RS 15 %	59.39±0.14	63.79±0.43^a	69.15±0.25	9.76±0.68	1.22±0.08^{bc}
	Bran	59.19±0.93	63.67±0.29^a	67.67±2.26	8.48±2.18	1.24±0.71^c
6	Control	59.28±0.16	64.70±0.75^a	71.12±0.55	11.83±0.72	1.14±0.02^a
	RS 5 %	60.48±0.61	63.96±0.36^a	68.19±1.19	7.71±1.58	0.48±0.01^b
	RS 15 %	61.40±0.71	64.94±0.01^a	68.35±0.32	6.95±0.27	0.54±0.62^c
	Bran	60.54±1.14	64.48±0.15^a	69.23±2.24	8.69±2.38	1.11±0.16^a
8	Control	60.61±0.42	65.40±0.45^a	70.96±0.15	10.35±0.26	0.58±0.01^a
	RS 5 %	62.38±0.71	65.06±0.16^{ab}	67.00±0.06	4.62±0.66	0.18±0.01^a
	RS 15 %	61.98±0.04	64.89±0.46^{ab}	68.87±0.58	6.89±0.18	0.05±0.15^b
	Bran	59.67±0.63	64.15±0.25^b	68.16±1.36	8.49±1.98	0.62±0.91^c

Different letters indicate statistically significant differences exist at α=0.05 based on multiple range test

Following cooking, the starch component of these products undergoes retrogradation, defined as partial crystallization of amylopectin within the gelatinized starch fraction, with an increase in firmness and a modification of taste. A mild heat treatment allows the sensory properties of the freshly prepared product to be fully recovered, but this requires careful control to avoid overcooking, which tends to further gelatinize the starch, resulting in a product that is too soft and sticky (Riva et al., 2000).

Figure 3.10 shows the gelatinization (%) with respect to cooking time (min). As it was expected gelatinization of spaghetti with RS 5 % and 15 % was found to be quicker. The lack of gelatinization endotherm meant the sample was completely gelatinized (Riva et al., 2000; Ndife et al., 1998). These results were in agreement of the findings from Image Analysis. If the two techniques DSC and Image analysis are going to be compared regarding to determination of optimum cooking time; image

analysis can be encountered as a more reliable technique. Because after 8 min of cooking the amount of ungelatinized starch is very little which makes both the sampling and detection of ungelatinized fraction quite difficult in DSC. However, DSC technique can be used to detect *al dente* spaghetti cooking time. In *al dente* cooked spaghetti, spaghetti comes to teeth and it has a characteristic firmness. In fact it is the Italian style of spaghetti cooking, for most people this type of cooked spaghetti is still uncooked. Because at this cooking time there is still some part of ungelatinized starch fraction. More discussions about determination of optimum cooking time by image analysis will be described in the next section.

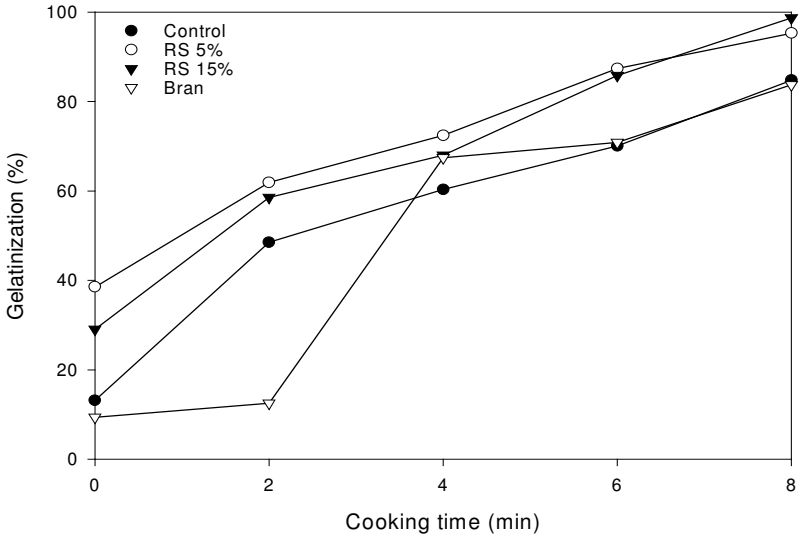

Figure 3.10 Percent gelatinization of spaghetti samples

3.2.1.5 Image analysis

Cooking time significantly affects spaghetti quality. Generally, undercooked spaghetti gives the consumer an unpleasant raw doughy taste, while overcooked ones are difficult to handle (Sui et al., 2006). Optimally cooked spaghetti should have a chewy, resilient bite without surface stickiness (Miskelly and Moss, 1985). For dry noodles, the optimum cooking time has been determined by the disappearance of the white core, when the strands are squeezed between a pair of glass plates (Oh et al., 1983).

Food scientists usually determine the optimum cooking time by a sensory panel test. However, training of professional panelists is expensive and time-consuming. It is also quite common to determine the optimum cooking time by sensations in household issues. Conventional techniques such as image analysis either by microscopy or scanning are rapid and also more reliable to determine optimum cooking time. In this thesis degree of cooking and optimum cooking time was determined by imaging the spaghetti samples cooked for different times by the help of a camera attached to a microscope. The criterion to determine the optimum cooking time was the disappearance of the black core in the center of images (Figure 3.11). Both mass increase and the changes in size were sufficient to decide about the cooking times of these samples.

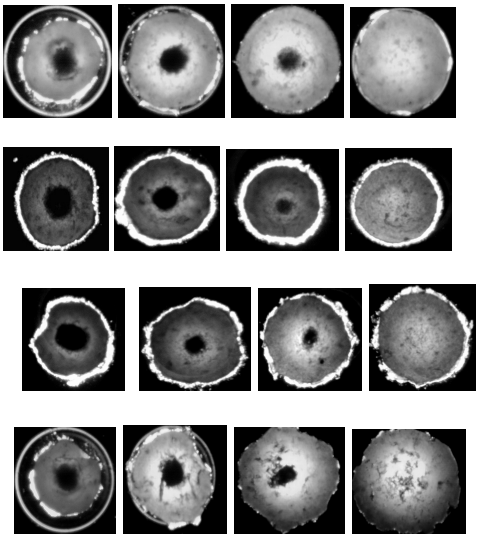

Figure 3.11 Selected images of spaghetti cross-sections at various cooking times (6,8,10,12) for control, RS 5 %, RS 15 % and bran spaghetti, respectively.

Degree of cooking values of spaghetti samples after 6, 8, 10 and 12 min were shown in Figure 3.12. These values were determined from the ratio of cooked area to total area. As cooking time proceeded by the plasticizing action of water both the cooked area and total area increased. As a result cooking occurred. All samples achieved nearly 100 % cooking after 12 min exposure to boiling water.

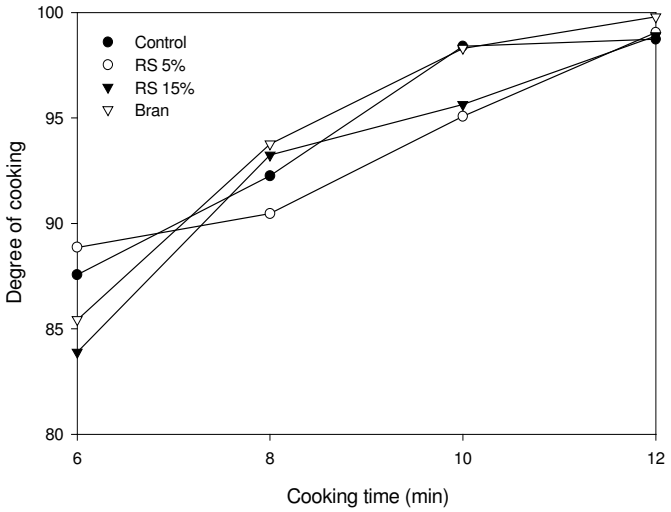

Figure 3.12 Degree of cooking values of spaghetti samples cooked for 6, 8,10, and 12 min

3.2.2 Analytical measurements

3.2.2.1 Cooking loss and water absorption

Another important quality parameters in spaghetti cooking are cooking loss and water absorption. Determination of water absorption and cooking loss are quite simple. During the spaghetti cooking process the granules imbibe water, swell and gelatinize. This water penetration and starch gelatinization is dependent on the quality of the surrounding protein network. Protein is an essential structural component of spaghetti and other pasta products. Removal of either lipid or protein adversely affects the retention of amylose. Removal of protein result in higher water absorption and cooking loss (Grzybowski and Donnelly, 1979).

Cooking loss is the amount of dry matter lost into the cooking water of optimally cooked spaghetti. Table 3.26 shows the cooking loss values of spaghetti samples obtained after pre-described cooking times. Cooking loss was highest in spaghetti enriched with 15 % RS. The increase in cooking loss with RS containing spaghetti was due to replacement of some portion of protein fraction with starch. Spaghetti with higher protein content interacts with water more tightly, reducing its mobile fraction that seems directly related to starch retrogradation (Riva et al., 2000). Bran containing spaghetti showed the lowest cooking loss values after optimum cooking of spaghetti, which can be related to higher amount of protein content. Cooking loss

was significantly influenced by cooking time. As cooking time increased gluten network start to breakdown and leaching of starch becomes easier leading to a greater cooking loss.

Swelling of spaghetti strands occurs during cooking of spaghetti. Water uptake shows how well spaghetti responds to cooking. Table 3.27 represents the water absorption (%) of all spaghetti types. As protein content relatively decreased water absorption of cooked spaghetti samples increased. Strongly formed protein network limited water diffusion to the starch granules, which also limited swelling. Water absorption of spaghetti samples was the same if results are analyzed by looking at standard deviations. But increase in cooking time also caused an increase in water absorption since more water can diffuse and interact with both gluten and starch. During cooking dried gluten acts as a sponge for water, opens its structure and embeds the starch granules inside this network.

Table 3.26 Percent cooking loss of spaghetti samples

Cooking time (min)	Control	RS 5%	RS 15%	Bran
6	6.48±0.55	4.68±0.35	6.58±0.35	5.57±0.43
8	6.67±0.62	5.89±0.24	6.03±0.50	6.47±0.41
10	8.30±0.69	7.93±0.36	10.59±0.38	7.73±0.43
12	8.00±0.32	7.89±0.20	10.80±0.54	7.65±0.35
14	9.07±0.45	7.90±0.53	9.04±0.51	9.03±0.37
16	10.26±0.44	9.77±0.55	9.46±0.55	9.47±0.42
18	10.13±0.48	9.74±0.41	12.07±0.52	9.97±0.43

Table 3.27 Percent water absorption of spaghetti types

Cooking time (min)	Control	RS 5 %	RS 15 %	Bran
6	138.74±4.85	132.28±4.90	129.74±4.15	118.45±1.09
8	156.15±5.18	158.48±3.15	159.10±2.67	146.46±1.18
10	185.37±4.05	173.10±3.97	176.12±5.04	164.16±2.05
12	192.90±2.35	205.48±4.27	198.17±1.07	176.20±2.03
14	200.97±3.98	218.09±0.40	227.20±5.83	201.04±2.97
16	230.61±2.00	245.69±3.72	248.09±0.98	224.19±1.39
18	235.05±0.48	270.54±5.37	263.01±4.00	239.48±3.50

3.2.2.2 Amount of resistant starch formed

Resistant starch can be found in many foods that people consume every day, but the amount of RS found in most commercial foods is usually very small. The amount of RS can vary as a result of the composition of the food or how the food is prepared and consumed (Brown, 2004). Quantification of RS is problematic, since it is not a distinct chemical entity but rather a set of physical states, which alter the rate of digestion of conventional starches. There are several methods in the literature to analyze RS content (Akerberg et al., 1998; Goni et al., 1996; Faisant et al., 1995; Berry, 1986; Englyst and Cummins, 1986; Englyst and Cummins, 1985; Englyst et al., 1982). But up to now very few products have been characterized. The problems in RS determination arise from the difficulties to sustain the enzymatic conditions that occur in vivo digestion. Another problem between different RS determination procedures is the sample preparation. In some procedures milling and boiling step included which allows only determination of RS_3 (Englyst et al., 1982). By eliminating the boiling step RS_2 can be determined (Berry, 1986). In both of these procedures the samples are usually milled and dried prior to analysis, which makes the determination of RS_1 impossible.

The type of RS used in this study was RS_3, which consisted of retrograded amylose. Additional amylose retrogradation occurs during cooking of pasta. Now that the main interest is on the determination of RS_3 but not on the total RS content the milling, boiling and drying steps were included in the procedure. The only artefact in this method can be during the drying step. The rate of amylose retrogradation is very slow at –20 ^{o}C. To minimize the extra formation of RS before analysis freeze-drying was done to samples at – 40 ^{o}C. In Table 3.28, amount of RS in uncooked and cooked samples were expressed in g/100 g dry sample. It was found that uncooked control spaghetti had an RS content of 0.45 (g/100g dry sample), which is quite low.

In one of the studies of Goni et al. (1996) suggested classification of materials according to the range of RS content (% dry matter). According to this classification products containing $\leq$ 1 % accepted as having negligible amount of RS, products with an RS content of 1.0-2.5 % were in the category of low, 2.5-5.0 % were intermediate, 5.0-15 % were high and > 15 % were in the very high group. In fact the cooking time of pasta products varies according to consumer like mainly it is

determined with the loss of white core in the centre. The recommended cooking time for the spaghetti samples in this work was 12 min (as explained in the Image Analysis section). The amount of RS_3 in 12 min cooked samples were 1.73 %, 6.65 % and 9.58 % for control, RS 5 % and RS 15 %, respectively. As a result, control spaghetti is low in RS content on the other hand spaghetti samples enriched with 5 % and 15 % RS were in the group of products high in RS.

Table 3.28 Amount of RS in uncooked and cooked samples (g/100g dry sample)

Cooking time (min)	Control	RS 5 %	RS 15 %
0	0.45±0.001	4.05±0.001	7.57±0.007
6	0.71±0.003	5.79±0.003	8.53±0.006
8	1.19±0.003	5.87±0.001	8.89±0.008
10	1.27±0.002	5.97±0.006	9.03±0.005
12	1.73±0.002	6.65±0.005	9.58±0.007

The amylose/amylopectin ratio is a remarkable factor in the starch retrogradation. During the starch retrogradation, a process of amylose and amylopectin chains reassociation occurs, leading to the formation of tightly packed structures and loss of water. The crystallization process of amylose molecules is facilitated because of its linear chain, while in the amylopectin, for its branched structure, this process is slower (Rosin et al., 2002). That's why the increase in amylose in the formulation (commercial RS_3, is high in amylose content) caused higher amounts of RS in the final product.

Table 3.29 Rate of resistant starch formation during cooking

Spaghetti type	Uncooked	6 min	8 min	10 min	12 min
Control	1	1.57	2.65	2.82	3.84
RS 5 %	1	1.18	1.20	1.22	1.36
RS 15 %	1	1.13	1.18	1.19	1.27

In Table 3.29 rate of RS formation (amount of RS formed during cooking/amount of RS in uncooked spaghetti) during cooking was shown. Resistant starch formation is more as cooking time proceeded mainly due to interaction between starch and water. It is a common concept that water acts as a plasticizer for retrogradation of starch and the retrogradation can be maximized in the range of 30-60 % of moisture (Kim et al.,

2005). It is quite clear from Table 3.29 that the cooking time is effective on the RS content. It was expected to see that as the RS content increased in the formulation the rate of increase in 12 min cooked spaghetti is not as dramatic as in control spaghetti. In control spaghetti after 12 min of cooking RS content increased 3.84 fold but this ratio is only in the level of 1.27 in RS 15 %. Possible cause can be due to different amounts of starch leaching into the cooking water. Cooking loss was higher for RS 15 % spaghetti.

3.2.3 Sensory analysis

Food appreciation is determined in large part by the sensory perception of the food product. As consumers are faced with an increasingly wide range of products, the role of sensory appreciation becomes more important in determining consumer-buying behavior. A necessary condition for repeated purchases of a food product is that it 'tastes nice'. Texture perception is an important factor in consumer buying behavior. It determines the identity of the food product. Texture is of dominating importance for pasta products since they have bland flavor (Wilkinson et al., 2000).

Instrumental measurement of cooked spaghetti texture can be a reliable and convenient alternative to the sensory panel. In fact sensory evaluation of spaghetti eating quality is a direct method for determining the quality of cooked spaghetti it's quite laborious and expensive. Objective methods are quicker and give more accurate results but an objective method without any correlation to sensory judgement makes no sense. From this point of view Pearson correlation analysis was performed on cooked spaghetti samples to compare objective and subjective evaluations. The results of texture profile analysis correlated well with the sensorial judgement of hardness, and chewiness (Table 3.30). There was a strong correlation between instrumental chewiness-sensory hardness, and a strong negative correlation between instrumental springness-sensory adhesiveness values. Panellists specially had difficulties in sensing adhesiveness values. The other factors assessed in the sensory results and TPA parameters did not give significant correlations.

Table 3.30 Pearson correlation coefficients between the sensory and instrumental parameters of cooked spaghetti texture

	Shard.	Sadh.	Schew.	Scoh.	Sspr.	Hard.	Adh.	Chew.	Coh.	Spr.
Shard.	1									
Sadh.	-0.801	1								
Schew.	0.773	-0.255	1							
Scoh.	-0.052	0.539	0.588	1						
Sspr.	-0.868	0.982*	-0.358	0.388	1					
Hard.	0.907	-0.480	0.967*	0.427	-0.580	1				
Adh.	0.272	0.045	0.324	0.644	-0.136	0.356	1			
Chew.	0.912	-0.484	0.955*	0.446	-0.596	0.996**	0.429	1		
Coh.	-0.690	0.633	-0.580	0.263	0.572	-0.631	0.480	0.191	1	
Spr.	0.577	-0.951*	-0.057	-0.752	-0.897	0.184	-0.167	-0.574	-0.479	1

* Correlation significant at the 0.05 level

** Correlation significant at the 0.01 level

The panelists were also asked to define which product they liked the best and explain why. They indicated that they disliked spaghetti containing bran mainly because of characteristic colour, odour and texture. They also didn't like 15 % RS spaghetti because of its high adhesiveness and starchy flavor. The most interesting result of this questionerie was all of the panelists choose spaghetti containing 5 % RS but not the control one as the best spaghetti. But it should also be taken into account that the spaghetti samples for the panel test were cooked in deionized water and served without dressing or sauce. Probably, 15 % RS spaghetti could also be nice to consume if served with sauce.

CHAPTER IV

CONCLUSIONS

Nowadays most of the diseases result from inadequate feeding and some of them may be related to insufficient fiber intake, it is reasonable to assume that an increased consumption of indigestible components would be important. As a result consumers are in need of good-tasting, high fiber foods. Pasta and its products are the main subgroup of many diets. In fact there are bran containing pasta products in the market; consumers still do not like to include these products into their diet because of many organoleptic and textural reasons such as colour, odour, cohesiveness, hardness, etc. From this point of view RS sources can be included in to diet, since they don't cause pronounced organoleptic alterations, as do traditional fiber sources like bran.

One of the good outcomes of the innovations in food technology is it forced consumers to be more aware of what they eat. Today, consumers are not only eating food to feed themselves but try to put a balance between health, lifestyle and diet. Resistant starch, which is a natural component that is present in many foods, has a role to play with regard to the nutritional benefits of fiber fortification.

Spaghetti was a good model product for the investigation of how addition of RS will affect rheological properties. Viscoelasticity is an important rheological behavior for spaghetti. Mainly starch is responsible of the viscous properties and gluten from elastic properties. However, rheological representation of food materials is complex and quite laborious since they do not just consist of Newtonian liquid and Hookean solids. They possess rheological properties of both elastic solid and viscous fluid. These materials are called as viscoelastic materials. Stress relaxation under constant strain and creep recovery under constant stress was used to map out viscoelastic characteristics. The resulting data were analyzed by various models.

The outcomes of this research will be summarized as follows:

1. Testing of breaking strength alone is not sufficient enough to predict the cooking quality of pasta, but it might be useful as a quality control procedure for the pasta industry, as the measurement can be done more rapidly than a cooking test. RS 15 % had the highest elasticity value and deflection point. Deflection point values gives an idea about brittleness of the sample as this shows how far a sample can be deformed before fracture.
2. Three-termed Maxwell model were found to fit better than two-termed model for stress relaxation data.
3. As cooking time proceeded it was easier to deform spaghetti samples than early stages of cooking.
4. Peleg model is a good alternative to Maxwell models, it has an additional benefit over other mathematical expressions (such as series of decaying exponential terms), since its constants are independent of the test duration and the calculation procedure.
5. Spaghetti enriched with 5 % RS had the lowest k_1 values especially for optimum cooked spaghetti (12 min). The k_2 values related with plastic behaviour was lowest for control spaghetti. The R^2 values of Burgers model ranged between 0.900-0.999 and for Peleg model the rank was around 0.999.
6. The firmness values of bran spaghetti were highest. Both firmness and adhesiveness values increased by increasing RS content .Cooking time had a strong effect on firmness values. Increasing the cooking time resulted a decrease in hardness values.
7. From the LSD analysis it was found that hardness, adhesiveness cohesiveness and chewiness values of RS 5 % and 15 % spaghetti samples were homogenously in the same group. However, the values for control and bran spaghetti were different.
8. The colour of spaghetti was not adversely affected by the addition of resistant starch.
9. The onset and peak temperatures of gelatinization were found 58 and 64 ^{o}C, respectively. The enthalpy values for RS containing spaghetti samples were lower than the control and bran containing spaghetti samples.

10. Enthalpy values of all spaghetti samples decreased with increase in cooking time.
11. Cooking loss is the amount of dry matter lost into the cooking water of optimally cooked spaghetti. Cooking loss was highest in spaghetti enriched with 15 % RS.
12. In vitro RS determinations showed that the amount of RS (g/100 g dry sample) in 5 % RS formulated spaghetti is 4.90 and in 15 % RS, 7.57. This means that amount of RS in the end product was increased from low levels to intermediate and high levels.
13. However, people consume spaghetti after cooking and during cooking it was found that additional formation RS occurred. This showed that with the introduction of RS enriched spaghetti into diet people could get sufficient amount of dietary fiber daily basis.
14. According to results of a panel test it was found that spaghetti produced with 5 % RS in the formula was found to be the best of all spaghetti samples.

4.1 Outlook

In the present work the modeling of viscoelastic characteristics were proved to be useful from the point of product acceptance by the consumer. Altough a TPA analysis can give more detail it should also be taken into account as one of the main criterias. So far, the parameters of the models showed that further knowledge in the field of morphological research of the structure is vital. This will enable one to understand better the physical meaning of these models. Confocal scanning laser microscopy is a good and powerful technique for structural analysis of the starch and protein networks. The use of these types of equipments in food research is quite new but it should become more available. Not only for rheology but also for most of the research fields it is quite important to observe the changes that occur in the microscale. Up to now most of the researches made in the macroscale and very rare in mesoscale.

After the years 1990 the scientific area become more aware of the importance of texture-mouthfeel and tried to find techniques and methods to test it efficiently. The drag force for this trend was the consumers being more aware of what they eat and increased expectations. But still there are a lot to be done in this field. For

example the texture analyzer which is widely used to define texture attributes can just mechanically simulate what jaws does during chewing or biting. It should be noted that chewing and biting takes place in presence of saliva and tongue which can alter the results. The test system should approach more to the original one.

Another important point regarding to viscoelasticity is the theory of nonlinear viscoelasticity is not set yet even most of the measurements done after deformation. More mathematical and physical research is needed.

Since in some circumstances starch can act as a dietary fiber it is important to characterize the nutritional properties of starch in different foods. It could be of interest to make in vivo studies on the effect of resistant starch rich diets in human health.

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1. EDUCATIONAL BACKGROUND

Country	University	Faculty/Institute	Working Field	Degree	Graduation Year
Turkey	Gaziantep University	Natural and Applied Sciences Institute	Food Technology	Ph.D.	2006
Turkey	Gaziantep University	Natural and Applied Sciences Institute	Food Technology	MSc.	2001
Turkey	Gaziantep Univerisity	Faculty of Engineering	Food Engineering	BSc.	1999

2. ACADEMIC CAREER

Institution/Organization	Country	City	Function	Year
Gaziantep University	Turkey	Gaziantep	Teaching Assist.	1999-
Wageningen Center for Food Sciences	The Netherlands	Wageningen	Research Scientist	09.2004-04.2005

3. PRINTED PAPERS

A. INTERNATIONAL JOURNALS

1) Sozer, N. and Dalgic, A. C. . Modeling of Rheological Characteristics of Various Spaghetti Types. *European Food Research and Technology.* (available online)

2) Sozer, N., Dalgic, A. C. and Kaya A. Thermal, Textural and Cooking Properties of Spaghetti Enriched with Resistant Starch. *Journal of Food Engineering.*(accepted)

3) Sozer, N., Dalgic, A. C. and Kaya A. Effect of resistant starch addition on viscoelastic properties of spaghetti. *Journal of Texture Studies* (in progress)

4) Kaya, A. and Sozer, N. (2005) Rheological Behaviour of Sour Pomegranate Juice Concentrates (Punica granatum L.).*International Journal of Food Science and Technology*, 40, 223-227.

5)Sozer,N. and Kaya, A. (2001) Changes in Cooking and Textural Properties of Spaghetti Cooked with Different Levels of Salt in the Cooking Water. *Journal of Texture Studies*, 34 (4), 381-390.

B. NATIONAL JOURNALS

1) Sozer, N. and Kaya, A. (2005) Dokusal özelliklerin belirlenmesinde akustik yayılım tekniğinin kullanılması (Application of Acoustic Emission Technique for Determination of Textural Properties).*Akademik Gıda*,15, 29-30.

2) Sozer, N, Dalgic, A. C. and Kaya, A. (2005) Diyet lifleri:Dirençli Nişasta (Dietary fibers: Resistant Starch) *Unlu Mamuller Teknolojisi,* 15 (72), 8-14.

C. CONGRESS and WORKSHOPS

1) Sozer, N., Dalgic, A. C. and Kaya, A. (2006) Dirençli nişasta katkılı spagettinin viskoelastik özellikleri Hububat (Cereals) 2006, September , 7-8, Gaziantep (Turkey).

2) Sozer, N., Dalgic, A. C. and Kaya, A. (2006) Modeling of viscoelastic characteristics of various spaghetti types 5th European Young Cereal Scientists and Technologists Workshop 2006, July 5-7, Gaziantep (Turkey).

3) Dietary Fiber 2006 Conference, 12-14 June 2006, Helsinki, Finland (delegate).

4) Sozer, N., Primo-Martin, C., Vliet van, T. and Hamer, R.J. (2005). Influence of Water Content on Crispness of Bread Crusts and its Quantification by Acoustic and Mechanical Measurements. 4th European Young Cereal Scientists and Technologists Workshop 2005, June29 - July1 Wien, Austria.

5) Sozer, N. and Kaya, A. (2002). Textural properties of commercially produced and bran containing spaghetti cooked in different cooking waters. 1st European Young Cereal Scientists and Technologists Workshop 2002, July 8-9 Leuven, Belgium.

6) Sozer, N. and Kaya, A. (2002). Spagettinin dokusal ve pişme özellikleri. Hububat (Cereals) 2002 Gaziantep (Turkey).

7) Sozer, N. and Kaya, A. (2001). Effect of salt composition of cooking water on cooking and textural properties of spaghetti. AACC Annual Meeting 2001, 14-18 Ekim Charlotte,USA

4.PROJECTS

1) Sozer, N., Dalgıç, A. C. and Kaya, A.(2006). “Production of gluten free pasta products and viscoelastic properties”. Supported by TÜBİTAK- TOVAG (researcher)

2) Sozer, N., Primo-Martin, C., Vliet van, T. and Hamer, R.J. (2004-2005). "Crispy Crunchy Behaviour of Cellular Solid Foods". Wageningen Center for Food Sciences (WCFS) (Visiting scientist)

3) Sozer, N., Dalgıç, A. C. and Kaya, A.(2005). "Production of spaghetti enriched with resistant starch". Supported by TÜBİTAK (Ph.D student)