FORMULATION AND CHARACTERIZATION OF STARCH AND SOY PROTEIN CONTAINING LOW CALORIE SOFT CANDY

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FORMULATION AND CHARACTERIZATION OF STARCH AND SOY PROTEIN CONTAINING LOW CALORIE SOFT CANDY

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ABSTRACT

FORMULATION AND CHARACTERIZATION OF STARCH AND SOY PROTEIN CONTAINING LOW CALORIE SOFT CANDY

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Type of sugar and gelling agents used in confectionery formulations have vital importance since they directly influence physicochemical properties during storage. In this study, effect of a non-caloric rare sugar, D-allulose (formerly called D-psicose) on the starch based confectionery gels were investigated in the presence and absence of soy protein isolate using different experimental techniques for 28 days. For characterization of the formulized gel systems, common techniques were used (optical microscopy, DSC, TGA, XRD, moisture content, water activity, hardness and color measurements). Time Domain Nuclear Magnetic Resonance (TD-NMR) technique was also employed to explain dynamics in the confectionery systems. Sugar type was found to be a very significant factor affecting gel characteristics and retrogradation. Results show that D-allulose containing formulations were less prone to retrogradation and crystallinity degree of those samples were lower upon storage. Also, TGA thermogram showed that, accelerated mass loss shifted to higher temperature indicating tight relationship of water and starch which reveals better gel network with the increasing D-allulose concentration. It was observed that D-allulose containing samples show smaller changes during storage by supporting presence of better gel network. According to X-ray results, sucrose containing formulations more susceptible to crystallization and promote retrogradation of starch molecules. T2 relaxation spectra obtained from NMR experiments showed that number of distinct peaks reduced with the addition of SPI while relaxation times of peaks change when different type of sugar was used.

Keywords: Time Domain NMR Relaxometry, Starch-based gels, D-allulose, Soy protein isolate, X-Ray Diffraction

ÖZ

NİŞASTA VE SOYA PROTEİNİ İÇEREN DÜŞÜK KALORİLİ YUMUŞAK ŞEKERLEME FORMÜLASYONU VE KARAKTERİZASYONU

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Yumuşak şekerleme formülasyonlarında kullanılan şeker tipi ve jelleşme ajanı, depolama süresince son ürünün fiziksel ve kimyasal özelliklerini etkilemesi sebebiyle büyük önem taşımaktadır. Bu çalışmada, düşük kalorili nadir şeker D-allulose'un nişasta bazlı yumuşak şekerlemeler üzerindeki etkisi 28 günlük depolama süresince izole soya protein varlığında incelenmiştir. Şekerlemelerin karakterizasyonu için, bilenen deneysel analizlerin (DSC, XRD, TGA, nem analizi, su aktivitesi, tekstüğr analizi, renk analizi) yanı sıra, düşük alanlı zaman boyutlu NMR relaksometre, şekerleme içindeki dinamikleri açıklamak için kullanılmıştır. Çalışmalar sonunda, şeker tipinin jelleşme ve depolama süresince retrogradasyon özelliklerini etkilediği tespit edilmiştir. D-allulose içeren formülasyonların daha az retrograde olup, daha düşük kristalleşme gösterdiği belirlenmiştir. Bunun yanı sıra, TGA sonuçları incelendiğinde artan D-allulose konsantrasyonları için, kütle kaybı eğrileri daha yüksek sıcaklıklarda gözlenmiştir bu da D-allulose varlığında daha iyi bir jel ağı oluştuğunu göstermektedir. Tekstür deneyleri bu sonuçları destekleyecek şekilde D-allulose içeren formülasyonların depolama boyunca daha az değişiklik gösterdiğini ortaya koymaktadır. X-Işını kırınımı sonuçlarına göre, sükroz içeren formülasyonların daha fazla kristallendiği ve nişasta retrogradasyonunu desteklediği tespit edilmiştir.

Bu sonuçların yanı sıra, formülasyonlara izole soya protein eklenmesi NMR deneylerinden elde edilen T2 relaksasyon spektrumlarında elde edilen pik sayısını değiştirirken, şeker tipinin değişmesi piklerin relaksasyon sürelerinde değişiklik yaratmıştır

Anahtar Kelimeler: NMR Relaksometre, D-allulose, Nişastalı şekerleme, Izole soya proteini, X-Işını Kırınımı

For those who want to break out of their shell..

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INTRODUCTION

1.1. Confectionery Gels

Confectionery gels are composed of high amount of sugar components such as sucrose and glucose syrup, gelling agents such as starch, gelatin or pectin along with food flavorings and colorings.

Gelatin is most common gelling agent used in gummy confections as it provides desired texture and appearance which are main concern of consumers. Gelatin is a biopolymer obtained by the mammalian protein; collagen and can undergo gelation thermoreversibly when its concentration exceeds 2-3%. Gelation start with the creation of a cross-linked structure by hydrogen bonding and formed gel strengthen upon cooling depending on gelatin concentration, ionic strength and pH (Marfil, Anhê, & Telis, 2012)

On the other hand, there are many concerns on consuming gelatin in some segments of the population because of its animal based nature. In this regard, pectin and thin boiled starch is preferred for formulation on confections. Thin boiled starch is produced by acid hydrolysis and give base structure to gels by providing greater acid and heat stability. Gel formation is obtained by gelatinization of starch molecules upon heating as a result of swelling of starch molecules in water. Therefore, water, concentration and the amount and type of sugar are important for formation of gel and further characteristics. Pectin is another gelling material for the production of confectionery products because of its low cost and easy availability. Pectin is a complex polysaccharide obtained from plant cell walls. Gels prepared by pectin can be classified as low methoxy (LM) and high methoxy (HM) depending on degree of esterification of carboxyl groups (Sessler, Weiss, & Vodovotz, 2013). HM pectins are generally used for confectionery products as they form gel at low pH in the presence of high solid content (sugar). In order to create pectin gels; ratio of sucrose: pectin, acidification level, sugar concentration are the parameters to be controlled (Burey, Bhandari, Rutgers, Halley, & Torley, 2009).

In ordinary gel systems, unlike confectionery gels, gelation is a simple process like dissolution and gel formation of biopolymers in an aqueous environment (Burey et al., 2009; V. Tolstoguzov, 2000). However, addition of sugar greatly influence the standard gelation because of low mobility of water and high solid content (Kasapis, Al-Marhoobi, Deszczynski, Mitchell, & Abeysekera, 2003). Sugar content can also greatly contribute to the formation of gel and final behavior of confectionery products depending on gelling agent used. High concentration of sugar (40-60%) have been shown to reduce the effect on chain-chain association in starch based confections due to increase on the critical gelling concentration for gel formation, while gelatin network was promoted as sugar concentration increased (Burey et al., 2009; Kasapis, Mitchell, Abeysekera, & MacNaughtan, 2004). For high methoxy pectin based gels, gelation is not possible without sugar (Fraeye et al., 2010; Jaramillo, Roberts, & Coupland, 2011).

Most of the commercial food gels contain one or more gelling components, in this respect they are usually considered as composite gel systems. However, it should be kept in mind that in the case of mixed biopolymer systems, phase separation which depends on critical gelling concentration, shape and competition between polymers could be observed (De Kruif & Tuinier, 2001; V. B. Tolstoguzov, 2017; Zasypkin, Braudo, & Tolstoguzov, 1997).

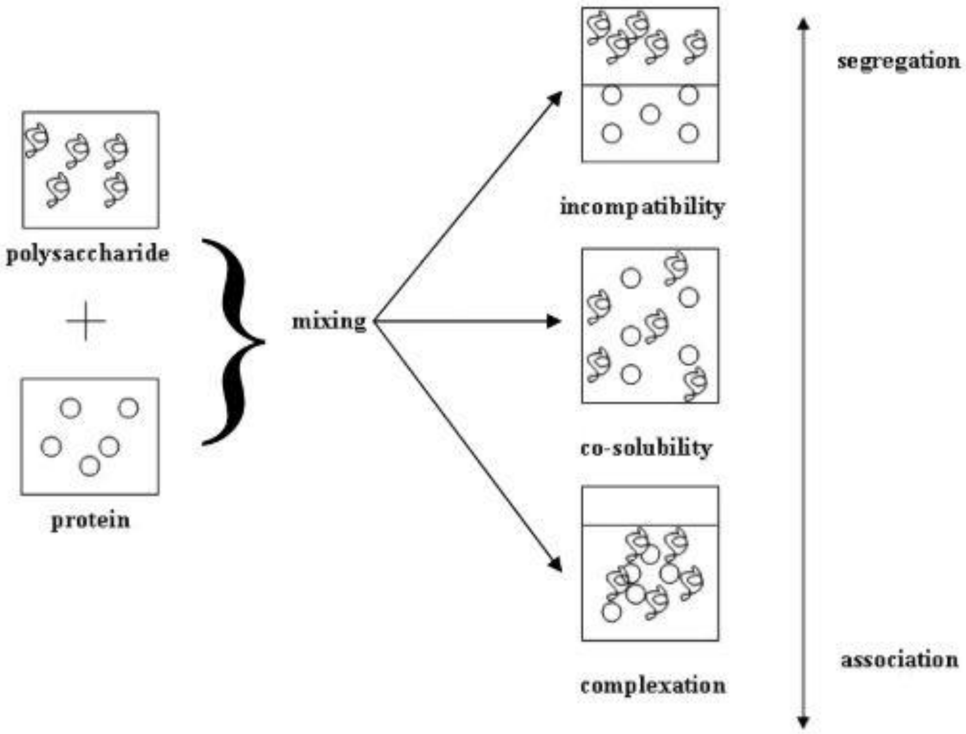


Figure 1.1. Possible behaviors of protein-polysaccharide mixture (Burey et al., 2009).

Protein and polysaccharides are widely used structural components, and their interaction can result in segregation or complexation depending on exceeding critical polymer concentration (Figure 1-1). Therefore, it is important to choose the proper polymer combination and concentration for the formation of the gel matrix and further stability (Burey et al., 2009). There are many researches that were conducted to investigate the confectionery gel systems containing more than one gelling agent including protein and polysaccharide (Gu, Ahn-Jarvis, & Vodovotz, 2015; Marfil et al., 2012; Ong, Whitehouse, Abeysekera, Al-Ruqaie, & Kasapis, 1998; Sessler et al., 2013; Siegwein, Vodovotz, & Fisher, 2011). In this study, starch and soy protein composite gels were used to develop a confectionary product. In the following sections these polymers will be discussed in detail.

1.1.1. Starch

Starch is a semi crystalline polymer containing amylose and amylopectin. Amylose is a linear polysaccharide whereas amylopectin is the highly branched fraction (Stawski, 2008). These two main components have distinct effect on functional properties of starch such as gelatinization, pasting, gelling or retrogradation (Ai & Jane, 2017).

Starch is one of the most important macro-constituents used for various functions in food industry including gelling agent, thickener, textural stabilizer, or film former. In confectionery products also, starch could have been assigned to provide gel structure and give desired textural character to the final product (Jangchud, Jangchud, & Prinyawiwatkul, 2013).

Gels prepared by native starch are characterized as firm and brittle and have low shear and thermal resistance. However, structural and functional properties of starch can be improved depending on the area to be used by applying different modifications (Chen, Kaur, & Singh, 2017; Siegwein et al., 2011). It was reported that acid-hydrolyzed; i.e; thin boiled starch is the most proper for production of confectionery products due to its low hot paste and high gel viscosity with greater acid and heat resistance (Burey et al., 2009; Jangchud et al., 2013).

In almost all applications, starch gelatinization is the major step for processing. Gelatinization is the term used to describe step change in viscosity at gelatinization temperature T_{gel} and creation of a gel network in the presence of water (Burey et al., 2009; Villanueva, Ronda, Moschakis, Lazaridou, & Biliaderis, 2018). Degree of gelatinization is important for confectionery products from production to shelf life in many stages. At this point, molecular interaction with water is important to be controlled for gelatinization of starch as water acts as both as a solvent and plasticizer. Water concentration affects the gel structure and heat treatment that is required to gelatinize the starch. In the presence of limited water (<30%), T_{gel} increases. Confectionery products contain high amount of sugar (>60%) and keep some of water in the system creating less available water for starch gelatinization due to insufficient swelling and disruption of starch granules (Beleia, Miller, & Hoseney, 1996; Burey et al., 2009). Thus, concentration should be controlled to achieve a gel having the desired structure.

Obtained gel matrix after gelatinization is a metastable structure and changes over time and this change results in retrogradation and syneresis as a result of molecular reconfiguration. The term retrogradation is described as the irreversible transition of solubilized components to insoluble microcrystalline structure. Several variables such as amylose/amylopectin ratio, temperature, botanical source of starch or presence of other ingredients like sugar, salt or surfactants can affect the rate of retrogradation (Belitz, Grosch, & Schieberle, 2009; Fennema, 1996). However, it has been stated that sugars have stabilizing effect on gel matrix by inhibiting the reorganization of starch granules to form crystalline structure and sucrose has been found to be more effective on stabilization compared to glucose and fructose (Burey et al., 2009; Prokopowich & Biliaderis, 1995).

1.1.2. Soy Protein Isolate

Soy protein isolate (SPI) is a widely used ingredient in formulations to increase the nutrition value and improve texture (Berghout, Boom, & van der Goot, 2015; Renkema & Van Vliet, 2002).

SPI is obtained from the residue after the extraction of soybean oil and has protein content over 90%. It is composed of , two major fractions which have different molecular weight and structure; 7S and 11S globulins which directly affect the functional properties such as water holding capacity and gelation (Jideani, 2011; Utsumi & Kinsella, 1985). It is known that interaction of protein and water is important for the gelation of the protein. It was stated that SPI had the highest water binding capacity and protein content among the soy protein based products and small amount of polysaccharide found could affect water absorption and gelation behavior of SPI (Jideani, 2011).

Protein gels has been defined as high moisture, continuous 3D network that preserve their structure upon deformation (Berghout et al., 2015). Gel formation of proteins can be induced by pH, heat or ionic strength by creating noncovalent interactions and hydrophobic interactions. It has been stated that for gelation of SPI, heat treatment is a prerequisite for protein unfolding and further hydrophobic interaction or formation of disulfide bridges (Berghout et al., 2015; Utsumi & Kinsella, 1985). Heat induced gelation is highly affected by protein substrate concentration. Coagulation can occur instead of gelation if protein concentration is not high enough (C. Tang et al., 2005).

In the literature, SPI has been widely investigated in various cases including composite gels systems because of better handling characteristics (Hua, Cui, & Wang, 2003; Jaramillo et al., 2011; Ryan & Brewer, 2007; Sessler et al., 2013; Siegwein et al., 2011; Sorgentini, Wagner, & Anon, 1995) and functional properties of SPI can be improved when it is used with polysaccharides (Hua et al., 2003). Studies demonstrated that improved textural characteristics (Abd Karim, Sulebele, Azhar, & Ping, 1999), increased water holding capacity (Sánchez, Bartholomai, & Pilosof, 1995), altered storage stability (Siegwein et al., 2011) are possible when starch-SPI mixture is used. Thus, it is possible to use SPI in confections with the combination of mixed biopolymer.

1.1.3. Rare Sugar

Increased consumption of ready to eat food, snacks and confectionery products is closely related to prevalence of many diseases like obesity, cancer or cardiovascular diseases. With the increase in obesity, people especially in urban area become more interested in consuming organic, unadulterated, sugar free and protein rich foods. Many gel confections consist of high amount of sucrose and glucose syrup and increasing concerns about reduction of sugar consumption cause a trend on using low and non-calorie sweeteners as a substitute for sucrose. While addition of sweeteners reduces calorie intake, their functionality may fail. Also, many most common artificial sweeteners have many concerns about the safety of consumption or unpleasant after taste. Therefore, there is a growing consumer preference for natural sweeteners. Recently, rare sugar which is type of monosaccharide found in nature in small amounts provides promising application in terms of processing and rheological characteristic with positive health effects. Different types of rare sugars and their existence is shown in Figure 1-2. More than 50 kinds of rare sugar exist but D-allulose is the one which has the lowest energy density (Hossain et al., 2015).

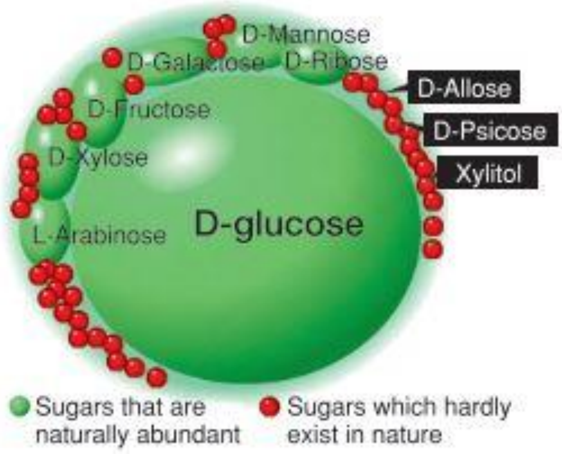


Figure 1.2. Type of monosaccharides existing in nature (Izumori, 2015)

D-allulose, is C-3 epimer of fructose (Figure1-3), is a reducing sugar with a ketone group which has a sweetness 70% of sucrose with a lower caloric value of 0.39 kcal/g due to poor digestion (Izumori, 2015; Mu, Zhang, Feng, Jiang, & Zhou, 2012). Systematic name of D-allulose is D-ribo-2-hexulose and it has been mentioned as D-psicose in many researches on the literature. As can be inferred from the name 'rare sugar', is rarely found in nature. However, it can be produced through isomerization with the use of enzyme *D-tagatose 3-epimerase* from D-fructose (Hossain et al., 2015) thus its mass production has become possible.

In 1999, the biotechnology Professor Ken Izumori, who has been studying rare sugar at Kagawa University since 1968, discovered that an enzyme found in a bacterium could synthesize rare sugar from other 6-carbon sugars like fructose. However, production process is very complex, due to the fact that the production cannot be made to a large extent for a very long time. First large-scale production has been made in the Rare Sugar Research Center established at Kagawa University. After D-allulose has been approved as generally recognized as safe (GRAS) by FDA in 2014, it began to attract the attention of producers as an alternative to Splenda, which is used as a natural sweetener in the market (Han, 2015).

The first commercial production is made by the Japanese-origin company, Matsutani, in varying forms of D-allulose like syrup and crystal table sugar. With the increase in popularity of D-allulose, it is also being produced by companies with different origins. Today, many companies such as Savanna Ingredients GmbH (Germany), Bonumose (USA), Ingredion (USA), and Tate and Lyle (UK) produce and sale D-allulose commercially. According to data cost of production of D-allulose has dropped to $ 10-20 for 1 kg (Daniells, 2016).

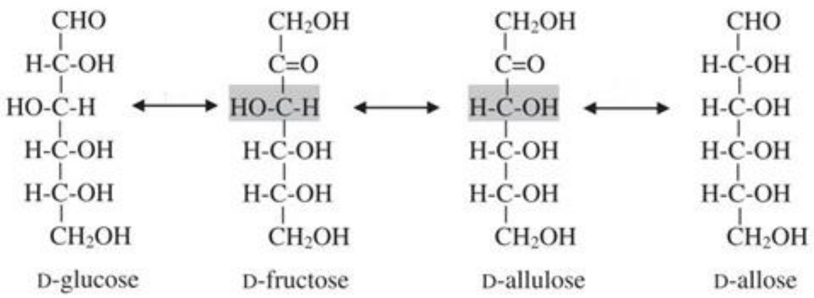


Figure 1.3. Structure of different monosaccharides (Hossain et al., 2015)

In the literature, many researches have been conducted on the use of D-allulose in both real and model food systems. According to studies, the most obvious and prominent result is that more antioxidant substances are produced through Maillard reaction and these substances give anti-oxidative properties to foods (Sun, Hayakawa, Ogawa, & Izumori, 2007). Also researches have shown that D-allulose promote gelatinization by providing greater amount of water for starch gelatinization which make retrogradation slower (Ikeda, Furuta, Fujita, & Gohtani, 2014). Other than antioxidant activity, the use of D-allulose alters emulsification, foaming capacity, and texture. In the study of physical and chemical properties of meringues, with the addition of D-allulose as a sucrose replacer, better foaming capacity and decreased air bubble size were obtained which indicated more stable foams (O'Charoen, Hayakawa, Matsumoto, & Ogawa, 2014). Considering the purpose of the use of sucrose such as contribution of texture and sensory and providing mouthfeel, D-allulose can be good substitute of sucrose, with better rheological and textural behavior.

1.2. Characterization of Confectionery Products

1.2.1. X-Ray Diffraction

X-ray diffraction (XRD) is a characterization technique that is useful for getting information about structures, crystallinity or texture. Each set of lattice planes in a matrix has different diffraction pattern depending on the specific atomic positions within the lattice plane when they are subjected to same wavelength of X-ray. In other words, when a crystal structure interacts with X-ray, diffraction pattern that is formed is unique for that crystal. Therefore, each diffraction pattern defines the specific crystals as a kind of fingerprint (Kohli, 2012).

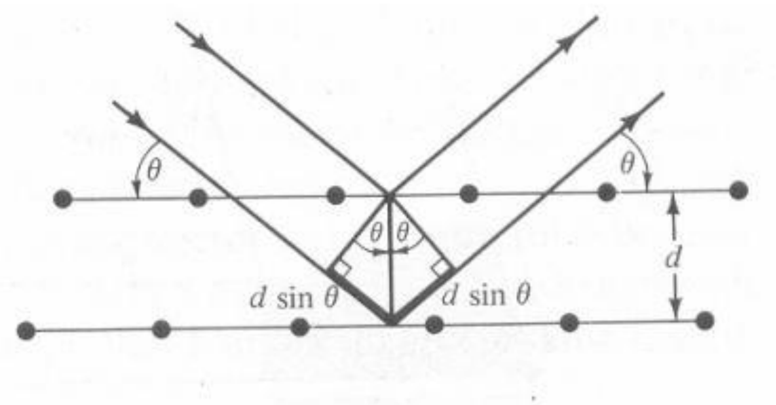


Figure 1.4. Bragg' law

Bragg's Law is the most commonly used theory to explain X-ray diffraction. The theory is about relating the angle θ where intensity of diffraction is maximum, to the wavelength λ and distance d between two atoms in a lattice (Figure 1-4). A typical X-ray diffraction pattern therefore contains diffraction peaks or lines at specific 2θ positions with different intensities. As an example X-ray diffractogram is shown in Figure 1-5., diffraction patterns of samples are given as a function of 2θ. While interpreting the diffractogram, sharp and high intensity peaks are associated with crystalline regions whereas broad peaks indicates amorphous structure. Also, higher intensity could be associated with more crystalline structure (Eliasson, 2010).

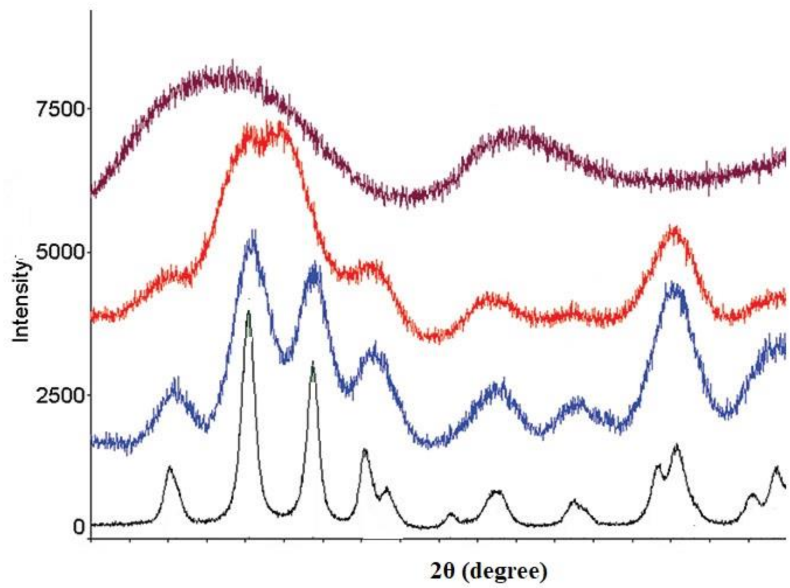


Figure 1.5. Example X-ray Diffraction pattern

In confectionery products, recrystallization of sugar molecules and retrogradation of starch are important changes to be controlled in terms of quality and texture. In this regard, X-ray diffraction (XRD) analysis stands out to characterize starch or sugar molecules in crystalline form (Mizuno, Mitsuiki, & Motoki, 1998; Skibsted, Risbo, & Andersen, 2010). XRD pattern of starch granules have been previously reported in several researches (Dankar, Haddarah, Omar, Pujolà, & Sepulcre, 2018; Das et al., 2010; Demirkesen, Campanella, Sumnu, Sahin, & Hamaker, 2014a; Nagaraj, Sasidharan, David, & Sambandam, 2017; Ozge Ozkoc, Sumnu, & Sahin, 2009; Ribotta, Cuffini, León, & Añón, 2004a), and can vary depending on botanical source of starch, crystallization of amorphous parts or interaction of amylose with lipids (Ozkoc, Sumnu, Sahin, & Turabi, 2009; Ribotta et al., 2004a). On the other hand, XRD can be used not only for detecting starch crystals but also, crystallization of sucrose (Leinen & Labuza, 2006).

It is possible to calculate total crystallinity of a sample by separation and integration of the areas under crystalline and amorphous X-ray diffraction peaks (Ribotta et al., 2004a). In order to calculate relative crystallinity following model described by Ribotta et al (YIL), can be used;

$$Total\ Crystallinity\ (TC) = \frac{I_c}{I_c + I_a}$$

Where I_c is the integrated intensity of crystalline phase and I_a is the integrated intensity of amorphous phase.

1.2.2. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a technique based on measurement of mass of sample as function of temperature. As temperature increases mass loss is observed in polymers and polymer containing systems. Resulted TGA curves consists of several weight loss steps caused by chemical reactions or physical transitions (Widmann, Schubnell, Riesen, Schawe, & Darribère, 2001).

TGA is widely used to characterize starch and starch combined food matrices by providing simple thermogram at the end of the experiment (Botosoa, Chèné, Blecker, & Karoui, 2015). With the use of TGA, it is possible to investigate the difference in thermal stability or resistance of starch components (Teramoto, Motoyama, Yosomiya, & Shibata, 2003), determine amylose and amylopectin content (Stawski, 2008). Beside these, research has shown that TGA can be used to detect retrogradation of starch with significant increase in bound water during storage (Tian, Li, Xu, & Jin, 2011).

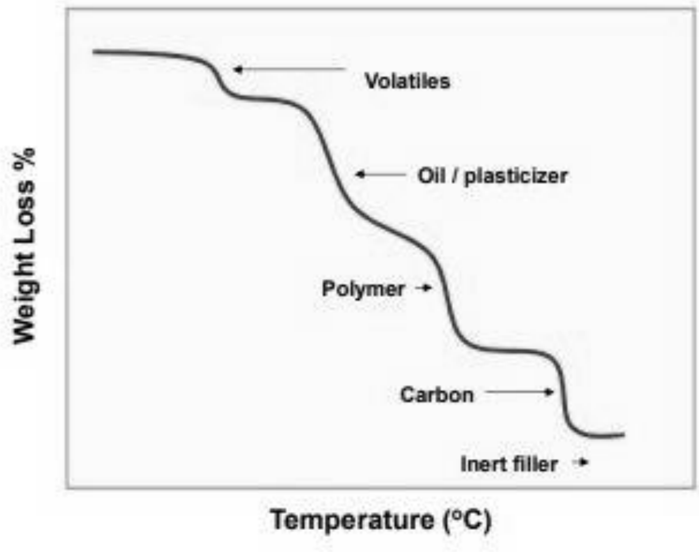


Figure 1.6. Typical TGA thermogram

A typical TGA thermogram is given in Figure 1-6., representing the decomposition stages and what type of decomposition/mass removal they belong. First two stages are related with the removal of volatiles and plasticizers. Water can be considered as both volatile and a plasticizer in food systems as it is found in free and bound form depending on the product. Moisture content is the term used for all water content in the system covering both free and bound and it is possible to use TGA for determination of moisture content (%) by using mass loss in the first or first two decomposition stage (Tomassetti, Campanella, & Aureli, 1989; Zhiqiang, Xiao-Su, & Yi, 1999).

Determination of the bound water content and related temperature is given schematically in Figure 1-7.

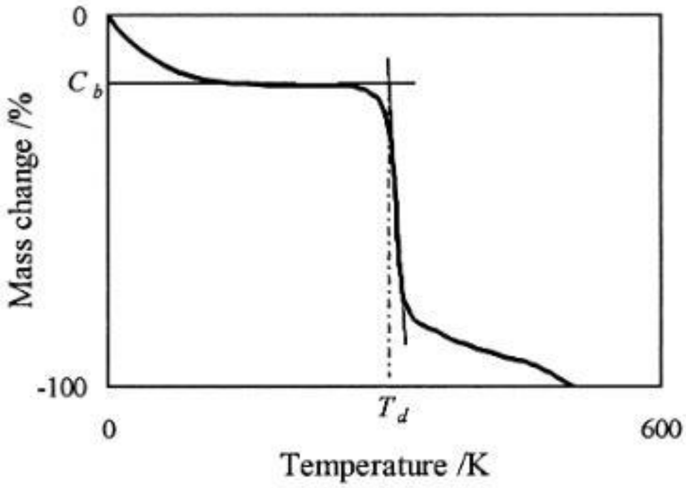


Figure 1.7. Simple TGA thermogram that represent the first decomposition stage (Zhiqiang et al., 1999)

Also derivative weight loss curves can be interpreted for the determination of strength of the interaction between water and polymer found in formulations by identifying the peak temperature. The temperature related to peak shifted to right indicates strong water association (which means hard to lose moisture due to strong interaction) while temperature shifted to left indicates lower water association (which means easy to lose moisture due to weaker interaction) (Siegwein et al., 2011).

1.2.3. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a type of measurement used for determination of thermal characteristic of a sample by measuring the energy absorbed from sample as a function of temperature. System is operated to keep temperature balance. When transition occurs, energy absorbed by sample is compensated with the increased energy input which is equivalent to the energy absorbed upon transition. This energy change is recorded as endothermic or exothermic peak in a DSC thermogram depending on the transition.

Determination of glass transition temperature is one of the most common reason to use DSC experiments. Glass transition temperature (T_g) is the term used to express thermal transition from rubbery to glassy state where behavior of systems completely changes. Especially for confectionery products, T_g is an important parameter which is used to predict the storage stability and crystallinity of samples upon storage. Starch based confections are initially amorphous semisolids that exhibit unstable heterogeneous structure and susceptible to rubber to glass transition upon storage (Karim, Norziah, & Seow, 2000a).

T_g is observed as a step wise change in a DSC thermogram (Spink, 2008). However, it is important to note that the term of 'step wise change' express a temperature range not a single temperature (Roos, 2010). The starting and final temperature of step change are named as onset (T_{onset}) and end set (T_{endset}) temperatures, and the midpoint of these temperatures is expressed as the glass transition temperature (T_g) (Figure 1-8.a). Also, heat capacity/temperature curves can be useful for determination of T_g since sample has different heat capacities depending on whether temperature is above or under T_g (Figure 1-8.b).

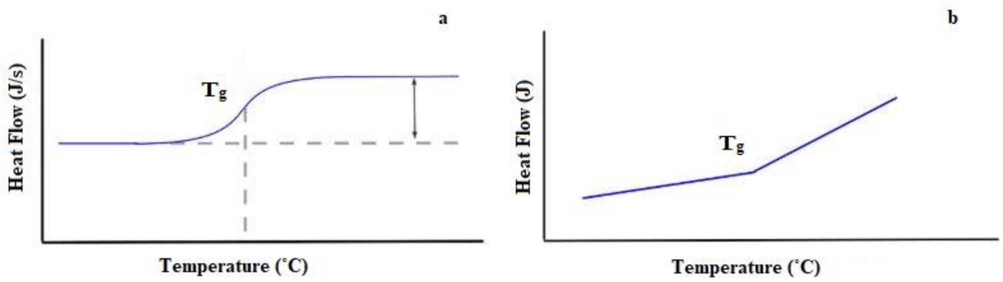


Figure 1.8. Schematic representation of the determination of glass transition temperature (Humboldt University of Berlin, 2009)

There are some factors affecting the glass transition temperature such as molecular weight of the polymers in the system, degree of crosslinking, or concentration of plasticizers (De Graaf, Madeka, Cocero, & Kokini, 1993). Also, change in the reorganization of polymer chains has significant effect on $T_{g.}$. Retrogradation is one of the most common phenomena occurs in food containing starch and there have been many researches which have investigated the effect of retrogradation on thermal behavior of food matrices (Demirkesen, Campanella, Sumnu, Sahin, & Hamaker, 2014b; Karim, Norziah, & Seow, 2000b; Mizuno et al., 1998; Ribotta, Cuffini, León, & Añón, 2004b). DSC can be used not only for determination of retrogradation but also for the gelatinization degree of starch. Therefore, obtained thermogram have been interpreted to examine whether gelatinization was complete or not (Zobel, Young, & Rocca, 1988). As an example, a peak is observed on a thermogram at gelatinization temperature when the sample is partially gelatinized.

1.2.4. NMR Relaxometry

Nuclear Magnetic Resonance (NMR) Relaxometry which is a nondestructive and noninvasive technique that has been used to characterize molecular dynamics in various matrices. Therefore, low field (LF) and time domain (TD) NMR relaxometry is widely used in food industry for many purposes including, droplet size measurement, water and fat content determination, compositional and structural characterization or mathematical modelling of heat and mass transfer (Kirtil & Oztop, 2016; F Mariette, 2010). Also, it has been widely used for characterization of starch alone and starch water interaction (Sung Gil Choi & Kerr, 2003; Fan et al., 2013; Farhat, Loisel, Saez, Derbyshire, & Blanshard, 1997; Hansen et al., 2009; Kovrlija & Rondeau-Mouro, 2017; Ozel, Dag, Kilercioglu, Sumnu, & Oztop, 2017; Zhu, 2017).

NMR Relaxometry is based on monitoring the relaxation of excited signal which is created by a radio frequency (RF) pulse in a static magnetic field. The relaxation term is used for the time for protons to turn back to their previous states. The relaxation of both longitudinal (T_1) and transverse (T_2) magnetization can give various information about the whole sample. Also, it is possible to differentiate different proton pools with the signal obtained during T_1 and T_2 relaxation times (Kirtil & Oztop, 2016). Longitudinal relaxation time T_1 which is also called as spin-lattice relaxation time has been defined as the time it takes for spins to give their energy back received from the RF pulse and it is strongly related to mobility of protons or crystal structure of solid phases. On the other hand, transverse relaxation time T_2, spin-spin relaxation time, is the time required for transverse magnetization to reach the equilibrium value of zero. It provides information about the mobility of hydrogen molecules by attributing to the immobile structure in the case of short T_2 and, whereas mobile structure in long T_2 (Hansen et al., 2009; Ozel, Dag, et al., 2017).

NMR measurements are based on the measurement of relaxation of protons in a sample. Therefore, it can be concluded that signal coming from sample is contributed by all protons in the matrix which make it possible to monitor dynamics of each components and internal structure at the end of NMR experiment (Farhat et al., 1997; Hansen et al., 2009). At that point, T_2 relaxation spectrum analysis may help to understand contributions of each proton pools and water distributions. In order to obtain relaxation spectrum, T_2 relaxation curves are analyzed by Non-Negative-Least-Square (NNLS). As a result of this analysis, depending on the sample, different numbers of peaks (proton pools) could be observed indicating solid-solid, solid-water or water entrapped in matrix (Ozel, Uguz, Kilercioglu, Grunin, & Oztop, 2017).

1.2.5. Fast Field Cycling Relaxometry

FFC Relaxometry is another NMR based method that has started to be used in food industry with growing interest on understanding molecular dynamics and phase transitions in a food matrix. Several research and applications of FFC Relaxometry reveals that it can be used as quality control tool for detection of spoilage and shelf life of milk, fruit or meat (Capitani et al., 2014; Conte, Bubici, Palazzolo, & Alonzo, 2009; Steele, Korb, Ferrante, & Bubici, 2016), determination of geographical origin of oils and food fraud (Baroni, Consonni, Ferrante, & Aime, 2009; Conte, Maccotta, De Pasquale, & Alonzo, 2010; Rachocki & Tritt-Goc, 2014), aging level of cheese products by degree of hydration (Godefroy, Korb, Creamer, Watkinson, & Callaghan, 2003).

The technique based on measurement of spin-lattice relaxation rate ,$1/T_1$, along a wide range of frequencies than standard NMR relaxometry by providing enhance characterization of molecular dynamics of variety of substances (Kimmich & Anoardo, 2004; Neudert, Mattea, & Stapf, 2018).

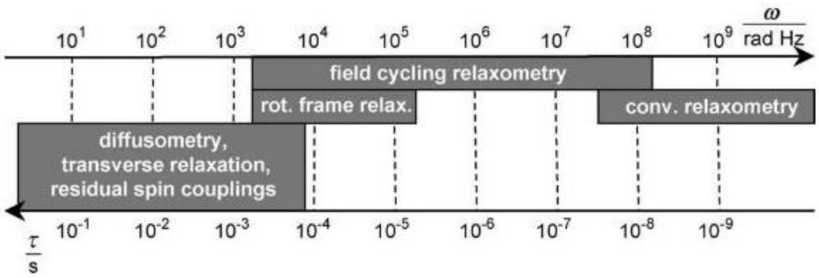


Figure 1.9. *Schematic representation of frequency scales for different NMR techniques (Kimmich & Anoardo, 2004)*

At the end of the measurement data can be displayed as rate ($1/T_1$) versus the frequency (MHz) which is known as NMR dispersion (NMRD) curve by providing detailed information about relaxation mechanism with the help of strong frequency dependence of R_1 at especially low fields (Chávez & Halle, 2006). However, it is important to interpret data with a proper model in dynamically complex and heterogenous systems (Villa et al., 2001). Different models can be interpreted to analyze NMRD profiles. Rouse model is used for homogeneous viscous medium where molecular weight of the polymer is below the critical molecular weight (M_c), while renormalized Rouse Model is used for modelling for entangled polymer chain where molecular weight is above than M_c. In other words, Renormalized Rouse Model is more useful when polymer chain dynamics is not dominated because of neighboring chains confinement (Kimmich & Anoardo, 2004). Presence of more than one gelling agent and high sugar concentration create a competition for water and may restrict chain dynamics in confectionery products. In this regard, it can be said that Renormalized Rouse Model could be useful to model the data and understand molecular dynamics. Moreover, it has been stated that different relaxation dispersion regimes can be observed for many complex systems and these distribution can be analyzed by Renormalized Rouse relaxation model that obey power laws with different exponents (Tavares, da Silva, Silva, & Sebastião, 2019).

1.3. Objective of the Study

This study was funded by and the Scientific & Technological Research Council of Turkey, with proposal number 116O759. The goal of the project is to design different confectionery products with rare sugar (D-allulose), use low resolution NMR relaxometry to characterize confectioneries with the combination of other physical and chemical characterization methods.

In this thesis, the objectives are listed as follows;

- To introduce and determine potential usage of rare sugar D-allulose in starch-based confections
- To formulate stable confections and investigate time dependent stability of confectionery gel systems

To characterize confections in terms of time domain low field NMR Relaxometry, X-ray Diffraction, Differential scanning calorimetry (DSC), and Thermogravimetric analysis (TGA) and other physical measurements

CHAPTER 2

MATERIALS AND METHODS

2.1. Materials

Sucrose (Bal Küpü, Aksaray, Turkey) was purchased from a local market in Ankara, Turkey. D-Allulose (All-u-Lose) was purchased from Santiva Inc. Downers Grove, IL, USA. Soy protein isolate having a protein content 90% (Alfsasol, Turkey) was used. Acid modified starch and corn syrup (DE=42) were provided by Kervan Gıda (İstanbul, Turkey). Sodium azide (≥99.99% trace metals basis) (Sigma-Aldrich Chemical Co., St. Louis, MO, USA) was used at a final concentration of 0.02% (w/w) in all formulations to prevent microbial growth.

2.2. Methods

2.2.1. Preparation of Samples

Starch gels was prepared according to the method of (Siegwein et al., 2011) with some modifications. Starch was mixed with two times amount of water by its weight and gelatinized in an oil bath at 140 ˚C for 5 minutes until it was dissolved completely. During this time, the sugar syrup-powder sugar mixture was mixed in a glass beaker with the remaining water and boiled up to 115 ˚C. After that, the gelatinized starch-water mixture was mixed with the 115 ˚C syrup mixture. For the soy protein formulations, the soy protein was introduced at this step and homogenized with a high shear homogenizer at 10,000 rpm for 1 min (WiseTisHG-15D, Wertheim, Germany). The Brix value was measured by a digital refractometer (Hanna, HI96801, USA) and cooking was continued at 140 ˚C until 75 ˚Brix was obtained. The mixture was then poured into molds prepared by powdered starch with dimensions of 2.5*2.5*2cm and kept at 38 °C for 36 hours. After drying, the starch on the samples were brushed and gels were stored in polyethylene bags at 25 ˚C. Composition of the gel samples were given in Table 2-1.

Table 2.1. *Concentrations of D-allulose and SPI in different formulations*

Name	Starch (%)	D-allulose (%)	Sucrose (%)	Soy Protein Isolate (%)
11_S0_R0	11	0	30	0
11_S0_R10	11	10	20	0
11_S0_R20	11	20	10	0
11_S0_R30	11	30	0	0
9_S2_R0	9	0	30	2
9_S2_R10	9	10	20	2
9_S2_R20	9	20	10	2
9_S2_R30	9	30	0	2

2.2.2. Characterization of Confectionery Products

2.2.2.1. Water Activity

Aqualab 4TE (METER Group, Pullman, WA) was used for water activity measurements. Water activities of samples were directly recorded from the instrument. Experiments were conducted at 25˚C in replicates during the 0,7,14,21,28 days of storage.

2.2.2.2. Moisture Content (%)

In vacuum oven drying, evaporation of water inside the food is promoted by vacuum and drying takes place at lower temperatures than conventional drying methods. It is a preferable method for high sugary products which is susceptible to thermal decomposition like caramelization and Maillard. Calculation of moisture content is based on the taking difference between initial and final weight of sample. In the study, moisture contents of the formulations were measured using a vacuum oven (DAIHAN, Germany) at 70 °C for 4 hours. Weight loss from samples were used to calculate the moisture content of samples.

2.2.2.3. Texture Analysis

Hardness of starch-based gels were measured by using a Texture Profile (Lloyd Instruments, TA Plus, Hants, UK). 10 mm cylinder shape probe was attached to the instrument for the measurement. The instrument was set to a speed of 100 mm/min and preload of 0.1 N, with 40% compression to simulate chewing. In addition to hardness, cohesiveness and adhesiveness were measured, but they were not recorded due to non-meaningful results. Experiments were carried out at 0,10, 20,30 days in replicates. For exporting and reporting the data NEXIGEN Texture analysis software was used.

2.2.2.4. Color Measurement

The color analysis of gels was performed using a spectrophotometer (Konica Minolta Spectrophotometer, CM-5, Japan). The a* (red-green), b* (yellow-blue) and L* (lightness) values were recorded for each sample by measuring the surface color for the first day following production.

2.2.2.5. X-Ray Diffraction Analysis

X-Ray Diffraction experiments were conducted by using a Rigaku Ultima-IV X-Ray Diffractometer (Japan) at 40kV and 30 mA. Data were collected by the method of

Suput et al. (2015) between 4-70 ^{o}C with the 2θ range. In order to evaluate the effect of crystallization of sugars, samples containing only sucrose (11_S0_R0 & 9_S2_R0) and only D-allulose (11_S0_R30 & 9_S2_R30) were analyzed on 0th and 28th days following production. Crystalline peaks were analyzed using PDXL software (Rigaku) by separation and integration of the areas under crystalline and amorphous regions. The crystallinity degree of the samples was determined based on the method described by (Demirkesen et al., 2014b; Ribotta et al., 2004a)

$$Total\ Crystallinity\ (TC) = \frac{I_c}{I_c + I_a}$$

Where I_c is integrated intensity of crystalline phase and I_a is the integrated intensity of amorphous phase.

2.2.2.6. Differential Scanning Calorimetry (DSC)

DSC 4000 (Perkin Elmer, MA, USA) was used by applying pure nitrogen gas through the system with a flow rate of 19.8 ml/min for measurement of approximately 10 mg sample in hermetically sealed pans. An empty aluminum pan was taken as the reference for all measurements. Samples were cooled from 25 ˚C to -65 ˚C with a rate of 5 °C/min and heated from -65 ˚C to 35 ˚C at a rate of 5 °C/min. Analyzes were repeated for 0th and 28th day samples after storage to understand the change in glass transition temperature as a result of crystallization. Pyris Manager software was used for the data treatments to calculate glass transition temperature (T_g).

2.2.2.7. Thermogravimetric Analysis

Thermogravimetric analysis was conducted by using Perkin Elmer Pyris1 (Perkin Elmer, MA, USA). Samples were analyzed at both 1st and 28th days of storage. The experiment was operated from 25 °C to 350 °C at a heating rate of 5 °C/min under nitrogen. Mass loss at first decomposition stage (up to 150 °C) was analyzed to determine bound water content and moisture content were related directly with mass loss.

2.2.2.8. Optical Microscopy

Starch based gels were analyzed under a light microscope (PrimpVert, Zeiss, Jena, Germany) to observe the gelatinization level of starch granules in different formulations. Small amount of gels was placed into a microscope slide and images were taken at 20X magnification by a microscopic camera (SONY CCD Color Digital Video C-Mount Microscope Camera, Tokyo, Japan).

2.2.2.9. Time Domain NMR Relaxometry

TD NMR Relaxometry experiments were conducted on a 0.5 T NMR low resolution system (Spin Track, Russia) operating at a Larmor frequency of 20.34 MHz. Relaxation period (TR) and observation time were chosen as 300ms and 400ms respectively in saturation recovery sequence for T_1 measurements. For T_2 measurements, Carr-Purcell- Meiboom-Gill (CPMG) sequence was used with 40 us echo time, 400-700 echoes depending on the formulation. 4 scans were used for both T_1 and T_2 measurements and experiments were performed for all samples in duplicates upon storage. Mono-exponential fitting was conducted for T_1 relaxation curves by MATLAB and Non-Negative-Least-Square (NNLS) analysis was conducted on T_2 curves to obtain a relaxation spectrum using PROSPA (Magritek , New Wellington, New Zealand).

2.2.2.10. Fast Field Cycling Relaxometry

Rate of proton spin-lattice relaxation measurements of starch based confectionery products have been carried out with the use of field-cycling relaxometry (Stelar, SpinMaster, FFC200, Italy) by using the method of Płowaś-Korus with some modifications (Płowaś-Korus et al., 2018). FFC measurements were conducted in the laboratory of Professor Danuta Kruk in the University of Warmia and Mazury in

Olsztyn (Poland). Data have been collected at a frequency range of 4 kHz–30 MHz The measurements were conducted only for 4 formulations in order to evaluate the effect extreme concentrations of different sugars (D-allulose and Sucrose) on the gelatinization behavior of starch and effect of substitution of SPI on structural properties of confectionery products for freshly prepared samples. In order to simulate storage conditions, temperature was kept constant at room temperature (25 ˚C). NMRD curves were obtained from the experiments and data were modelled to Renormalized Rouse Model using FITTEA software.

2.2.2.11. Statistical Analysis

Statistical analysis for all the experimental results were done by analysis of variance (ANOVA) with the general linear model tool of Minitab (Minitab Inc., Coventry, UK). For the comparison of results, Tukey's comparison test was used at 95% confidence interval.

As seen on the formulation table (Table 2.1), total polymer concentration was kept at 11% and SPI was tested at a level of 2% concentration on the formulations. That is why, while naming the factors in the ANOVA 'starch' concentration was used as one of the factors with 2 levels (9 and 11%) and D-Allulose concentration was the other factor (10 , 20, 30 %). In addition, storage experiments were also conducted for most of the physical parameters measured. Thus 'storage time' was another factor studied. Frequency of the storage experiments changed for different experiments. They are summarized in the following table (Table 2.2)

Table 2.2. *Frequency of storage experiments*

Experiments	**The days conducted**
Moisture Content (%)	0, 7, 14, 21, 28
Water activity	0, 7, 14, 21, 28
TD-NMR	0, 7, 14, 21, 28
Texture Analysis	0, 10, 20, 30
X-ray Diffraction	0, 28
DSC	0, 28
TGA	0, 28

Two-way ANOVA was conducted for the formulations at each day to understand the effect of starch concentration and allulose substitution. For evaluating the storage time, for each formulation, one-way ANOVA was used. Assumptions of ANOVA; normality of the residuals and constant variance in the data set were checked using Anderson Darling and Barnett test at 5 % significance level respectively. Outliers were removed from the data and while considering the replicates for the data analysis, coefficient of variance (Standard Deviation/Mean) was kept at maximum 10%. All ANOVA results are provided in the Appendix section with the same order of the results presented.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Texture Analysis

Table 3-1. shows the hardness of starch based soft candies containing SPI and D-allulose. For fresh samples, SPI replacement caused increase in hardness values of the samples ($p<0.05$). Hardness (N) of the sample (11_S0_R10) containing only starch as a gelling agent was approximately half of the sample prepared by using 2% soy protein isolate (9_S2_R10). Increase in the hardness value can be explained with increased covalent crosslinks within the protein network in the presence of reducing sugar through Maillard reactions which led to increased rigidity of the protein gel network. Sun et al. (2004) showed that extent of Maillard reaction was directly correlated with breaking strength of egg white protein gel. Therefore, increased hardness was associated with increased gel strength as a result of Maillard reaction. This observation was followed by increase of hardness values of only starch containing formulations (11_S0_R0, 11_S0_R10, 11_S0_R20, 11_S0_R30) while hardness of SPI and sucrose containing formulation (9_S2_R0) decreased at 10th day of measurement ($p<0.05$). It has been reported that interactions between protein and polysaccharides can affect the gel structure, depending on the polymer concentration and compatibility of polymers (Burey et al., 2009; De Kruif & Tuinier, 2001). A discontinuous phase might have been formed and this might have caused decrease in hardness during the first 10 days for the formulation of 9_S2_R0. A similar disrupted starch network has been observed in the research conducted on SPI addition to starch-based confections (Siegwein et al., 2011).

The textural changes did not follow the same trend during of storage. It was found that hardness of the SPI and sucrose containing sample (9_S2_R0) significantly increased between 10th and 20th days of storage and remained unchanged afterwards ($p<0.05$). It was hypothesized that discontinuous and disrupted starch network as a result of SPI addition might have accelerated the retrogradation and syneresis which led to obtain a firmer structure through storage.

Table 3.1. *Hardness of starch based soft candies during storage*

	Hardness (N)			
Time (days)	**0**	**10**	**20**	**30**
11_S0_R0	06.08 ± 0.11 ^{cd,D}	19.54 ± 0.73 ^{b,C}	35.90 ± 2.14 ^{a,B}	46.40 ± 0.51 ^{a,A}
11_S0_R10	07.29 ± 0.53 ^{c,C}	25.32 ± 1.33 ^{a,B}	32.99 ± 4.10 ^{ab,AB}	39.06 ± 3.60 ^{b,A}
11_S0_R20	04.14 ± 0.73 ^{cd,C}	09.92 ± 0.87 ^{c,B}	13.23 ± 1.03 ^{cd,AB}	13.82 ± 0.67 ^{d,A}
11_S0_R30	02.58 ± 0.24 ^{d,C}	04.54 ± 0.17 ^{e,B}	05.83 ± 0.07 ^{d,A}	06.43 ± 0.20 ^{e,A}
9_S2_R0	23.92 ± 0.81 ^{a,B}	05.20 ± 0.51 ^{de,C}	41.89 ± 4.59 ^{a,A}	43.51 ± 0.79 ^{ab,A}
9_S2_R10	17.45 ± 2.82 ^{b,AB}	07.35 ± 0.20 ^{cd,B}	22.57 ± 5.71 ^{bc,A}	20.21 ± 1.84 ^{c,AB}
9_S2_R20	06.94 ± 0.15 ^{cd,AB}	04.17 ± 0.12 ^{e,B}	08.49 ± 0.89 ^{d,A}	08.54 ± 1.04 ^{de,A}
9_S2_R30	06.07 ± 0.57 ^{cd,AB}	03.73 ± 0.08 ^{e,B}	07.37 ± 0.51 ^{d,A}	06.76 ± 1.04 ^{e,A}

Means within the same column, followed by the different small letters (a–e) are significantly different for each sample ($p < 0.05$)
Means within the same row, followed by the different capital letters (A–D) are significantly different for each storage day ($p < 0.05$)

30th day measurements showed that significant increase occurred in samples of 11_S0_R0, 11_S0_R10, 11_S0_R20, 11_S0_R30, and 9_S0_R0 ($p<0.05$). This increase in hardness of samples was associated with the retrogradation of starch. Thus, hardness of only starch and sucrose containing formulation increased sharply during storage. On the other hand, D-allulose containing samples experienced relatively smaller textural changes upon storage. It has been also shown that D-allulose, promoted gelatinization by providing greater amount of water for starch gelatinization and also slowed retrogradation (Ikeda et al., 2014). Besides, as rare sugar concentration increased there was a decreasing trend in hardness values of different formulations during of storage ($p<0.05$). Research conducted on the effect of D-allulose on gelatinization also showed that rice cakes prepared by using sucrose was much harder than the samples prepared by using D-allulose (Ikeda et al., 2014).

Therefore, it was not surprising to conclude that in the presence of rare sugar D-allulose, retrogradation was slower and confections stayed more stable.

3.2. Water Activity

Water activity plays an important role in the physiochemical changes, texture, aroma, taste and microbial safety (Durance, 2002). As shown in Table 3-2., water activity of the formulations significantly decreased by replacement of starch with SPI at each day of the measurement for the 28 days storage ($p<0.05$). It was stated that heat induced soy protein gels had poor water holding capacity accompanying with coarse and stiff structure (Tang et al., 2005). In the case of thermally induced protein gels, most important factor for gelation is the concentration of the protein. When low concentration of protein is used, coagulation rather than gelation is expected to occur (Tang et al., 2005). Also, it was clearly mentioned in another research that in order to obtain a self-supporting gel, high protein concentration (more than 7% w/w in soy proteins) was needed (Puppo & Añón, 1999). These researches indicated that SPI at concentration (2%) used in the study was not sufficient for gel formation. Although the SPI concentration of 2% was not sufficient for gel formation, polysaccharide chains which are contained in SPI can significantly absorb water (Jideani, 2011). SPI that was used in this study has 90% protein content with no fat, thus the remaining was most probably carbohydrates. Therefore, it can be concluded that the reason for the decrease in water activity was not the gelation of the soy protein isolate but binding of polysaccharide chains with water. It is also known that amines in protein chains react with reducing sugar upon heat treatment through Maillard Reaction. Addition of SPI to the formulation provided amine groups which reacted with the monosaccharides that were present in the mixture. It was stated that reaction of amines with reducing sugars resulted in the formation of covalent cross links with in the protein network which could cause higher protein-protein interaction and a better gel network (Sun, Hayakawa, & Izumori, 2004).

Water activity of the formulations significantly decreased by D-allulose substitution at each day of measurement for the 28 days of storage ($p<0.05$). D-allulose is a reducing sugar showing high water solubility but low water binding ability compared to sucrose. This property of D-allulose enables more available water for starch gelatinization and results in better gel network which eventually causes a decrease in free water (Ikeda, Gohtani, Fukada, & Amo, 2011; Yuanxia Sun et al., 2007). On the other hand, it was found in the research that D-allulose decreased water-protein interaction by making hydrogen bonding directly with protein through Maillard reaction. In this way hydrophobic interactions and intermolecular bonds were enhanced which contributed higher aggregation and cross-linking (Yuanxia Sun, Hayakawa, Ogawa, Fukada, & Izumori, 2008). As mentioned before, 2 % SPI was not sufficient to form a gel. However, presence of D-allulose in the formulation might have contributed to gel formation by decreasing the critical gel concentration.

Table 3.2. *Water activities of starch based soft candies during 28 days of storage*

aw	**Time (days)**				
Name	**0**	**7**	**14**	**21**	**28**
11_S0_R0	$0.69 \pm 0.00^{a,A}$	$0.65 \pm 0.01^{a,AB}$	$0.64 \pm 0.01^{a,B}$	$0.66 \pm 0.02^{a,AB}$	$0.64 \pm 0.00^{a,B}$
11_S0_R10	$0.66 \pm 0.00^{b,A}$	$0.60 \pm 0.00^{b,C}$	$0.63 \pm 0.01^{b,B}$	$0.57 \pm 0.00^{b,D}$	$0.60 \pm 0.01^{b,C}$
11_S0_R20	$0.62 \pm 0.01^{c,A}$	$0.58 \pm 0.01^{c,AB}$	$0.61 \pm 0.01^{c,A}$	$0.56 \pm 0.01^{c,B}$	$0.58 \pm 0.00^{c,AB}$
11_S0_R30	$0.61 \pm 0.01^{c,A}$	$0.57 \pm 0.00^{c,B}$	$0.58 \pm 0.02^{c,AB}$	$0.55 \pm 0.01^{c,B}$	$0.58 \pm 0.00^{c,AB}$
9_S2_R0	$0.66 \pm 0.00^{b,A}$	$0.62 \pm 0.01^{b,AB}$	$0.62 \pm 0.01^{b,AB}$	$0.59 \pm 0.04^{b,B}$	$0.62 \pm 0.01^{b,AB}$
9_S2_R10	$0.57 \pm 0.00^{d,A}$	$0.55 \pm 0.00^{d,AB}$	$0.55 \pm 0.01^{d,AB}$	$0.52 \pm 0.02^{d;B}$	$0.56 \pm 0.00^{d,A}$
9_S2_R20	$0.57 \pm 0.00^{d,A}$	$0.55 \pm 0.00^{d,A}$	$0.57 \pm 0.01^{d,A}$	$0.53 \pm 0.00^{d,A}$	$0.56 \pm 0.00^{d,A}$
9_S2_R30	$0.54 \pm 0.00^{e,A}$	$0.53 \pm 0.00^{e,AB}$	$0.51 \pm 0.02^{e,AB}$	$0.51 \pm 0.01^{e,B}$	$0.54 \pm 0.00^{e,A}$

Means within the same column, followed by the different small letters (a–e) are significantly different for each sample ($p<0.05$)
Means within the same row, followed by the different capital letters (A–C) are significantly different for each storage day ($p<0.05$)

3.3. Moisture Content (%)

Water is one of the most important components, and the final water content effects texture and shelf life of confections significantly. Moisture content of all formulations were found to be between 11-15.4 % which were consistent with values of standard sugar confections (Ergun, Lietha, & Hartel, 2010). As can be seen in the Table 3-3., moisture content of formulations decreased significantly with the replacement of both SPI and D-allulose for the 0 day of measurement ($p<0.05$). Although D-allulose is highly soluble in water, Ikeda et al. (2011) showed that water binding abilities of single D-allulose molecule was smaller than a single sucrose molecule which means less amount of hydrated water in the sugar solution. Therefore, it was hypothesized that during the preparation of sugar syrup mixture, D-allulose containing formulations might have lost more water due to evaporation, which could have resulted in lower moisture content in the final product. As indicated before, gel formation of SPI required concentrations more than 2% (Puppo & Añón, 1999; Tang et al., 2005), and it was reported that presence of SPI in starch based soft candies resulted in the disruption of starch gel network (Siegwein et al., 2011). Therefore, it was concluded that addition of soy protein isolate affected gelatinization of starch molecules due to reduced H-bonding with water which consequently resulted in more water that were susceptible to evaporation during heat treatment and lower moisture content in final product.

Table 3.3. Moisture Content of starch based soft candies during 28 days of storage

Mc (%)	**Time (days)**				
Name	**0**	**7**	**14**	**21**	**28**
11_S0_R0	$14.94 \pm 0.01^{ab,A}$	$13.01 \pm 2.20^{a,A}$	$13.24 \pm 0.32^{a,A}$	$12.63 \pm 0.62^{ab,A}$	$12.32 \pm 0.67^{a,A}$
11_S0_R10	$15.20 \pm 0.20^{a,A}$	$14.67 \pm 0.03^{a,A}$	$11.82 \pm 0.90^{a,B}$	$12.22 \pm 0.16^{ab,B}$	$11.31 \pm 0.09^{a,B}$
11_S0_R20	$15.44 \pm 1.83^{a,A}$	$13.70 \pm 0.90^{a,A}$	$12.53 \pm 0.29^{a,A}$	$11.97 \pm 0.04^{ab,A}$	$12.52 \pm 0.34^{a,A}$
11_S0_R30	$13.85 \pm 0.07^{abc,AB}$	$14.43 \pm 0.15^{a,A}$	$12.52 \pm 0.04^{a,C}$	$12.48 \pm 0.41^{ab,C}$	$13.15 \pm 0.46^{a,BC}$
9_S2_R0	$14.09 \pm 0.01^{abc,A}$	$14.37 \pm 0.62^{a,A}$	$12.95 \pm 0.90^{a,AB}$	$13.24 \pm 0.50^{a,AB}$	$11.65 \pm 0.63^{a,B}$
9_S2_R10	$12.44 \pm 0.12^{bc,AB}$	$14.86 \pm 1.82^{a,A}$	$12.23 \pm 0.72^{a,AB}$	$11.11 \pm 0.63^{b,B}$	$11.39 \pm 0.18^{a,AB}$
9_S2_R20	$12.41 \pm 0.06^{bc,AB}$	$13.68 \pm 0.49^{a,A}$	$12.16 \pm 0.04^{a,B}$	$11.72 \pm 0.24^{ab,B}$	$12.09 \pm 0.46^{a,B}$
9_S2_R30	$12.05 \pm 0.00^{c,A}$	$12.72 \pm 0.29^{a,A}$	$11.48 \pm 0.06^{a,A}$	$11.59 \pm 0.25^{b,A}$	$12.30 \pm 1.72^{a,A}$

Means within the same column, followed by the different small letters (a–c) are significantly different for each sample ($p < 0.05$)
Means within the same row, followed by the different capital letters (A–C) are significantly different for each storage day ($p < 0.05$)

3.4. Color Measurement

Color of a food is an important parameter to understand the product quality and color changes could be used to quantify the extent of gelatinization, denaturation, Maillard, or caramelization reactions that take place during processing of food. In this study, $L^*a^*b^*$ color model was used to evaluate the color change in the formulations at the 1st day (next day after curing), and results are given in Table 3-4.

Table 3.4. *L, a, b values of starch based confections at the first day of storage*

Name	L*	a*	b*
11_S0_R0	60.52 ± 0.13 ^{a}	0.00 ± 0.00 ^{e}	08.37 ± 0.11 ^{de}
11_S0_R10	60.39 ± 1.72 ^{a}	0.10 ± 0.01 ^{e}	15.63 ± 1.63 ^{c}
11_S0_R20	58.74 ± 1.49 ^{a}	1.67 ± 0.11 ^{d}	19.23 ± 0.93 ^{b}
11_S0_R30	58.29 ± 1.73 ^{a}	5.18 ± 0.25 ^{c}	23.04 ± 1.56 ^{a}
9_S2_R0	48.02 ± 0.40 ^{b}	7.23 ± 0.44 ^{b}	09.17 ± 0.06 ^{d}
9_S2_R10	46.72 ± 0.86 ^{b}	8.58 ± 0.38 ^{a}	09.36 ± 0.16 ^{d}
9_S2_R20	44.07 ± 1.51 ^{b}	5.09 ± 0.17 ^{c}	04.62 ± 0.07 ^{f}
9_S2_R30	46.70 ± 0.02 ^{b}	5.45 ± 0.35 ^{c}	05.27 ± 0.31 ^{ef}

Different letters (a-f) represent significant difference among different formulations ($p < 0.05$)

Color analysis showed that L* value did not change significantly with the substitution with D-allulose ($p>0.05$), but changed with the SPI displacement ($p<0.05$). Besides, remarkable increase in a* (redness) and decrease in b*(yellowness) and L*(lightness) were observed. Visually SPI containing samples were brown in color similar with previous studies (Yuanxia Sun et al., 2008). This was direct consequence of Maillard reactions. Maillard reactions are known to effect the color and flavor significantly (Yuanxia Sun, Hayakawa, Puangmanee, & Izumori, 2006). Presence of SPI in the system provided amine groups which were capable of reacting with the reducing sugars and formed brown pigment associated with browning. It is known that D-allulose is a reducing sugar that shows high reactivity especially in Maillard reactions.

There are considerable researches conducted about accelerated Maillard reaction in the presence of rare sugar D-allulose (O'Charoen, Hayakawa, & Ogawa, 2015; Y. Sun et al., 2004; Zeng, Zhang, Guan, Zhang, & Sun, 2013). The increase in a* and decrease in b* values with the replacement of sucrose with D-allulose in the presence of soy protein isolate were associated with the increased Maillard reaction products formed.

Images of some formulations (11_S0_R0, 11_S0_R30, 9_S2_R0, 9_S2_R30) after cooking were given in appendix part in Figure A.1.

3.5. X-ray Diffraction

According to X-Ray Diffraction results, the narrower and more concentrated peaks are associated with the crystal regions, while the larger and less dense peaks are associated with the amorphous regions (Brown, 1966). X-ray diffraction analysis taken at 0 day and 28 days of storage are shown in Figure 3-1. For all samples, characteristic fractures were observed around 18-24^{o} band. X-ray diffraction pattern of starch granules have been previously reported in some researches pointing the peaks in similar bands (Dankar et al., 2018; Das et al., 2010; Demirkesen et al., 2014; Nagaraj et al., 2017; Ozkoc et al., 2009; Ribotta et al., 2004). For this reason, high density peaks observed in the 18 °-24 ° range were associated with retrogradation of starch. In the case of 30% sucrose (11_S0_R0), the number of narrow peaks was large, whereas in the sample with 30% D-allulose (11_S0_R30), the broad and less number of peaks were observed at the end of 28 days of storage (Figure 3-1). This was associated with the high crystallinity of sucrose and high retrogradation tendency of starch in the presence of sucrose. The diffraction pattern of formulations of 11_S0_R0 and 9_S2_R0 which were prepared by using 30% sucrose showed peaks around 15.6˚, 18.9˚, and 22.2˚ corresponding to B-type structure (Figure 3-1.(b)-(d)). This was indicative of recrystallization of amylopectin during storage (Ozkoc et al., 2009). Similar behavior has been previously reported and peaks corresponding to 15.0-15.8, 17.0-18, 22.0-22.8, and 24.0 were associated with the B-type structure (Demirkesen et al., 2014; Ribotta et al., 2004). In the literature, it was reported that crystallinity of sucrose could be seen as distinct peaks at 11.6˚, 13.6˚, 18.8˚, 19.6˚,and 24.6˚ degrees and might shift left or right if non-homogeneous crystals were present in the system (Leinen & Labuza, 2006; Li, Zhou, & Labuza, 2009). Figure 3-1.(b) and Figure 3-1.(d) showed that after 28 days of storage, distinct peaks were observed at approximately same bands which was associated with crystallization of sucrose molecules and light shifts might have resulted from non-homogeneous crystal sizes. Results showed that D-allulose containing samples generally showed peaks around 20.0˚ and 23.2˚, however there was no report of X-ray diffraction pattern of D-allulose in starch samples in literature. Therefore, it was hypothesized that peaks corresponding these angles could be associated with the D-allulose crystals.

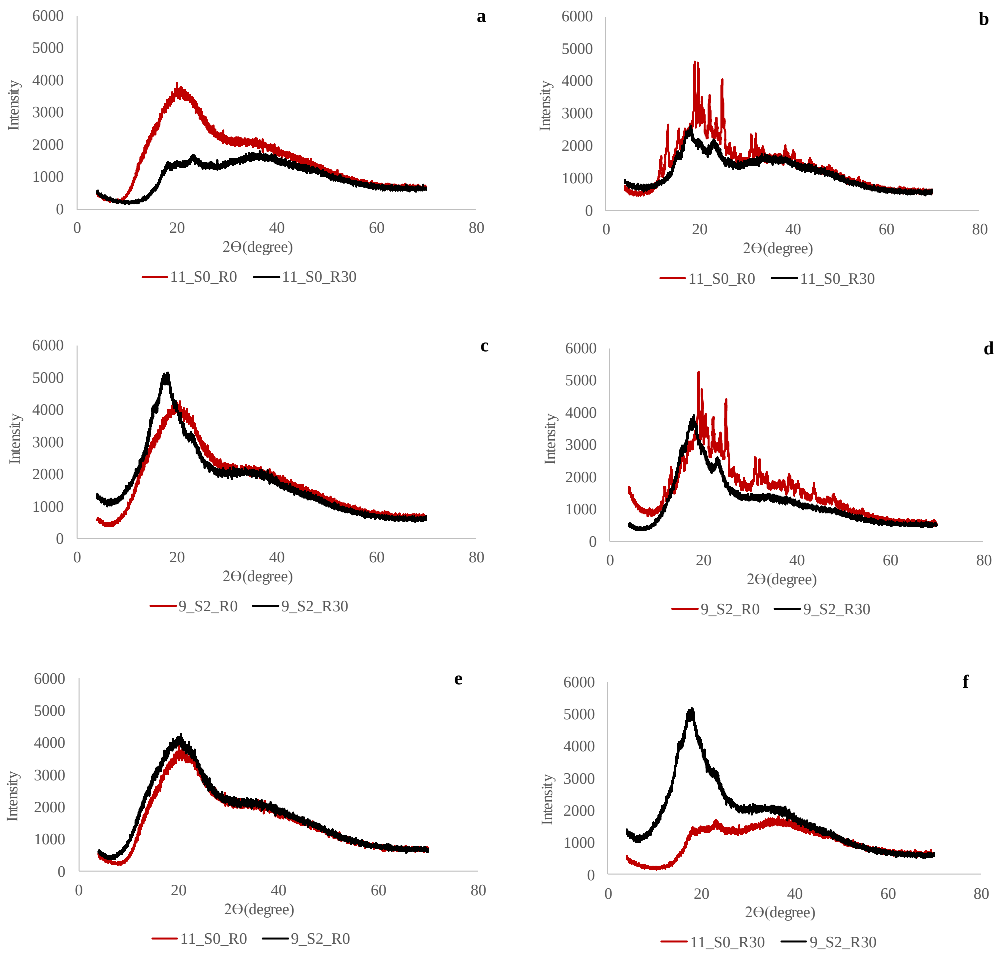


Figure 3.1. *X-Ray Diffraction Pattern of starch based soft candies (a)-(c) at the 0th day of storage (b)-(d) 28th day of storage (e)-(f) change in pattern as a result of SPI addition*

Recrystallization of starch is an important parameter to be controlled and affected by many factors like amylose-amylopectin ratio, water-starch ratio, storage time, temperature and presence of non-starch components. In this regard, sugar has a great impact on starch retrogradation. The formation of crystal, and increase in crystallinity has been related to re-association of amylopectin and amylose fractions during storage (Demirkesen et al., 2014) .

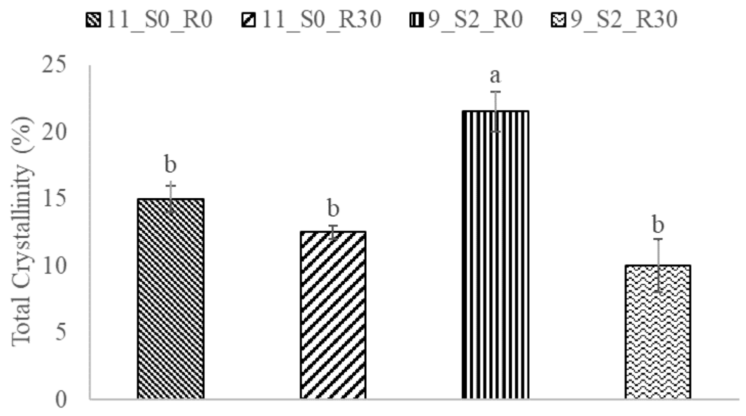


Figure 3.2. *Calculated Total Crystallinity of formulations at the 28th day of storage*

Total crystallinity of samples after 28 days storage was calculated to detect the effect of sugar type and addition of SPI, and results were given in Figure 3-2. According to results, replacement of D-allulose had significant effect on total crystallinity, while addition of SPI did not ($p<0.05$). As illustrated in Figure 3-2., the highest crystallinity was obtained in the gels prepared with SPI and sucrose (9_S2_R0) indicating higher retrogradation of starch molecules in the presence of sucrose. As reported in the research conducted by Wang et al (2016), as hydroxyl groups increased, hydrogen bonding with water molecules increased and this led a decrease in the degree of relative crystallinity. In other words, effect of reducing sugar on the crystallinity of starch gels can be explained by the more potential steric hindrance than sucrose that occurs as a result of the interaction of sugar with water existing on the molecular surface of starch and thereby preventing starch molecules from combining (Guo & Du, 2014). This approach has been compromised with the result of this study, and after 28 days of storage, formulations containing sucrose were found to be more susceptible to crystallization of sugar and retrogradation of starch.

3.6. Differential Scanning Calorimetry

The glass transition temperature is a critical parameter associated with the quality and stability of confection gels. Generally, confection gels are found in amorphous metastable state where both glassy and rubbery state of sugars are present in materials. Glassy state is more hygroscopic and susceptible to moisture uptake from environment whereas rubbery state shows more fluid like behavior (Ergun et al., 2010). While, the higher T_g of a food is associated with easier water uptake during storage, low-T_g gels are more desirable to have soft and elastic structures (Kirtil, Aydogdu, & Oztop, 2016).

T_g values of formulations varied between -35 °C to -41 °C (Table 3-5.), thus all formulations were in the desired rubbery gel structure and far away from glassy state. T_g values of formulations showed decrease or increase depending on their water content which was known to have a plasticizing effect. An interesting finding was that contrary to expectations, at the initial day of measurement, replacement of sucrose with D-allulose did not change T_g significantly for SPI free formulations ($p>0.05$) whereas, significant decrease in T_g was observed as the amount of D-allulose increased for the formulations containing SPI ($p<0.05$). It is known that molecular weight, degree of cross linking of polymers, and concentration of water as a plasticizer affect glass transition temperature (De Graaf et al., 1993)(De Graaf et al., 1993). According to a research conducted by Roos & Karel (1991), higher concentration of hydrophilic amino acids on the protein chain provided enhanced plasticization and resulted in higher glass transition temperatures (De Graaf et al., 1993). From this point of view, it was thought that hydrophobic nature and rapid insolubilization of soy protein upon heating (Jideani, 2011) might have caused a decrease in T_g. Moreover, it was stated that each sugar type found in confectionery products had a different T_g and was highly affected from the amount of water present in the system (Ergun et al., 2010, 2017). Also, water release as a result of increased Maillard reaction between D-allulose and SPI could affect the T_g.

There was only significant change in formulations of 11_S0_R20 and 9_S2_R20 ($p<0.05$) upon 28 days of storage. Therefore, it is important to note that starch based soft candies were capable of preserving their gel matrix upon storage except, approximately 2°C of decrease on glass transition temperature of 20% D-allulose containing samples. This case will be discussed again in the TGA section for clarification.

Table 3.5. *Glass Transition Temperature (Tg) of starch based confections at the 0th and 28th days of storage*

	Tg (°C)	
Time (days)	**0**	**28**
11_S0_R0	-36.68 ± 1.34 ^{ab,A}	-35.19 ± 4.70 ^{a,A}
11_S0_R10	-39.91 ± 0.73 ^{b,A}	-39.39 ± 1.00 ^{a,A}
11_S0_R20	-37.83 ± 0.06 ^{ab,A}	-39.96 ± 0.69 ^{a,B}
11_S0_R30	-39.24 ± 1.40 ^{b,A}	-39.88 ± 0.42 ^{a,A}
9_S2_R0	-35.12 ± 0.14 ^{a,A}	-37.93 ± 2.68 ^{a,A}
9_S2_R10	-39.30 ± 1.16 ^{b,A}	-40.30 ± 0.02 ^{a,a}
9_S2_R20	-38.00 ± 0.37 ^{ab,A}	-40.52 ± 0.16 ^{a,B}
9_S2_R30	-39.07 ± 0.95 ^{b,A}	-39.69 ± 0.43 ^{a,A}

Means within the same column, followed by the different small letters (a–b) are significantly different for each sample ($p < 0.05$)
Means within the same row, followed by the different capital letters (A–B) are significantly different for each storage day ($p< 0.05$)

3.7. Thermogravimetric Analysis

TGA is a widely used method to determine the moisture content and the state of water in a food matrix. Many researches have been conducted on the use of TGA to evaluate the kinetic profile of starch alone and starch containing food systems (Fisher, Ahn-Jarvis, Gu, Weghorst, & Vodovotz, 2014; Stawski, 2008; Tian et al., 2011; Tomassetti et al., 1989; Zhiqiang et al., 1999). In this study TGA analysis was also conducted for different formulations. A typical TGA curve is given in Figure 3-3.

Table 3.6. *Mass loss at first decomposition stage in TGA experiments*

Mass Loss (%)	**Time (days)**	
Name	**0**	**28**
11_S0_R0	11.62 ± 1.20 ^{a,A}	10.27 ± 0.51 ^{ab,A}
11_S0_R10	09.11 ± 0.03 ^{ab,A}	09.31 ± 0.13 ^{ab,A}
11_S0_R20	07.56 ± 0.67 ^{b,A}	08.15 ± 1.25 ^{b,A}
11_S0_R30	09.66 ± 0.97 ^{ab,A}	10.59 ± 0.35 ^{a,A}
9_S2_R0	10.41 ± 0.52 ^{ab,A}	09.66 ± 0.97 ^{ab,A}
9_S2_R10	07.98 ± 0.04 ^{b,B}	09.61 ± 0.10 ^{ab,A}
9_S2_R20	07.64 ± 0.65 ^{b,B}	10.21 ± 0.26 ^{ab,A}
9_S2_R30	07.58 ± 1.32 ^{b,A}	09.95 ± 0.05 ^{ab,A}

Means within the same column, followed by the different small letters (a–b) are significantly different for each sample ($p < 0.05$)
Means within the same row, followed by the different capital letters (A–B) are significantly different for each storage day ($p < 0.05$)

In a thermogravimetric analysis, mass loss (%) up to 150 ˚C can be assumed to be water while mass loss above that temperature is mostly related with decomposition (Fisher et al., 2014). Therefore, mass loss up to 150 ˚C was used to determine the water content of samples. Mass losses at the first decomposition stage varied between 7.58 (%) and 11.62 (%) for fresh samples (t=0), while it was between 8.15 (%) and 10.59 (%) after 28 days of storage (Table 3-6). Results showed that as the amount of D-allulose and SPI increased, mass loss decreased, and consequently water content (%) were found to be lower ($p <0.05$).

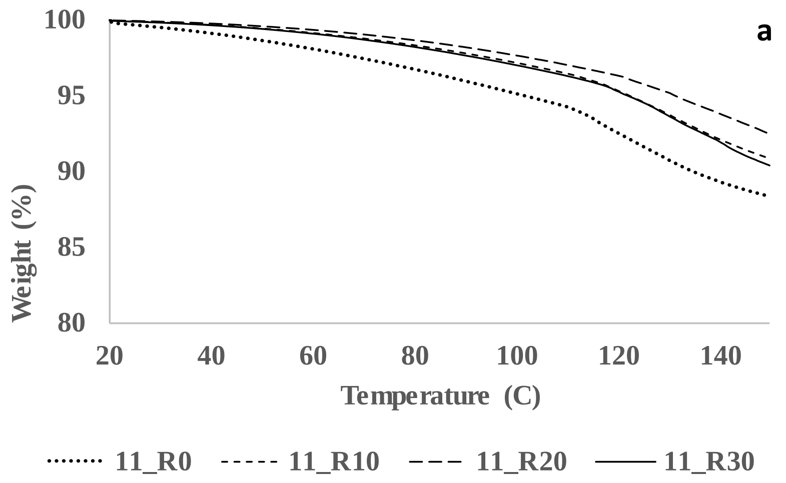
As can be seen from Table 3-6., mass loss (%) showed a significant increase ($p <0.05$) during 28 days of storage for the samples 9_S2_R10 and 9_S2_R20. It is important to note that the sample of 9_S2_R20 experienced mass loss relatively at a higher rate compared to 9_S2_R10. This observation can be supported by the research where it was stated that bound water was found positively correlated with the retrogradation degree of the samples and higher mass loss was observed for retrograded samples than freshly gelatinized starch samples (Tian et al., 2011). Therefore, it was concluded that 9_S2_R20 was more likely to be retrograded. This finding could be also supported by 2 ˚C decrease in T_g temperature of the same sample which was attributed to the higher retrogradation of starch molecules in the presence of D-allulose and SPI.

Table 3.7. *Peak temperatures obtained from derivative weight loss curves of different formulation at initial day of measurement*

Peak Temperature (°C)	**Time (days)**
Name	**0**
11_S0_R0	119.75 ± 5.72 ^{d}
11_S0_R10	130.37 ± 1.53 ^{bc}
11_S0_R20	131.19 ± 0.07 ^{bc}
11_S0_R30	141.07 ± 0.49 ^{a}
9_S2_R0	123.15 ± 3.08 ^{cd}
9_S2_R10	128.89 ± 0.34 ^{bcd}
9_S2_R20	133.48 ± 0.30 ^{ab}
9_S2_R30	133.68 ± 0.71 ^{ab}

Means within the same column, followed by the different small letters (a–d) are significantly different for each sample ($p < 0.05$)

In a TGA analysis in addition to weight loss curves, derivative curves are also utilized. In a previous study, where effect of SPI concentration on starch based confections was discussed, it was stated that derivative weight loss peaks shifted to lower temperatures with the addition of SPI by indicating weaker water association (Siegwein et al., 2011). However, results showed, addition of SPI did not significantly affect the peak temperature ($p>0.05$), whereas accelerated mass loss shifted to a higher temperature as D-allulose amount in the system increased ($p<0.05$) (Figure 3-3.) (Table 3-7.) According to the observed shift in TGA thermogram, water can be attributed as tightly bound to starch molecules in the presence of high amount of D-allulose. By considering the effect of D-allulose on promoting gelatinization (Ikeda et al., 2014), the result was not surprising.



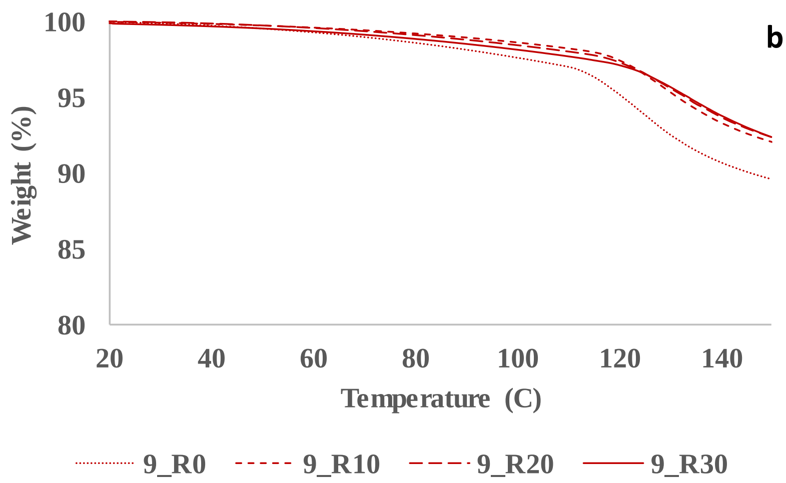


Figure 3.3. TGA thermogram of starch based soft candies (a) replacement of D-allulose for 11% starch and (b) replacement of D-allulose for 9% Starch

3.8. Optical Microscopy

Light microscopy has been used for evaluation of morphology of the samples. Microscopic images could be used for understanding the effect of other ingredients on the gelatinization of starch. When starch is gelatinized, granules become disrupted and dissolved in water, they lose their rigid appearance and start to swell. As stated before , starch's behavior in a matrix is affected by components such as protein or sugar (Koganti, Mitchell, Macnaughtan, Hill, & Foster, 2015; Ratnayake, Wassinger, & Jackson, 2007).

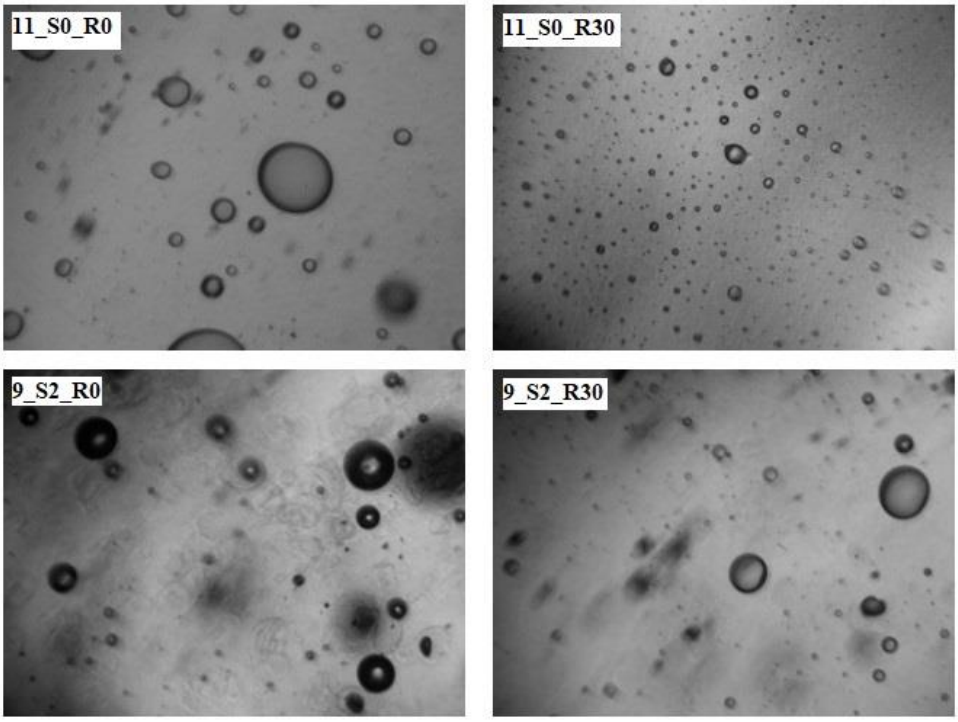


Figure 3.4. Optical microscopic images of starch based soft candies

Figure 3-4 showed that starch granules were completely dissolved for all formulations. Images exhibited circles with a dark out-layer line which can be interpreted as the granules that remained visibly intact. However, it has been stated that starch granules are completely dissolved when they were kept at 95 °C for 23 min (Koganti et al., 2015). When the preparation procedure of the study has been considered (140 °C oil bath, 20-25 min) and not obtaining any gelatinization peak corresponding to partial gelatinization in DSC thermograms, it was hypothesized that circles might be air bubbles entrapped in gel network as result of homogenization or thermal process (boiling). An interesting finding was that air bubbles in the images belonging to 11_S0_R30 were smaller in size and well distributed compared to 11_S0_R0. This might suggest that gel network was more homogeneous in the presence of D-allulose.

3.9. Nuclear Magnetic Resonance Relaxometry

3.9.1. T_1 (Spin-Lattice) Relaxation Time

T_1 which is called as longitudinal relaxation time is defined as the time takes for spins to give energy back received from radiofrequency pulse and is strongly related to mobility of water protons (Ozel, Dag, et al., 2017). Low resolution time domain NMR has been used to characterize mobility of water molecules and interaction of water with lipids, starch or proteins. There are several studies involving NMR relaxometry about systems containing starch, sugar and protein (Botlan & Desbois, 1995; Farhat, Loisel, Saez, Derbyshire, & Blanshard, 1997; Teo & Seow, 1992). In this study, T_1 relaxation times of the starch-based confections with different formulations were measured and the results are shown in Table 3-8. The addition of SPI to formulation showed an increasing trend in T_1 values indicating higher mobility of the water molecules. This phenomenon can be explained by the change in starch gelatinization in the presence of SPI. It is well known that during gelatinization mobility of water protons were reduced because of increase in H-bonding between water and starch molecules which lead to the formation of a gel network (Ozel, Dag, et al., 2017). However, interaction of protein and polysaccharides affects gel structure depending on polymer concentration and compatibility of polymers (Burey et al., 2009). It was reported that SPI formed aggregates rather than forming a gel when amount of SPI was not enough and interrupted the starch gel network (Puppo & Añón, 1999; C. Tang et al., 2005). Therefore, longer T_1 can be associated with disrupted starch gel network upon displacement of SPI.

Table 3.8. *T1 relaxation times of starch based soft candies upon 28 days of storage*

T1 (ms)	**Time (days)**				
Name	**0**	**7**	**14**	**21**	**28**
11_S0_R0	$49,68 \pm 0,75^{b,A}$	$51,02 \pm 1,09^{bc,A}$	$51,07 \pm 0,16^{bc,A}$	$49,46 \pm 0,10^{bc,A}$	$49,57 \pm 0,63^{b,A}$
11_S0_R10	$48,20 \pm 0,72^{bc,A}$	$47,49 \pm 0,00^{d,A}$	$47,92 \pm 0,02^{cde,A}$	$47,05 \pm 0,45^{c,A}$	$47,03 \pm 0,58^{c,A}$
11_S0_R20	$45,90 \pm 0,48^{c,A}$	$44,87 \pm 0,35^{e,A}$	$45,20 \pm 0,49^{e,A}$	$46,88 \pm 1,15^{c,A}$	$46,75 \pm 0,05^{c,A}$
11_S0_R30	$41,30 \pm 0,31^{d,A}$	$41,74 \pm 0,22^{f,A}$	$41,48 \pm 1,02^{f,A}$	$41,99 \pm 1,42^{d,A}$	$41,51 \pm 0,65^{d,A}$
9_S2_R0	$50,95 \pm 0,78^{b,A}$	$51,57 \pm 0,42^{b,A}$	$51,57 \pm 0,21^{b,A}$	$51,88 \pm 0,54^{b,A}$	$51,33 \pm 0,35^{b,A}$
9_S2_R10	$54,88 \pm 0,69^{a,A}$	$56,10 \pm 0,00^{a,A}$	$57,20 \pm 0,84^{a,A}$	$57,30 \pm 0,56^{a,A}$	$55,10 \pm 0,83^{a,A}$
9_S2_R20	$49,79 \pm 1,42^{b,A}$	$48,95 \pm 0,49^{cd,A}$	$50,02 \pm 1,16^{bcd,A}$	$52,44 \pm 1,70^{b,A}$	$49,63 \pm 0,48^{b,A}$
9_S2_R30	$46,34 \pm 0,13^{c,A}$	$46,98 \pm 0,95^{de,A}$	$47,47 \pm 1,51^{de,A}$	$48,49 \pm 0,98^{bc,A}$	$46,09 \pm 0,40^{c,A}$

Means within the same column, followed by the different small letters (a–f) are significantly different for each sample ($p < 0.05$)
Means within the same row, followed by the different capital letters are significantly different for each storage day ($p < 0.05$)

Results showed that, while T_1 was highly affected by D-allulose substitution and showed a decreasing trend as D-allulose concentration increased for each day of measurement during storage ($p<0.05$), significant changes were not observed during storage when each formulation was considered itself ($p>0.05$). As cited before, researches have shown that D-allulose promoted gelatinization by providing greater amount of water for starch gelatinization which made retrogradation slower (Ikeda et al., 2014). Therefore, the reason of obtaining shorter T_1 values with the displacement of sucrose by D-allulose could be formation of better starch gel network and less mobility of water molecules. On the other hand, as cited in moisture content section, D-allulose showed less water binding abilities compared to sucrose (Ikeda et al., 2014). Considering the decrease in moisture content with the displacement by D-allulose on the first day of measurement, it could be stated that, water in the system might have been lost by evaporation during the preparation of the sugar syrup mixture due to less binding of D-allulose with water. Therefore, final products contained less mobile water in the presence of D-allulose and shorter T_1 values were observed.

Spin-lattice relaxation times can be also used to characterize crystal structure of solid phases. According to a research conducted by Botlan et al. (1998) recrystallization of sugar could be detected by T_1 values obtained by time domain NMR (Botlan, Casseron, & Lantier, 1998). Results of the study showed that crystallization resulted in longer T_1 relaxation times. In our case, at the same moisture content, increase in T_1 values could be associated with increased crystalline region. When the data recorded at 7th and 14th days of storage were examined, it was observed that while moisture content of formulation did not change ($p>0.05$), there was significant change on T_1 values ($p<0.05$). It can be clearly seen that while 30% sucrose containing samples (11_S0_R0) had the longest T_1 values among only starch containing samples, 20% sucrose containing samples (9_S2_R10) had the longest T_1 values among 2% soy protein isolate containing samples. Longer T_1 values of starch-sucrose gels were explained by contribution of signal from solid state in the presence of sucrose and less gelatinization of starch molecules (Botlan & Desbois, 1995). Therefore, it can be clearly said that crystalline regions were more dominant at higher sucrose concentrations. Also, the difference in T_1 values of 11_S0_R0 and 11_S0_R30 at the end of 28 days of storage indicated that crystallinity of 11_S0_R0 sample was higher than 11_S0_R30 and this result could also be supported by the X-ray diffraction pattern (Figure 3-1. (a)-(b)). Characteristic properties of crystallization which were sharp and narrow peaks with high intensity were not observed in the diffraction pattern of 11_S0_R30 which indicated the presence of less amount of less crystalline region. In a study conducted by Ikeda et al (2014), it was stated that that in the limited water, more enhanced re-association of starch molecules were obtained in the presence of sucrose than D-allulose during storage (Ikeda et al., 2014). Therefore, it could be concluded that results of this study were consistent with the literature. Moreover, the results were validated by another method that is T_1 NMR relaxometry. When each formulation was examined individually, T_1 values of formulations did not show significant change during 28 days of storage ($p>0.05$). This result was also parallel with glass transition temperature results that did not change as well ($p>0.05$) except for 11_S0_R20 and 9_S2_R20 samples (Table 3-8).

3.9.2. T_2 Relaxation Times

Time required for transverse magnetization to reach the equilibrium value of zero is called as transverse relaxation time, T_2, or spin-spin relaxation time. It provides information about the mobility of hydrogen molecules by attributing to immobile structure in case of short T_2, whereas mobile components in long T_2 (Ozel, Dag, et al., 2017). Food products generally show multi-compartmental proton distribution and transverse magnetization decaying curve could be used to obtain one dimensional distribution, T_2 relaxation spectra, by Laplace transformation. Change in relaxation spectrum could be used in characterization of proton related changes within food systems (Kirtil et al., 2014). In complex food systems at least two relaxation times were identified which belonged to non-exchangeable and exchangeable protons. In the literature there are several studies about the effect of biopolymers on relaxation behavior (Choi, Kim, Hanna, Weller, & Kerr, 2003; Mariette & Lucas, 2005; Tang, Godward, & Hills, 2000). According to the studies, while SPI films showed bi-exponential T_2 behavior (S. G. Choi et al., 2003), multi-exponential behavior was detected for starch molecules (Tang et al., 2000). Figures 3-5. shows representative 1D NMR T_2 relaxation spectra of the starch based soft candies at the 0^{th} day (Figure 3.5 (a-d)) and 28^{th} day (Figure 3-5.(e)-(f)) of storage obtained by Non-Negative-Least-Square (NNLS) analysis and overall results are given in Table 3-5.(b)-(c). Total of three or four distinct peaks with different T_2 (spin-lattice) relaxation times were observed depending on the formulations. Relative Areas (RAs) of the corresponding peaks were also given.

Table 3.9. *T2 (spin-spin) relaxation times of each compartment observed in relaxation spectrum*

	(ms)	Time (days)				
	Name	**0**	**7**	**14**	**21**	**28**
Peak 1	**11_S0_R0**	0.19 a,A	0.20 a,A	0.20 a,A	0.20 a,A	0.20 ab,A
	11_S0_R10	0.21 a,A	0.20 a,A	0.21 a,A	0.20 a,A	0.21 a,A
	11_S0_R20	0.20 a,A	0.21 a,A	0.20 a,A	0.18 a,A	0.19 ab,A
	11_S0_R30	0.19 a,A	0.19 ab,A	0.19 ab,A	0.19 a,A	0.21 a,A
	9_S2_R0	0.18 a,A	0.19 ab,A	0.20 a,A	0.17 a,A	0.19 ab,A
	9_S2_R10	0.14 b,A	0.13 c,A	0.14 b,A	0.14 a,A	0.16 b,A
	9_S2_R20	0.18 a,A	0.17 b,A	0.17 ab,A	0.16 a,A	0.17 ab,A
	9_S2_R30	0.20 a,A	0.20 a,A	0.19 ab,A	0.18 a,A	0.16 b,A
Peak 2	**11_S0_R0**	0.49 bc,A	0.82 ab,A	0.77 ab,A	0.78 ab,A	0.73 bc,A
	11_S0_R10	0.61 bc,B	0.47 b,B	0.53 bc,B	0.87 ab,A	0.91 ab,A
	11_S0_R20	0.97 a,A	1.02 a,A	0.99 a,A	0.74 ab,A	0.77 bc,A
	11_S0_R30	0.65 abc,B	0.77 ab,B	0.77 ab,B	0.63 b,B	1.15 a,A
	9_S2_R0	0.74 ab,A	0.70 ab,A	0.79 ab,A	0.70 ab,A	0.63 c,A
	9_S2_R10	0.38 c,B	0.44 b,B	0.44 c,B	1.10 a,A	0.57 c,B
	9_S2_R20	0.64 abc,A	0.59 ab,A	0.59 bc,A	0.63 b,A	0.55 c,A
	9_S2_R30	0.70 abc,A	0.68 ab,A	0.70 abc,A	0.61 b,A	0.63 c,A
Peak 3	**11_S0_R0**	1.30 d,B	4.25 a,A	4.40 a,A	3.70 a,A	4.40 ab,A
	11_S0_R10	1.35 d,C	1.25 d,C	1.20 e,C	3.70 a,B	4.40 ab,A
	11_S0_R20	4.25 a,A	4.25 a,A	3.85 ab,AB	2.90 abc,B	3.35 bc,AB
	11_S0_R30	1.90 cd,B	2.70 bc,B	2.75 c,B	1.65 d,B	5.00 a,A
	9_S2_R0	3.30 b,A	3.20 ab,A	3.10 bc,A	2.70 abcd,A	3.35 bc,A
	9_S2_R10	1.55 d,B	1.60 cd,B	1.50 de,B	3.40 ab,A	1.75 d,B
	9_S2_R20	2.40 c,A	2.40 bcd,A	2.25 cd,A	2.05 cd,A	2.30 cd,A
	9_S2_R30	2.65 bc,A	2.55 bcd,A	2.65 c,A	2.25 bcd,A	2.60 cd,A
Peak 4	**11_S0_R0**	5.70 a,A	*	*	*	*
	11_S0_R10	5.30 b,A	5.15 a,A	4.55 b,C	*	*
	11_S0_R20	*	*	*	*	*
	11_S0_R30	5.90 a,A	15.00 a,A	16.00 a,A	5.70 a,A	*
	9_S2_R0	*	*	*	*	*
	9_S2_R10	*	*	*	*	*
	9_S2_R20	*	*	*	*	*
	9_S2_R30	*	*	*	*	*

Means within the same column, followed by the different small letters (a–d) are significantly different for each sample ($p < 0.05$)
Means within the same row, followed by the different capital letters(A-C) are significantly different for each storage day ($p < 0.05$)

Table 3.10. *Relative area (RA) of each peak observed in relaxation spectrum for starch based soft candies*

	(%)	Time (days)				
	Name	0	7	14	21	28
RA 1	11_S0_R0	36.21 cd,A	40.11 d,A	45.71 cd,A	48.00 bc,A	37.13 bc,A
	11_S0_R10	37.46 c,AB	31.03 e,B	35.93 e,B	43.83 c,A	36.88 bc,AB
	11_S0_R20	38.03 bc,AB	39.57 d,AB	39.38 de,AB	42.14 c,A	36.49 bc,B
	11_S0_R30	24.24 d,A	25.30 f,A	24.77 f,A	27.08 d,A	25.82 d,A
	9_S2_R0	50.16 ab,B	52.52 b,AB	54.21 ab,AB	55.83 ab,A	40.48 b,C
	9_S2_R10	53.33 a,A	58.54 a,A	59.68 a,A	64.16 a,A	60.96 a,A
	9_S2_R20	47.56 abc,B	46.08 c,B	48.43 bc,B	56.14 ab,A	42.23 b,B
	9_S2_R30	38.73 bc,B	39.88 d,AB	39.73 de,AB	44.57 c,A	32.41 c,C
RA 2	11_S0_R0	14.42 c,B	30.54 ab,A	25.96 ab,AB	23.73 abcd,AB	33.06 abc,A
	11_S0_R10	13.55 c,B	31.03 a,A	13.38 c,B	27.67 abc,A	32.29 bc,A
	11_S0_R20	32.93 a,A	32.58 a,A	32.98 a,A	30.35 ab,B	33.82 ab,A
	11_S0_R30	20.84 bc,A	26.82 ab,A	26.90 ab,A	20.15 cd,A	37.65 a,A
	9_S2_R0	21.71 bc,B	18.24 bc,BC	18.13 bc,BC	15.69 d,C	28.42 c,A
	9_S2_R10	18.27 bc,A	13.57 c,AB	11.66 c,AB	31.97 a,C	10.90 d,BC
	9_S2_R20	26.45 ab,A	28.52 ab,A	26.11 ag,A	22.39 bcd,B	29.74 bc,A
	9_S2_R30	34.40 a,B	33.68 a,B	35.79 a,A	30.96 ab,B	37.41 a,A
RA 3	11_S0_R0	22.86 a,A	29.37 b,A	28.34 b,A	28.27 ab,A	29.82 b,A
	11_S0_R10	21.93 a,C	19.37 d,D	23.52 b,C	28.35 ab,B	30.85 b,A
	11_S0_R20	29.05 a,AB	27.86 bc,B	27.64 b,B	27.52 ab,B	29.70 b,A
	11_S0_R30	28.81 a,A	33.92 a,A	36.19 a,A	32.70 a,A	36.54 a,A
	9_S2_R0	28.13 a,BC	29.25 b,B	27.61 b,C	28.49 ab,BC	31.10 b,A
	9_S2_R10	28.41 a,A	27.90 bc,A	28.64 b,A	3.88 d,B	28.14 b,A
	9_S2_R20	26.00 a,A	25.41 c,A	25.46 b,A	21.48 c,B	28.05 b,A
	9_S2_R30	26.87 a,AB	26.46 bc,AB	24.50 b,B	24.48 cd,B	30.18 b,A
RA 4	11_S0_R0	26.52 a,A	*	*	*	*
	11_S0_R10	27.06 a,A	26.76 a,A	27.17 a,A	*	*
	11_S0_R20	*	*	*	*	*
	11_S0_R30	25.24 a,A	13.97 b,AB	12.15 a,AB	20.08 a,A	*
	9_S2_R0	*	*	*	*	*
	9_S2_R10	*	*	*	*	*
	9_S2_R20	*	*	*	*	*
	9_S2_R30	*	*	*	*	*

Means within the same column, followed by the different small letters (a–d) are significantly different for each sample ($p < 0.05$)
Means within the same row, followed by the different capital letters(A-C) are significantly different for each storage day ($p < 0.05$)

Relaxation spectrum analysis provides detailed information about the contribution of each proton pool. The first peak seen in the spectrum which has the lowest relaxation time can be attributed to solid-solid interaction like interactions between polymers in the system, while final peak which has the highest relaxation time can be treated as water entrapped in gel network. Besides, intermediate peaks can be associated with interaction of polymers in the system with water (Ozel, Dag, et al., 2017). Since the system in this study contains starch and SPI as gelling agents and high amount of sugar, formulations can be attributed as composite gel system and similar approach can be used to analyze the samples. A short echo time (40 us) was used in the experiments thus detection of small relaxation times became possible. Obtained peak and relative areas were given in Table 3-9. and 3-10, respectively. T_2 relaxation times with the highest relative area and relaxation times changing between 0.13-0.21 ms were associated with solid-solid interactions. It can be attributed to sugar-starch, sugar-protein, sugar-sugar or protein-starch interactions (Aroulmoji, Mathlouthi, Feruglio, Murano, & Grassi, 2011; Kirtil et al., 2014). Although, relaxation time (T_2) of the first peak did not change significantly ($p>0.05$) during 28 days of storage, the relative areas of first peak varied depending on the day of measurement ($p<0.05$). Results showed that shortest T_2 relaxation time and highest relative area RA_1 were observed for the sample 9_S2_R10. Among all formulations, shortest T_2 relaxation time of peak 1 and highest relative area RA_1 were observed for the sample 9_S2_R10 which indicated higher solid-solid interaction. It is not surprising to obtain higher solid-solid interaction in such a complex system containing 3 types of sugar component (glucose syrup, sucrose, D-allulose) and 2 types of gelling agents due to high competitive environment for water. Also, as mentioned before, presence of soy protein in the system could have disrupted the gel structure of starch and this case might have resulted in higher solid-solid interactions. It was reported that starch protons showed solid like behavior when it was not gelatinized and more liquid like behavior when fully gelatinized (François Mariette, 2009). Therefore, it was hypothesized that starch molecules showed more solid like behavior and exhibited high relative area in T_2 relaxation spectra in the presence of SPI. The reason of not observing such a result in 9_S2_R20 and higher D-allulose concentration might be explained by the gelatinization promoting behavior of D-allulose (Ikeda et al., 2014) which led starch molecules to exhibit liquid a like behavior and this case reflected as a second peak in the relaxation spectrum. Also, higher solid-solid interaction (Figure 3-5.(a)) detected in 11_S0_R0 compared to 11_S0_R30 can be explained with same phenomena.

Presence of intermediate peaks indicated that polymer-water interactions can be starch-water, sugar-water or soy protein-water for this study. As shown in Figure 3-5 and Table 3-10, relative area of the intermediate peaks increased with D-allulose substitution. Also relaxation spectra of D-allulose containing formulations shifted to right (Figure 3-5.(a)) indicating longer relaxation times. It was reported that sucrose had slower relaxation rates (shorter relaxation times) compared to D-glucose and D-fructose because of its higher molecular weight and more exchangeable -OH groups which could affect the contribution of the exchange. It is important to mention here that chemical exchange with -OH groups of the sugar can also contribute to the relaxation behavior as water protons (Aroulmoji, Mathlouthi, Feruglio, Murano, & Grassi, 2011). Hence, longer relaxation times in the presence of D-allulose could be explained by enhanced polymer-water and sugar-water interaction. Figure 3-5(b)-(d) showed that, addition of soy protein resulted in disappearance of one of the peaks. To see this clearly, formulations of 11_S0_R30 and 9_S2_R30 can be examined. While 4 peaks were observed in 11_S0_R30 sample, 3 peaks were observed in 9_S2_R30 and the disappearance of one of the peaks that was associated with starch-water interaction with the partial displacement of starch by SPI could be explained by sugar-protein interaction, in other words with Maillard reaction. With the displacement by SPI, reducing sugars present in the system could participate in Maillard reaction which could result in new interactions between the molecules and consequently creation of new proton pools in the system. Because of Maillard reaction, polymer-water interaction became more complex and thereby resulted in merging of the proton pools. Also, it is not surprising to observe the disappearance of starch-water interaction peak following the displacement of SPI. As considered before soy protein was found to have a disruptive effect on the on starch-water network. Figure 3-5.(d) shows that D-allulose exhibited a more distinct proton population with a higher relative area ($p<0.05$). It can be associated with elevated Maillard reaction in the presence of D-allulose (O'Charoen et al., 2015; Y. Sun et al., 2004; Yuanxia Sun et al., 2006). The final peak which had the longest relaxation time was attributed to the mobile water entrapped in gel matrix. While relaxation times of different formulations did not show any noticeable change during 28 days of storage ($p>0.05$) (Table 3-9.), relative areas of the proton populations changed ($p<0.05$). Results showed that sucrose containing formulation relaxed faster than D-allulose containing sample indicating less polymer-water interaction and less mobile water entrapped in the gel network. It was proposed that less polymer water interaction could be followed by faster re-association of starch molecules upon storage in the presence of sucrose compared to D-allulose. As a result of retrogradation and syneresis, mobile water in the gel network was lost more in the samples formulated with sucrose during 28 days of storage. Therefore, it is worth to hypothesize that D-allulose prevented retrogradation and enabled to hold more water in the gel network compared to sucrose

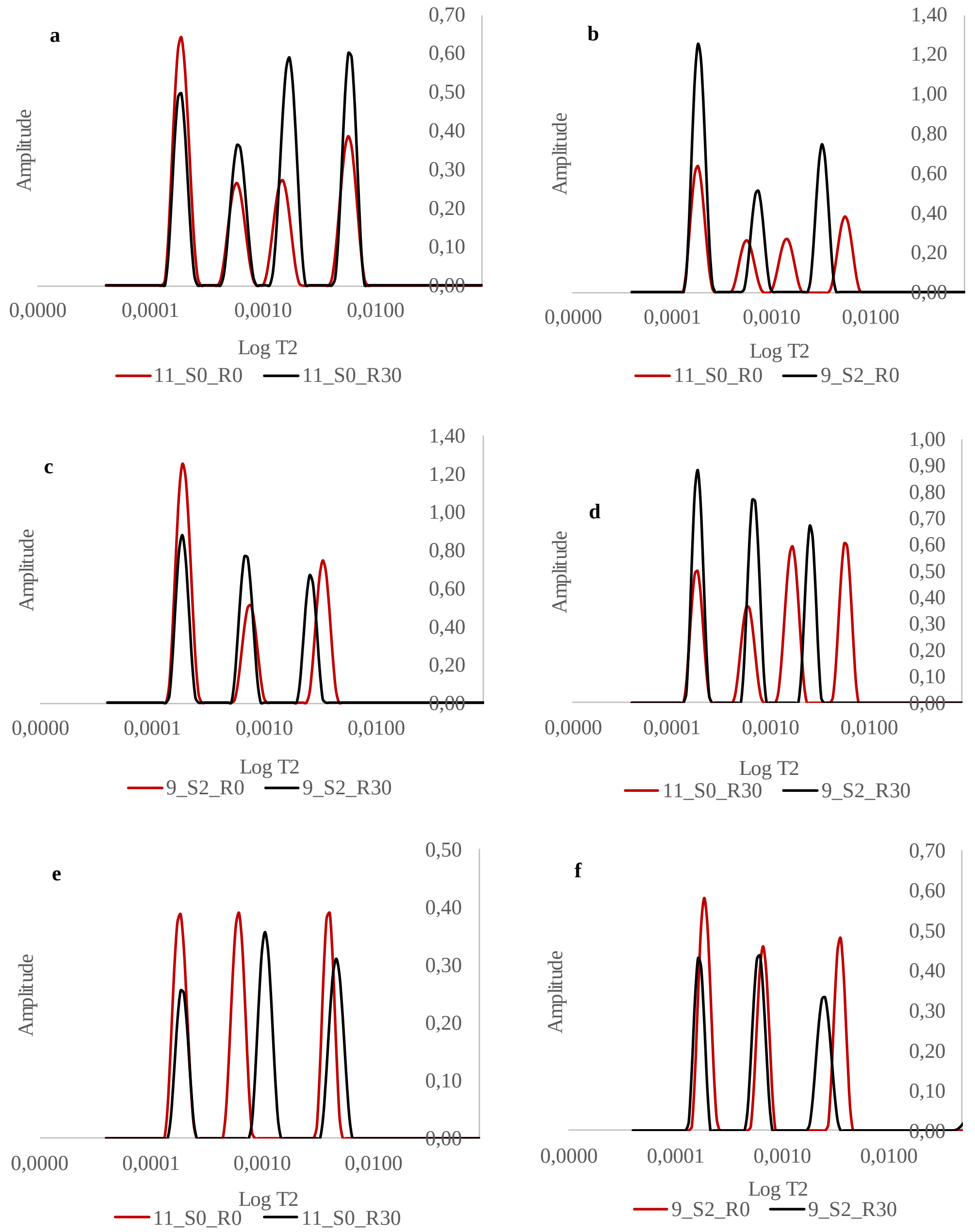


Figure 3.5. Representative T2 Relaxation Spectrum of starch based soft candies at the 0th day of storage (a)-(c) as a result of D-allulose replacement (b)-(d) as a result of SPI replacement (e)-(f) at the 28th days of storage as a result of D-allulose replacement

3.10. Fast Field Cycling Relaxometry

Confectionery systems generally consist of considerable water content as plasticizer and different biopolymers as structural components. It is known that product stability is highly affected by the exchange between bulk and entrapped water molecules during processing and further storage. Therefore, determination of dynamics in hydration layers is important to characterize structure and molecular order of matrix (Satheesh, Galkin, Sykora, & Ferrante, 2001). Fast field cycling NMR is one of the prominent techniques that stands out in that point due to its sensitivity of translational motion of water molecules and dynamics of water molecule with its vicinity (Godefroy et al., 2003).

As mentioned in introduction, the FFC technique based on measurement of spin-lattice relaxation rate, $1/T_{1,}$ along a wider range of frequencies than standard NMR relaxometry by providing enhance characterization of molecular dynamics of variety of substances (Kimmich & Anoardo, 2004; Neudert et al., 2018). In order to characterize the effect of sugar type and addition of a new macromolecules to system, ^{1}H relaxation dispersion data of and spin-lattice relaxation time curves of 4 formulations (11_S0_R0, 11_S0_R30, 9_S2_R0, 9_S2_R30) were recorded at a frequency range of 4 kHz – 30 MHz. It is stated that small differences in structure and composition for polymer containing system can be discriminated easily for lower fields (lower than 10 MHz) compare to higher fields (Pasin & Ferrante, 2017). Also, considering relaxation behavior of formulations did not change for frequencies lower than 0.01 MHz and higher than 10 MHz, experimental data were represented for that frequency range and given in Figure 3-6 & Figure 3-7.

Differences in molecular mobility which was a consequence of composition resulted in different T_1 dispersion and rate (R_1) profiles especially at lower frequency than 1 MHz as it has been discussed in previous researches (Pasin & Ferrante, 2017). It was stated that for food systems especially for gel systems, relaxation of water resulted from relaxation of bulk or entrapped water rather than water at hydration level as water molecules at hydration level was less mobile than bulk water (Chávez & Halle, 2006). Therefore, it can be concluded that situation of bulk water should be examined to interpret water relaxation dispersion curves.

It can be clearly seen that T_1 relaxation for only starch and D-Allulose containing confectionery (11_R30) were longer than the other three formulations. Longer spin-lattice relaxation time referred longer correlation times which indicated motions of different molecular chain organizations and further intermolecular interaction (Sebastião et al., 2016). Also, it is mentioned that polymer network of hydrogels can be classified as homogeneous or heterogeneous depending on polymer water interaction. In homogeneous gels, water is surrounded by polymer chains which result in one highly mobile phase, while in heterogenous hydrogels two or more phase are created where restricted solute movements observed (Bellich, Borgogna, Cok, & Cesàro, 2011). Considering the relation between higher water content and longer T_1, it can be concluded that 11_S0_R30 formulations have a more homogeneous structure and therefore more mobility than other formulations indicating better gel network.

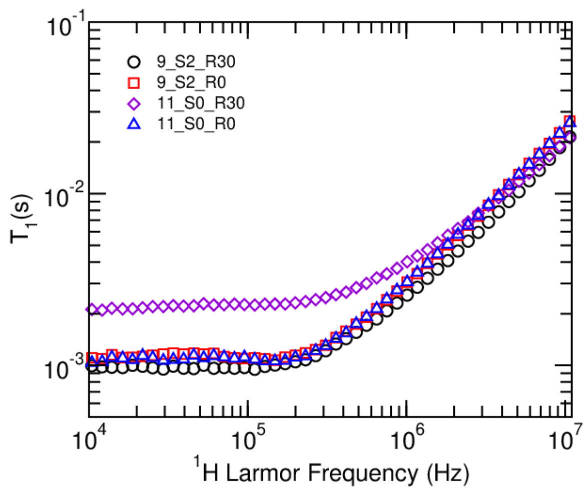


Figure 3.6. ^{1}H spin-lattice relaxation time curves of starch based confectionery products

According to NMRD profile, replacement of SPI did not affect dispersion profile when sucrose is used as sugar type (compare 11_S0_R0 and 9_S2_R0), but rate of dispersion increases when D-allulose is used in formulations (compare 11_S0_R30 and 9_S2_R30). Increase in rate of dispersion resulted from increase in solid-solid interaction due to quick relaxation of solids in the systems. This can be explained by the fact that the protein binding with D-allulose increases the solid-solid interaction in the system compared to sucrose containing formulations.

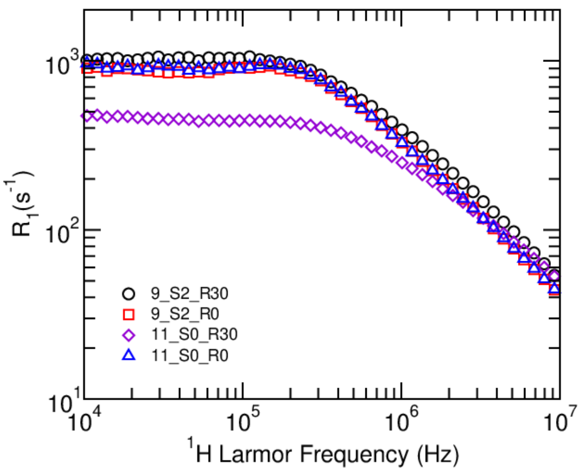


Figure 3.7. ^{1}H relaxation dispersion data of starch based confectionery products

Moreover, NMRD curves also showed that addition of D-allulose to the formulations resulted in slower relaxation, pointing out a better gel structure as discussed previously with the T_1 dispersion curves.

Besides obtaining experimental data, representing the data with a proper model is essential for the characterization of system. As mentioned before, Renormalized Rouse Model are generally used when polymer chain dynamics is not dominated because of neighboring chains confinement (Kimmich & Anoardo, 2004). Presence of more than one gelling agent and high sugar concentration create competition for water and may restrict chain dynamics in confectionery products. In this regard, it can be said that Renormalized Rouse Model could be useful to model data and understand molecular dynamics in different frequency ranges. Representative models for different formulations and model constants were given in Figure 3-8 and Table 3-1, respectively.

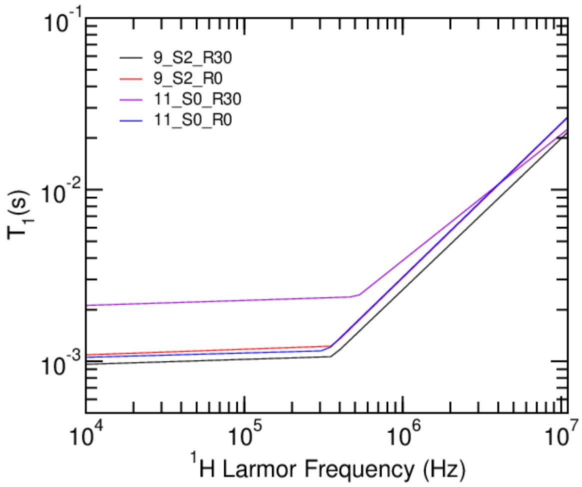


Figure 3.8. .Renormalized Rouse Model for **^{1}**H spin-lattice relaxation time curves of starch based confectionery products

When table is examined, f represents the frequency where f0 and f1 are the highest and lowest characteristic frequency in Hz respectively. P values explain the exponents at different frequency regimes where p0, p1 and p3 denote exponent of high, intermediate and low frequency regimes, respectively.

Table 3.11. *Renormalized Rouse model constants*

Formulation	**a1**	**fo**	**f1**	**p0**	**p1**	**p2**
11_S30	7.67E+07	3.32E+05	1	-8.96E-01	-2.74E-02	-1.05E-03
11_R30	7.08E+06	5.95E+05	1	-7.39E-01	-5.50E-02	-1.05E-03
9_S30	7.30E+07	3.36E+05	1	-8.93E-01	-1.86E-02	-1.05E-03
9_R30	8.73E+07	3.77E+05	1	-8.93E-01	-3.51E-02	-1.05E-03

Relaxation models are generally described by Fourier transform of function decaying with time with a specific time constant τ, correlation time. Relaxation model for renormalized Rouse model can be described as follow;

$$\tau_1(f) = A \begin{cases} f^{p_1}, & f \geq f_M \\ {f_M}^{p_1 - p_2} f^{p_2}, & f_m \leq f \leq f_M \\ {f_M}^{p_1 - p_2} {f_m}^{p_3 - p_2} f^{p_2}, & f \leq f_m \end{cases}$$

CHAPTER 4

CONCLUSION

This study was built on the design of a confectionery product containing starch and SPI as gelling agents and examined the role of D-allulose in a biopolymer based composite gel matrix.

Several physical measurements were conducted and advanced characterization techniques were utilized to understand the interactions in the gel matrix.

Both water activity and moisture content of the formulations significantly decreased by D-allulose substitution. TGA thermograms revealed that, accelerated mass loss shifted to a higher temperature with the use of D-allulose which was associated with tightly bound water molecules to starch, indicating better gel network. This constituted that presence of D-allulose in the formulation have contributed gel formation. This hypothesis have been proved with the enhanced textural properties of formulations with the use of D-allulose showing smaller changes upon storage by providing better gel network and slower retrogradation. There was no reported research of X-ray diffraction pattern of D-allulose in starch samples in the literature. The striking outcome of X-ray results at this point was that D-allulose containing samples generally revealed peaks around 20.0˚ and 23.2˚. Therefore, it was hypothesized that peaks corresponding these angles could be associated with the D-allulose crystals. T_2 relaxation spectra showed that four distinct peaks observed in only starch containing formulations reduced to three peaks with the addition of SPI. This was explained by more complex polymer water interaction through Maillard reaction thereby resulted in merging of the proton pools. Time domain NMR relaxometry and FFC measurement were found to be useful for characterization of confectionery products for both initial and during storage. Signal obtained from samples showed different trends with respect to the the sugar type and additional polymer due to change in matrix.

To conclude, use of D-allulose resulted in better gel network and less retrogradation during storage. By considering low calorie intake and gelatinization promoting behavior of D-allulose, rare sugar can be good substitute for other sugar types used in industry. This study showed that TD-NMR and FFC measurement were also simple and accurate methods for examination of water distribution of complex composite gel systems.

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APPENDICES

ANOVA TABLES

A. Analysis of variance for effect of change formulation

Table A. 1. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on (1) water activity (aw); (2) moisture content (MC %); (3) T1; (4) T2 using adjusted SS for Tests for day 0*

(1) General Linear Model: Water Activity (aw) versus Starch, Rare Sugar

```
Factor      Type   Levels  Values
Starch      fixed       2  9, 11
Rare Sugar  fixed       4  0, 10, 20, 30

Analysis of Variance for aw, using Adjusted SS for Tests

Source             DF     Seq SS     Adj SS     Adj MS       F      P
Starch              1  0.0156313  0.0156313  0.0156313  532.12  0.000
Rare Sugar          3  0.0216743  0.0216743  0.0072248  245.94  0.000
Starch*Rare Sugar   3  0.0021123  0.0021123  0.0007041   23.97  0.000
Error               8  0.0002350  0.0002350  0.0000294
Total              15  0.0396528

S = 0.00541993   R-Sq = 99.41%   R-Sq(adj) = 98.89%

Grouping Information Using Tukey Method and 95.0% Confidence

Starch  N  Mean  Grouping
11      8   0.6  A
 9      8   0.6    B

Means that do not share a letter are significantly different.
Grouping Information Using Tukey Method and 95.0% Confidence

Rare
Sugar  N  Mean  Grouping
 0     4   0.7  A
10     4   0.6    B
20     4   0.6      C
30     4   0.6        D

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

        Rare
Starch  Sugar  N  Mean  Grouping
11       0     2   0.7  A
 9       0     2   0.7    B
11      10     2   0.7    B
11      20     2   0.6      C
```

```
11      30     2   0.6      C
 9      10     2   0.6        D
 9      20     2   0.6        D
 9      30     2   0.5          E

Means that do not share a letter are significantly different.
```

(2) General Linear Model: Moisture Content (MC %) versus Starch, Rare Sugar

```
Factor      Type   Levels  Values
Starch      fixed       2  9, 11
Rare Sugar  fixed       4  0, 10, 20, 30

Analysis of Variance for MC %, using Adjusted SS for Tests
Source             DF   Seq SS   Adj SS   Adj MS      F      P
Starch              1  17.2673  17.2673  17.2673  39.99  0.000
Rare Sugar          3   4.5783   4.5783   1.5261   3.53  0.068
Starch*Rare Sugar   3   3.0593   3.0593   1.0198   2.36  0.147
Error               8   3.4547   3.4547   0.4318
Total              15  28.3595


S = 0.657145   R-Sq = 87.82%   R-Sq(adj) = 77.16%

Grouping Information Using Tukey Method and 95.0% Confidence

Starch  N  Mean  Grouping
11      8  14.9  A
 9      8  12.8    B

Means that do not share a letter are significantly different.
Grouping Information Using Tukey Method and 95.0% Confidence

Rare
Sugar  N  Mean  Grouping
 0     4  14.5  A
20     4  13.9  A B
10     4  13.8  A B
30     4  13.0    B

Means that do not share a letter are significantly different.
Grouping Information Using Tukey Method and 95.0% Confidence

        Rare
Starch  Sugar  N  Mean  Grouping
11      20     2  15.4  A
11      10     2  15.2  A
11       0     2  14.9  A B
 9       0     2  14.1  A B C
11      30     2  13.8  A B C
 9      10     2  12.4    B C
 9      20     2  12.4    B C
 9      30     2  12.2      C

Means that do not share a letter are significantly different.
```

(3) General Linear Model: T_1 versus Starch, Rare Sugar

```
Factor      Type   Levels  Values
Starch      fixed       2  9, 11
Rare Sugar  fixed       4  0, 10, 20, 30


Analysis of Variance for T1, using Adjusted SS for Tests

Source             DF   Seq SS   Adj SS  Adj MS       F      P
Starch              1   70.707   70.707  70.707  124.74  0.000
Rare Sugar          3  139.141  139.141  46.380   81.82  0.000
Starch*Rare Sugar   3   15.597   15.597   5.199    9.17  0.006
Error               8    4.535    4.535   0.567
Total              15  229.980


S = 0.752885   R-Sq = 98.03%   R-Sq(adj) = 96.30%


Grouping Information Using Tukey Method and 95.0% Confidence

Starch  N  Mean  Grouping
 9      8  50.5  A
11      8  46.3    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

Rare
Sugar  N  Mean  Grouping
   10     4  51.5  A
    0     4  50.3  A
   20     4  47.9    B
   30     4  43.8      C

   Means that do not share a letter are significantly different.


   Grouping Information Using Tukey Method and 95.0% Confidence

           Rare
   Starch  Sugar  N  Mean  Grouping
    9      10     2  54.9  A
    9       0     2  50.9    B
    9      20     2  49.8    B
   11       0     2  49.7    B
   11      10     2  48.2    B C
    9      30     2  46.3      C
   11      20     2  46.0      C
   11      30     2  41.3        D

   Means that do not share a letter are significantly different.
```

(4) General Linear Model: T_2 versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for T2, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	2.96270	2.96270	2.96270	337.33	0.000
Rare Sugar	3	0.36604	0.36604	0.12201	13.89	0.002
Starch*Rare Sugar	3	0.30764	0.30764	0.10255	11.68	0.003
Error	8	0.07026	0.07026	0.00878		
Total	15	3.70664				

S = 0.0937160   R-Sq = 98.10%   R-Sq(adj) = 96.45%

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	N	Mean	Grouping
11	8	2.0	A
9	8	1.1	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Rare Sugar	N	Mean	Grouping
0	4	1.7	A
30	4	1.6	A
20	4	1.4	B
10	4	1.4	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	Rare Sugar	N	Mean	Grouping
11	30	2	2.2	A
11	0	2	2.0	A B
11	10	2	2.0	A B
11	20	2	1.8	B C
9	0	2	1.5	C
9	30	2	1.1	D
9	20	2	1.0	D
9	10	2	0.8	D

Means that do not share a letter are significantly different.

Table A. 2. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on (1) water activity (aw); (2) moisture content (MC %); (3) T1; (4) T2 using adjusted SS for Tests for day 7*

(1) General Linear Model: Water activity (aw) versus Starch, Rare Sugar

```
Factor      Type   Levels  Values
Starch      fixed       2  9, 11
Rare Sugar  fixed       4  0, 10, 20, 30


Analysis of Variance for aw_day 7, using Adjusted SS for Tests

Source             DF     Seq SS     Adj SS     Adj MS       F      P
Starch              1  0.0065894  0.0065894  0.0065894  177.04  0.000
Rare Sugar          3  0.0176537  0.0176537  0.0058846  158.10  0.000
Starch*Rare Sugar   3  0.0005389  0.0005389  0.0001796    4.83  0.033
Error               8  0.0002978  0.0002978  0.0000372
Total              15  0.0250797


S = 0.00610087   R-Sq = 98.81%   R-Sq(adj) = 97.77%


Grouping Information Using Tukey Method and 95.0% Confidence

Starch  N  Mean  Grouping
11      8   0.6  A
 9      8   0.6    B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Rare
Sugar  N  Mean  Grouping
 0     4   0.6  A
10     4   0.6    B
20     4   0.6    B
30     4   0.6      C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

        Rare
Starch  Sugar  N  Mean  Grouping
11       0     2   0.7  A
 9       0     2   0.6    B
11      10     2   0.6    B C
11      20     2   0.6      C D
11      30     2   0.6        D
 9      20     2   0.5          E
 9      10     2   0.5          E
 9      30     2   0.5          E

Means that do not share a letter are significantly different.
```

(2) General Linear Model: Moisture Content (MC %) versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for MC_day 7, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.007	0.007	0.007	0.01	0.941
Rare Sugar	3	3.756	3.756	1.252	1.03	0.428
Starch*Rare Sugar	3	4.758	4.758	1.586	1.31	0.337
Error	8	9.690	9.690	1.211		
Total	15	18.211				

S = 1.10059   R-Sq = 46.79%   R-Sq(adj) = 0.23%

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	N	Mean	Grouping
11	8	14.0	A
9	8	13.9	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Rare Sugar	N	Mean	Grouping
10	4	14.8	A
0	4	13.7	A
20	4	13.7	A
30	4	13.6	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	Rare Sugar	N	Mean	Grouping
9	10	2	14.9	A
11	10	2	14.7	A
11	30	2	14.4	A
9	0	2	14.4	A
11	20	2	13.7	A
9	20	2	13.7	A
11	0	2	13.0	A
9	30	2	12.7	A

Means that do not share a letter are significantly different.

(3) General Linear Model: T1 versus Starch, Rare Sugar

```
Factor      Type   Levels  Values
Starch      fixed       2  9, 11
Rare Sugar  fixed       4  0, 10, 20, 30


Analysis of Variance for T1_day 7, using Adjusted SS for Tests

Source             DF   Seq SS   Adj SS  Adj MS       F      P
Starch              1   85.438   85.438  85.438  254.57  0.000
Rare Sugar          3  153.106  153.106  51.035  152.06  0.000
Starch*Rare Sugar   3   33.200   33.200  11.067   32.97  0.000
Error               8    2.685    2.685   0.336
Total              15  274.428


S = 0.579325   R-Sq = 99.02%   R-Sq(adj) = 98.17%


Grouping Information Using Tukey Method and 95.0% Confidence

Starch  N  Mean  Grouping
 9      8  50.9  A
11      8  46.3    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

Rare
Sugar  N  Mean  Grouping
10     4  51.8  A
 0     4  51.3  A
20     4  46.9    B
30     4  44.4      C

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

        Rare
Starch  Sugar  N  Mean  Grouping
 9      10     2  56.1  A
 9       0     2  51.6    B
11       0     2  51.0    B C
 9      20     2  49.0      C D
11      10     2  47.5        D
 9      30     2  47.0        D E
11      20     2  44.9          E
11      30     2  41.7            F

Means that do not share a letter are significantly different.
```

(4) General Linear Model: T2_day 7 versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for T2_day 7, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	6.3353	6.3353	6.3353	1413.34	0.000
Rare Sugar	3	0.7830	0.7830	0.2610	58.23	0.000
Starch*Rare Sugar	3	0.4057	0.4057	0.1352	30.17	0.000
Error	8	0.0359	0.0359	0.0045		
Total	15	7.5599				

S = 0.0669515   R-Sq = 99.53%   R-Sq(adj) = 99.11%

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	N	Mean	Grouping
11	8	2.4	A
9	8	1.1	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Rare Sugar	N	Mean	Grouping
0	4	2.0	A
30	4	1.9	A
10	4	1.6	B
20	4	1.5	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	Rare Sugar	N	Mean	Grouping
11	30	2	2.7	A
11	0	2	2.5	A
11	10	2	2.4	A
11	20	2	1.9	B
9	0	2	1.5	C
9	30	2	1.2	D
9	20	2	1.0	D
9	10	2	0.8	E

Means that do not share a letter are significantly different.

Table A. 3. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on (1) water activity (aw); (2) moisture content (MC %); (3) T1; (4) T2 using adjusted SS for tests for day 14*

(1) General Linear Model: Water acitivity versus Starch, Rare Sugar

```
Factor      Type   Levels  Values
Starch      fixed       2  9, 11
Rare Sugar  fixed       4  0, 10, 20, 30


Analysis of Variance for aw_day 14, using Adjusted SS for Tests

Source             DF     Seq SS     Adj SS     Adj MS      F      P
Starch              1  0.0111725  0.0111725  0.0111725  63.09  0.000
Rare Sugar          3  0.0159640  0.0159640  0.0053213  30.05  0.000
Starch*Rare Sugar   3  0.0023407  0.0023407  0.0007802   4.41  0.042
Error               8  0.0014167  0.0014167  0.0001771
Total              15  0.0308939


S = 0.0133074   R-Sq = 95.41%   R-Sq(adj) = 91.40%


Grouping Information Using Tukey Method and 95.0% Confidence

Starch  N  Mean  Grouping
11      8   0.6  A
 9      8   0.6    B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Rare
Sugar  N  Mean  Grouping
 0     4   0.6  A
20     4   0.6    B
10     4   0.6    B
30     4   0.5      C

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

        Rare
Starch  Sugar  N  Mean  Grouping
11       0     2   0.6  A
11      10     2   0.6  A
 9       0     2   0.6  A B
11      20     2   0.6  A B C
11      30     2   0.6    B C D
 9      20     2   0.6      C D E
 9      10     2   0.5        D E
 9      30     2   0.5          E

Means that do not share a letter are significantly different.
```

(2) General Linear Model: Moisture Content (MC%) versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for MC_day 14, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.4158	0.4158	0.4158	1.44	0.265
Rare Sugar	3	3.1118	3.1118	1.0373	3.58	0.066
Starch*Rare Sugar	3	1.0601	1.0601	0.3534	1.22	0.364
Error	8	2.3177	2.3177	0.2897		
Total	15	6.9053				

S = 0.538245   R-Sq = 66.44%   R-Sq(adj) = 37.07%

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	N	Mean	Grouping
11	8	12.5	A
9	8	12.2	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Rare Sugar	N	Mean	Grouping
0	4	13.1	A
20	4	12.3	A
10	4	12.0	A
30	4	12.0	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	Rare Sugar	N	Mean	Grouping
11	0	2	13.2	A
9	0	2	13.0	A
11	20	2	12.5	A
11	30	2	12.5	A
9	10	2	12.2	A
9	20	2	12.2	A
11	10	2	11.8	A
9	30	2	11.5	A

Means that do not share a letter are significantly different.

(3) General Linear Model: T1 versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for T1_day 14, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	106.136	106.136	106.136	149.10	0.000
Rare Sugar	3	161.829	161.829	53.943	75.78	0.000
Starch*Rare Sugar	3	39.617	39.617	13.206	18.55	0.001
Error	8	5.695	5.695	0.712		
Total	15	313.278				

S = 0.843718   R-Sq = 98.18%   R-Sq(adj) = 96.59%

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	N	Mean	Grouping
9	8	51.6	A
11	8	46.4	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Rare Sugar	N	Mean	Grouping
10	4	52.6	A
0	4	51.3	A
20	4	47.6	B
30	4	44.5	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	Rare Sugar	N	Mean	Grouping
9	10	2	57.2	A
9	0	2	51.6	B
11	0	2	51.1	B C
9	20	2	50.0	B C D
11	10	2	47.9	C D E
9	30	2	47.5	D E
11	20	2	45.2	E
11	30	2	41.5	F

Means that do not share a letter are significantly different.

(4) General Linear Model: T2 versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for T2_day 14, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	2.25300	2.25300	2.25300	244.18	0.000
Rare Sugar	3	0.40171	0.40171	0.13390	14.51	0.001
Starch*Rare Sugar	3	0.26717	0.26717	0.08906	9.65	0.005
Error	8	0.07381	0.07381	0.00923		
Total	15	2.99569				

S = 0.0960553   R-Sq = 97.54%   R-Sq(adj) = 95.38%

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	N	Mean	Grouping
11	8	1.8	A
9	8	1.0	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Rare Sugar	N	Mean	Grouping
0	4	1.6	A
30	4	1.5	A
20	4	1.2	B
10	4	1.2	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	Rare Sugar	N	Mean	Grouping
11	30	2	2.0	A
11	0	2	1.8	A B
11	10	2	1.7	A B
11	20	2	1.6	B
9	0	2	1.4	B
9	30	2	1.0	C
9	20	2	0.9	C
9	10	2	0.8	C

Means that do not share a letter are significantly different.

Table A. 4. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on (1) water activity (aw); (2) moisture content (MC %); (3) T1; (4) T2 using adjusted SS for Tests for day 21*

(1) General Linear Model: Water activity versus Starch, Rare Sugar

```
Factor      Type   Levels  Values
Starch      fixed       2  9, 11
Rare Sugar  fixed       4  0, 10, 20, 30


Analysis of Variance for aw_day 21, using Adjusted SS for Tests

Source             DF     Seq SS     Adj SS     Adj MS      F      P
Starch              1  0.0095355  0.0095355  0.0095355  51.32  0.000
Rare Sugar          3  0.0254231  0.0254231  0.0084744  45.61  0.000
Starch*Rare Sugar   3  0.0003591  0.0003591  0.0001197   0.64  0.608
Error               8  0.0014865  0.0014865  0.0001858
Total              15  0.0368042


S = 0.0136311   R-Sq = 95.96%   R-Sq(adj) = 92.43%


Grouping Information Using Tukey Method and 95.0% Confidence

Starch  N  Mean  Grouping
11      8   0.6  A
 9      8   0.5    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

Rare
Sugar  N  Mean  Grouping
 0     4   0.6  A
10     4   0.5    B
20     4   0.5    B
30     4   0.5    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

        Rare
Starch  Sugar  N  Mean  Grouping
11       0     2   0.7  A
 9       0     2   0.6    B
11      10     2   0.6    B C
11      20     2   0.6    B C
11      30     2   0.6    B C D
 9      20     2   0.5      C D
 9      10     2   0.5      C D
 9      30     2   0.5        D
```

Means that do not share a letter are significantly different.

(2) General Linear Model: Moisture Content (MC %) versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for Mc_day 21, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.6672	0.6672	0.6672	3.98	0.081
Rare Sugar	3	3.8209	3.8209	1.2736	7.59	0.010
Starch*Rare Sugar	3	1.7852	1.7852	0.5951	3.55	0.068
Error	8	1.3417	1.3417	0.1677		
Total	15	7.6151				

S = 0.409531   R-Sq = 82.38%   R-Sq(adj) = 66.96%

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	N	Mean	Grouping
11	8	12.3	A
9	8	11.9	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Rare Sugar	N	Mean	Grouping
0	4	12.9	A
30	4	12.0	A B
20	4	11.8	B
10	4	11.7	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	Rare Sugar	N	Mean	Grouping
9	0	2	13.2	A
11	0	2	12.6	A B
11	30	2	12.5	A B
11	10	2	12.2	A B
11	20	2	12.0	A B
9	20	2	11.7	A B
9	30	2	11.6	B
9	10	2	11.1	B

Means that do not share a letter are significantly different.

(3) General Linear Model: T1 versus Starch, Rare Sugar

```
Factor      Type   Levels  Values
Starch      fixed       2  9, 11
Rare Sugar  fixed       4  0, 10, 20, 30


Analysis of Variance for T1_day 21, using Adjusted SS for Tests

Source             DF   Seq SS   Adj SS   Adj MS       F      P
Starch              1  152.992  152.992  152.992  152.71  0.000
Rare Sugar          3  106.759  106.759   35.586   35.52  0.000
Starch*Rare Sugar   3   31.123   31.123   10.374   10.36  0.004
Error               8    8.015    8.015    1.002
Total              15  298.889


S = 1.00091   R-Sq = 97.32%   R-Sq(adj) = 94.97%


Grouping Information Using Tukey Method and 95.0% Confidence

Starch  N  Mean  Grouping
 9      8  52.5  A
11      8  46.3    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

Rare
Sugar  N  Mean  Grouping
10     4  52.2  A
 0     4  50.7  A B
20     4  49.7    B
30     4  45.2      C

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

        Rare
Starch  Sugar  N  Mean  Grouping
 9      10     2  57.3  A
 9      20     2  52.4    B
 9       0     2  51.9    B
11       0     2  49.5    B C
 9      30     2  48.5    B C
11      10     2  47.0      C
11      20     2  46.9      C
11      30     2  42.0        D

Means that do not share a letter are significantly different.
```

(4) General Linear Model: T2 versus Starch, Rare Sugar

```
Factor      Type   Levels  Values
Starch      fixed       2  9, 11
Rare Sugar  fixed       4  0, 10, 20, 30


Analysis of Variance for T2_day 21, using Adjusted SS for Tests

Source             DF   Seq SS   Adj SS   Adj MS       F      P
Starch              1  2.46961  2.46961  2.46961  262.83  0.000
Rare Sugar          3  0.71516  0.71516  0.23839   25.37  0.000
Starch*Rare Sugar   3  0.27235  0.27235  0.09078    9.66  0.005
Error               8  0.07517  0.07517  0.00940
Total              15  3.53230


S = 0.0969343   R-Sq = 97.87%   R-Sq(adj) = 96.01%


R denotes an observation with a large standardized residual.


Grouping Information Using Tukey Method and 95.0% Confidence

Starch  N  Mean  Grouping
11      8   1.6  A
 9      8   0.8    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

Rare
Sugar  N  Mean  Grouping
 0     4   1.5  A
30     4   1.4  A B
10     4   1.2    B C
20     4   0.9      C

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

        Rare
Starch  Sugar  N  Mean  Grouping
11      30     2   1.8  A
11       0     2   1.7  A
11      10     2   1.7  A
 9       0     2   1.2    B
11      20     2   1.2    B
 9      30     2   0.9    B C
 9      20     2   0.7      C
 9      10     2   0.6      C

Means that do not share a letter are significantly different.
```

Table A. 5. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on (1) water activity (aw); (2) moisture content (MC %); (3) T1; (4) T2 using adjusted SS for Tests for day 28*

(1) General Linear Model: Water activity versus Starch, Rare Sugar

```
Factor      Type   Levels  Values
Starch      fixed       2  9, 11
Rare Sugar  fixed       4  0, 10, 20, 30


Analysis of Variance for aw_day 28, using Adjusted SS for Tests

Source             DF     Seq SS     Adj SS     Adj MS       F      P
Starch              1  0.0031894  0.0031894  0.0031894  109.60  0.000
Rare Sugar          3  0.0119506  0.0119506  0.0039835  136.89  0.000
Starch*Rare Sugar   3  0.0003129  0.0003129  0.0001043    3.58  0.066
Error               8  0.0002328  0.0002328  0.0000291
Total              15  0.0156857


S = 0.00539438   R-Sq = 98.52%   R-Sq(adj) = 97.22%

Grouping Information Using Tukey Method and 95.0% Confidence

Starch  N  Mean  Grouping
11      8   0.6  A
 9      8   0.6    B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Rare
Sugar  N  Mean  Grouping
 0     4   0.6  A
10     4   0.6    B
20     4   0.6      C
30     4   0.6      C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

        Rare
Starch  Sugar  N  Mean  Grouping
11       0     2   0.6  A
 9       0     2   0.6  A B
11      10     2   0.6    B
11      20     2   0.6      C
11      30     2   0.6      C D
 9      10     2   0.6      C D E
 9      20     2   0.6        D E
 9      30     2   0.5          E

Means that do not share a letter are significantly different.
```

(2) General Linear Model: Moisture Content (MC %) versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for mc_day 28, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.8754	0.8754	0.8754	1.59	0.242
Rare Sugar	3	4.0344	4.0344	1.3448	2.45	0.138
Starch*Rare Sugar	3	0.4759	0.4759	0.1586	0.29	0.832
Error	8	4.3910	4.3910	0.5489		
Total	15	9.7767				

S = 0.740863   R-Sq = 55.09%   R-Sq(adj) = 15.79%

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	N	Mean	Grouping
11	8	12.3	A
9	8	11.9	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Rare Sugar	N	Mean	Grouping
30	4	12.7	A
20	4	12.3	A
0	4	12.0	A
10	4	11.4	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	Rare Sugar	N	Mean	Grouping
11	30	2	13.1	A
11	20	2	12.5	A
11	0	2	12.3	A
9	30	2	12.3	A
9	20	2	12.1	A
9	0	2	11.7	A
9	10	2	11.4	A
11	10	2	11.3	A

Means that do not share a letter are significantly different.

(3) General Linear Model: T1 versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for T1_day 28, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	76.545	76.545	76.545	259.88	0.000
Rare Sugar	3	131.754	131.754	43.918	149.10	0.000
Starch*Rare Sugar	3	21.758	21.758	7.253	24.62	0.000
Error	8	2.356	2.356	0.295		
Total	15	232.414				

S = 0.542720   R-Sq = 98.99%   R-Sq(adj) = 98.10%

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	N	Mean	Grouping
9	8	50.6	A
11	8	46.2	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Rare Sugar	N	Mean	Grouping
10	4	51.1	A
0	4	50.5	A
20	4	48.2	B
30	4	43.8	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Starch	Rare Sugar	N	Mean	Grouping
9	10	2	55.1	A
9	0	2	51.5	B
9	20	2	49.6	B
11	0	2	49.6	B
11	10	2	47.0	C
11	20	2	46.8	C
9	30	2	46.1	C
11	30	2	41.5	D

Means that do not share a letter are significantly different.

(4) General Linear Model: T2 versus Starch, Rare Sugar

```
Factor      Type   Levels  Values
Starch      fixed       2  9, 11
Rare Sugar  fixed       4  0, 10, 20, 30


Analysis of Variance for T2_day 28, using Adjusted SS for Tests

Source             DF  Seq SS  Adj SS  Adj MS       F      P
Starch              1  5.4459  5.4459  5.4459  444.09  0.000
Rare Sugar          3  1.1217  1.1217  0.3739   30.49  0.000
Starch*Rare Sugar   3  0.6678  0.6678  0.2226   18.15  0.001
Error               8  0.0981  0.0981  0.0123
Total              15  7.3336


S = 0.110739   R-Sq = 98.66%   R-Sq(adj) = 97.49%


Grouping Information Using Tukey Method and 95.0% Confidence

Starch  N  Mean  Grouping
11      8   2.1  A
 9      8   1.0    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

Rare
Sugar  N  Mean  Grouping
30     4   2.0  A
 0     4   1.5    B
10     4   1.4    B
20     4   1.3    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

        Rare
Starch  Sugar  N  Mean  Grouping
11      30     2   2.8  A
11      10     2   2.1    B
11       0     2   2.0    B
11      20     2   1.6      C
 9      30     2   1.1      C D
 9      20     2   1.0        D
 9       0     2   1.0        D
 9      10     2   0.8        D

Means that do not share a letter are significantly different.
```

Table A. 6. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on hardness using adjusted SS for Tests; day0*

General Linear Model: Hardness versus Starch, RareSugar

```
Factor     Type   Levels  Values
Starch_h   fixed       2  9, 11
Rare_h     fixed       4  0, 10, 20, 30


Analysis of Variance for Hardness_ day 0, using Adjusted SS for Tests

Source           DF  Seq SS  Adj SS  Adj MS       F      P
Starch_h          1  294.13  294.13  294.13  239.32  0.000
Rare_h            3  322.97  322.97  107.66   87.59  0.000
Starch_h*Rare_h   3  147.54  147.54   49.18   40.02  0.000
Error             8    9.83    9.83    1.23
Total            15  774.47


S = 1.10862   R-Sq = 98.73%   R-Sq(adj) = 97.62%


Grouping Information Using Tukey Method and 95.0% Confidence

Starch_h  N  Mean  Grouping
 9        8  13.6  A
11        8   5.0    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

Rare_h  N  Mean  Grouping
 0      4  15.0  A
10      4  12.4    B
20      4   5.5      C
30      4   4.3      C

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

Starch_h  Rare_h  N  Mean  Grouping
 9         0      2  23.9  A
 9        10      2  17.5    B
11        10      2   7.3      C
 9        20      2   6.9      C D
11         0      2   6.1      C D
 9        30      2   6.1      C D
11        20      2   4.1      C D
11        30      2   2.6        D

Means that do not share a letter are significantly different.
```

Table A. 7. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on hardness using adjusted SS for Tests; day 10*

General Linear Model: Hardness versus Starch, Rare Sugar

```
Factor     Type   Levels  Values
Starch_h   fixed       2  9, 11
Rare_h     fixed       4  0, 10, 20, 30


Analysis of Variance for Hardness_day 10, using Adjusted SS for Tests

Source           DF  Seq SS  Adj SS  Adj MS       F      P
Starch_h          1  377.75  377.75  377.75  887.65  0.000
Rare_h            3  355.64  355.64  118.55  278.56  0.000
Starch_h*Rare_h   3  184.43  184.43   61.48  144.46  0.000
Error             8    3.40    3.40    0.43
Total            15  921.23


S = 0.652355   R-Sq = 99.63%   R-Sq(adj) = 99.31%


Grouping Information Using Tukey Method and 95.0% Confidence

Starch_h  N  Mean  Grouping
11        8  14.8  A
 9        8   5.1    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

Rare_h  N  Mean  Grouping
10      4  16.3  A
 0      4  12.4    B
20      4   7.0      C
30      4   4.1        D

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

Starch_h  Rare_h  N  Mean  Grouping
11        10      2  25.3  A
11         0      2  19.5    B
11        20      2   9.9      C
 9        10      2   7.4      C D
 9         0      2   5.2        D E
11        30      2   4.5          E
 9        20      2   4.2          E
 9        30      2   3.7          E

Means that do not share a letter are significantly different.
```

Table A. 8. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on hardness using adjusted SS for Tests day 20*

General Linear Model: Hardness versus Starch, Rare Sugar

```
Factor     Type   Levels  Values
Starch_h   fixed       2  9, 11
Rare_h     fixed       4  0, 10, 20, 30


Analysis of Variance for Hardness_day 20, using Adjusted SS for Tests

Source           DF   Seq SS   Adj SS  Adj MS      F      P
Starch_h          1    14.54    14.54   14.54   1.51  0.255
Rare_h            3  2706.37  2706.37  902.12  93.47  0.000
Starch_h*Rare_h   3   154.72   154.72   51.57   5.34  0.026
Error             8    77.21    77.21    9.65
Total            15  2952.84


S = 3.10673   R-Sq = 97.39%   R-Sq(adj) = 95.10%


Grouping Information Using Tukey Method and 95.0% Confidence

Starch_h  N  Mean  Grouping
11        8  22.0  A
 9        8  20.1  A

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

Rare_h  N  Mean  Grouping
 0      4  38.9  A
10      4  27.8    B
20      4  10.9      C
30      4   6.6      C

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

Starch_h  Rare_h  N  Mean  Grouping
 9         0      2  41.9  A
11         0      2  35.9  A
11        10      2  33.0  A B
 9        10      2  22.6    B C
11        20      2  13.2      C D
 9        20      2   8.5        D
 9        30      2   7.4        D
11        30      2   5.8        D

Means that do not share a letter are significantly different.
```

Table A. 9. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on hardness using adjusted SS for Tests day 28*

General Linear Model: Hardness versus Starch, Rare

```
Factor     Type   Levels  Values
Starch_h   fixed       2  9, 11
Rare_h     fixed       4  0, 10, 20, 30


Analysis of Variance for Hardness_day 28, using Adjusted SS for Tests

Source           DF   Seq SS   Adj SS   Adj MS       F      P
Starch_h          1   177.95   177.95   177.95   71.74  0.000
Rare_h            3  3739.42  3739.42  1246.47  502.49  0.000
Starch_h*Rare_h   3   213.77   213.77    71.26   28.73  0.000
Error             8    19.84    19.84     2.48
Total            15  4150.99


S = 1.57499   R-Sq = 99.52%   R-Sq(adj) = 99.10%

Grouping Information Using Tukey Method and 95.0% Confidence

Starch_h  N  Mean  Grouping
11        8  26.4  A
 9        8  19.8    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

Rare_h  N  Mean  Grouping
 0      4  45.0  A
10      4  29.6    B
20      4  11.2      C
30      4   6.6        D

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

Starch_h  Rare_h  N  Mean  Grouping
11         0      2  46.4  A
 9         0      2  43.5  A B
11        10      2  39.1    B
 9        10      2  20.2      C
11        20      2  13.8        D
 9        20      2   8.5        D E
 9        30      2   6.8          E
11        30      2   6.4          E

Means that do not share a letter are significantly different.
```

Table A. 10. *Analysis of Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on glass transition Tg using adjusted SS for Tests; day 0*

General Linear Model: Glass transition (Tg) versus Starch, Rare Sugar

```
Factor          Type   Levels  Values
Starch_Tg       fixed       2  9, 11
Rare Sugar_Tg   fixed       4  0, 10, 20, 30


Analysis of Variance for Tg_ day 0, using Adjusted SS for Tests

Source                   DF   Seq SS   Adj SS  Adj MS      F      P
Starch_Tg                 1   1.1827   1.1827  1.1827   1.41  0.269
Rare Sugar_Tg             3   7.3195   7.3195  2.4398   2.91  0.101
Starch_Tg*Rare Sugar_Tg   3  27.2890  27.2890  9.0963  10.84  0.003
Error                     8   6.7154   6.7154  0.8394
Total                    15  42.5064


S = 0.916198   R-Sq = 84.20%   R-Sq(adj) = 70.38%

Grouping Information Using Tukey Method and 95.0% Confidence

Starch_Tg  N   Mean  Grouping
 9         8  -37.9  A
11         8  -38.4  A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Rare
Sugar_Tg  N   Mean  Grouping
30        4  -37.2  A
 0        4  -37.9  A
20        4  -38.6  A
10        4  -39.0  A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

           Rare
Starch_Tg  Sugar_Tg  N   Mean  Grouping
 9         30        2  -35.1  A
11          0        2  -36.7  A B
11         20        2  -37.8  A B
 9         10        2  -38.0  A B
 9          0        2  -39.1    B
11         30        2  -39.2    B
 9         20        2  -39.3    B
11         10        2  -39.9    B

Means that do not share a letter are significantly different.
```

Table A. 11. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on glass transition Tg using adjusted SS for Tests; day 28*

General Linear Model: Glass transition (Tg) versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch_Tg	fixed	2	9, 11
Rare Sugar_Tg	fixed	4	0, 10, 20, 30

Analysis of Variance for Tg_day 28, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch_Tg	1	4.030	4.030	4.030	1.03	0.339
Rare Sugar_Tg	3	18.396	18.396	6.132	1.57	0.270
Starch_Tg*Rare Sugar_Tg	3	21.412	21.412	7.137	1.83	0.219
Error	8	31.166	31.166	3.896		
Total	15	75.004				

S = 1.97378   R-Sq = 58.45%   R-Sq(adj) = 22.09%

Grouping Information Using Tukey Method and 95.0% Confidence

Starch_Tg	N	Mean	Grouping
11	8	-38.6	A
9	8	-39.6	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Rare Sugar_Tg	N	Mean	Grouping
0	4	-37.4	A
30	4	-38.9	A
10	4	-40.0	A
20	4	-40.1	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Starch_Tg	Rare Sugar_Tg	N	Mean	Grouping
11	0	2	-35.2	A
9	30	2	-37.9	A
11	10	2	-39.4	A
9	0	2	-39.7	A
11	30	2	-39.9	A
11	20	2	-40.0	A
9	20	2	-40.3	A
9	10	2	-40.5	A

Means that do not share a letter are significantly different.

Table A. 12. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on T2 (spin-spin) relaxation times of each compartment (peaks) obtained by NNLS using adjusted SS for Tests; day 0*

General Linear Model: Peak_1, Peak 2, Peak 3, Peak 4 versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for Peak_1, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.0022562	0.0022562	0.0022562	32.82	0.000
Rare Sugar	3	0.0012187	0.0012187	0.0004062	5.91	0.020
Starch*Rare Sugar	3	0.0031687	0.0031687	0.0010562	15.36	0.001
Error	8	0.0005500	0.0005500	0.0000687		
Total	15	0.0071937				

S = 0.00829156   R-Sq = 92.35%   R-Sq(adj) = 85.66%

Analysis of Variance for Peak 2, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.017556	0.017556	0.017556	2.39	0.160
Rare Sugar	3	0.202569	0.202569	0.067523	9.21	0.006
Starch*Rare Sugar	3	0.214619	0.214619	0.071540	9.76	0.005
Error	8	0.058650	0.058650	0.007331		
Total	15	0.493394				

S = 0.0856227   R-Sq = 88.11%   R-Sq(adj) = 77.71%

Analysis of Variance for Peak 3, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.3025	0.3025	0.3025	7.12	0.028
Rare Sugar	3	7.0725	7.0725	2.3575	55.47	0.000
Starch*Rare Sugar	3	7.7225	7.7225	2.5742	60.57	0.000
Error	8	0.3400	0.3400	0.0425		
Total	15	15.4375				

S = 0.206155   R-Sq = 97.80%   R-Sq(adj) = 95.87%

Analysis of Variance for Peak 4, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	71.402	71.402	71.402	7140.25	0.000
Rare Sugar	3	23.987	23.987	7.996	799.58	0.000
Starch*Rare Sugar	3	23.987	23.987	7.996	799.58	0.000

```
Error               8    0.080   0.080   0.010
Total              15  119.457


S = 0.1   R-Sq = 99.93%   R-Sq(adj) = 99.87%


Grouping Information Using Tukey Method and 95.0% Confidence for
Peak_1

Starch  N  Mean  Grouping
11      8   0.2  A
 9      8   0.2    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for
Peak_1

Rare
Sugar  N  Mean  Grouping
30     4   0.2  A
20     4   0.2  A
 0     4   0.2  A B
10     4   0.2    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for
Peak_1

        Rare
Starch  Sugar  N  Mean  Grouping
11      10     2   0.2  A
11      20     2   0.2  A
 9      30     2   0.2  A
11      30     2   0.2  A
11       0     2   0.2  A
 9      20     2   0.2  A
 9       0     2   0.2  A
 9      10     2   0.1    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for Peak
2

Starch  N  Mean  Grouping
11      8   0.7  A
 9      8   0.6  A

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for Peak
2
```

Rare Sugar	N	Mean	Grouping
20	4	0.8	A
30	4	0.7	A B
0	4	0.6	A B
10	4	0.5	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak 2

Starch	Rare Sugar	N	Mean	Grouping
11	20	2	1.0	A
9	0	2	0.7	A B
9	30	2	0.7	A B C
11	30	2	0.6	A B C
9	20	2	0.6	A B C
11	10	2	0.6	B C
11	0	2	0.5	B C
9	10	2	0.4	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak 3

Starch	N	Mean	Grouping
9	8	2.5	A
11	8	2.2	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak 3

Rare Sugar	N	Mean	Grouping
20	4	3.3	A
0	4	2.3	B
30	4	2.3	B
10	4	1.5	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak 3

Starch	Rare Sugar	N	Mean	Grouping
11	20	2	4.3	A
9	0	2	3.3	B
9	30	2	2.7	B C
9	20	2	2.4	C
11	30	2	1.9	C D

9	10	2	1.6	D
11	10	2	1.3	D
11	0	2	1.3	D

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak 4

Starch	N	Mean	Grouping
11	8	4.2	A
9	8	0.0	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak 4

Rare Sugar	N	Mean	Grouping
30	4	3.0	A
0	4	2.8	A B
10	4	2.6	B
20	4	0.0	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak 4

Starch	Rare Sugar	N	Mean	Grouping
11	30	2	5.9	A
11	0	2	5.7	A
11	10	2	5.3	B
9	20	2	0.0	C
11	20	2	0.0	C
9	30	2	0.0	C
9	0	2	-0.0	C
9	10	2	-0.0	C

Means that do not share a letter are significantly different.

Table A. 13. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on T2 (spin-spin) relaxation times of each compartment (peaks) obtained by NNLS using adjusted SS for Tests; day 7*

General Linear Model: Peak 1, Peak 2, Peak 3, Peak 4 versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for Peak_1_day 7, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.0033063	0.0033063	0.0033063	75.57	0.000
Rare Sugar	3	0.0026687	0.0026687	0.0008896	20.33	0.000
Starch*Rare Sugar	3	0.0030687	0.0030687	0.0010229	23.38	0.000
Error	8	0.0003500	0.0003500	0.0000438		
Total	15	0.0093937				

S = 0.00661438   R-Sq = 96.27%   R-Sq(adj) = 93.01%

Analysis of Variance for Peak 2_day 7, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.11391	0.11391	0.11391	7.98	0.022
Rare Sugar	3	0.30367	0.30367	0.10122	7.09	0.012
Starch*Rare Sugar	3	0.09532	0.09532	0.03177	2.22	0.163
Error	8	0.11425	0.11425	0.01428		
Total	15	0.62714				

S = 0.119504   R-Sq = 81.78%   R-Sq(adj) = 65.84%

Analysis of Variance for Peak 3_day 7, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	1.8225	1.8225	1.8225	14.58	0.005
Rare Sugar	3	12.2000	12.2000	4.0667	32.53	0.000
Starch*Rare Sugar	3	2.8475	2.8475	0.9492	7.59	0.010
Error	8	1.0000	1.0000	0.1250		
Total	15	17.8700				

S = 0.353553   R-Sq = 94.40%   R-Sq(adj) = 89.51%

Analysis of Variance for Peak 4_day 7, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	101.51	101.51	101.51	6.34	0.036
Rare Sugar	3	150.02	150.02	50.01	3.12	0.088
Starch*Rare Sugar	3	150.02	150.02	50.01	3.12	0.088

```
Error               8  128.04  128.04   16.01
Total              15  529.58


S = 4.00070   R-Sq = 75.82%   R-Sq(adj) = 54.67%


Grouping Information Using Tukey Method and 95.0% Confidence for
Peak_1_day 7

Starch  N  Mean  Grouping
11      8   0.2  A
 9      8   0.2    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for
Peak_1_day 7

Rare
Sugar  N  Mean  Grouping
 0     4   0.2  A
30     4   0.2  A
20     4   0.2  A
10     4   0.2    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for
Peak_1_day 7

        Rare
Starch  Sugar  N  Mean  Grouping
11      20     2   0.2  A
11       0     2   0.2  A
 9      30     2   0.2  A
11      10     2   0.2  A
11      30     2   0.2  A B
 9       0     2   0.2  A B
 9      20     2   0.2    B
 9      10     2   0.1      C

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for Peak
2_day 7

Starch  N  Mean  Grouping
11      8   0.8  A
 9      8   0.6    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for Peak
2_day 7
```

Rare Sugar	N	Mean	Grouping
20	4	0.8	A
0	4	0.8	A
30	4	0.7	A
10	4	0.4	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak 2_day 7

Starch	Rare Sugar	N	Mean	Grouping
11	20	2	1.0	A
11	0	2	0.8	A B
11	30	2	0.8	A B
9	0	2	0.7	A B
9	30	2	0.7	A B
9	20	2	0.6	A B
11	10	2	0.5	B
9	10	2	0.4	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak 3_day 7

Starch	N	Mean	Grouping
11	8	3.1	A
9	8	2.4	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak 3_day 7

Rare Sugar	N	Mean	Grouping
0	4	3.7	A
20	4	3.3	A B
30	4	2.6	B
10	4	1.4	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak 3_day 7

Starch	Rare Sugar	N	Mean	Grouping
11	20	2	4.3	A
11	0	2	4.2	A
9	0	2	3.2	A B
11	30	2	2.7	B C
9	30	2	2.6	B C D

9	20	2	2.4	B C D
9	10	2	1.6	C D
11	10	2	1.2	D

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak 4_day 7

Starch	N	Mean	Grouping
11	8	5.0	A
9	8	-0.0	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak 4_day 7

Rare Sugar	N	Mean	Grouping
30	4	7.5	A
10	4	2.6	A
20	4	0.0	A
0	4	-0.0	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak 4_day 7

Starch	Rare Sugar	N	Mean	Grouping
11	30	2	15.0	A
11	10	2	5.1	A
9	20	2	0.0	A
11	20	2	0.0	A
9	0	2	0.0	A
9	10	2	-0.0	A
11	0	2	-0.0	A
9	30	2	-0.0	A

Means that do not share a letter are significantly different.

Table A. 14. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on T2 (spin-spin) relaxation times of each compartment (peaks) obtained by NNLS using adjusted SS for Tests; day 14*

General Linear Model: Peak 1, Peak 2, Peak 3, Peak4 versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for Peak1_day 14, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.0030250	0.0030250	0.0030250	16.13	0.004
Rare Sugar	3	0.0015250	0.0015250	0.0005083	2.71	0.115
Starch*Rare Sugar	3	0.0031250	0.0031250	0.0010417	5.56	0.023
Error	8	0.0015000	0.0015000	0.0001875		
Total	15	0.0091750				

S = 0.0136931   R-Sq = 83.65%   R-Sq(adj) = 69.35%

Analysis of Variance for Peak2_day 14, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.074256	0.074256	0.074256	10.73	0.011
Rare Sugar	3	0.249369	0.249369	0.083123	12.01	0.002
Starch*Rare Sugar	3	0.096819	0.096819	0.032273	4.66	0.036
Error	8	0.055350	0.055350	0.006919		
Total	15	0.475794				

S = 0.0831790   R-Sq = 88.37%   R-Sq(adj) = 78.19%

Analysis of Variance for Peak3_day 14, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	1.8225	1.8225	1.8225	27.00	0.001
Rare Sugar	3	12.1875	12.1875	4.0625	60.19	0.000
Starch*Rare Sugar	3	2.5275	2.5275	0.8425	12.48	0.002
Error	8	0.5400	0.5400	0.0675		
Total	15	17.0775				

S = 0.259808   R-Sq = 96.84%   R-Sq(adj) = 94.07%

Analysis of Variance for Peak 4_day 14, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	105.576	105.576	105.576	18769.00	0.000
Rare Sugar	3	171.127	171.127	57.042	10140.85	0.000
Starch*Rare Sugar	3	171.127	171.127	57.042	10140.85	0.000
Error	8	0.045	0.045	0.006		

```
Total              15  447.874


S = 0.075   R-Sq = 99.99%   R-Sq(adj) = 99.98%


Grouping Information Using Tukey Method and 95.0% Confidence for
Peak1_day 14

Starch  N  Mean  Grouping
11      8   0.2  A
 9      8   0.2    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for
Peak1_day 14

Rare
Sugar  N  Mean  Grouping
 0     4   0.2  A
30     4   0.2  A
20     4   0.2  A
10     4   0.2  A

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for
Peak1_day 14

        Rare
Starch  Sugar  N  Mean  Grouping
11      10     2   0.2  A
11      20     2   0.2  A
11       0     2   0.2  A
 9       0     2   0.2  A
 9      30     2   0.2  A B
11      30     2   0.2  A B
 9      20     2   0.2  A B
 9      10     2   0.1    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for
Peak2_day 14

Starch  N  Mean  Grouping
11      8   0.8  A
 9      8   0.6    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for
Peak2_day 14

Rare
```

Sugar	N	Mean	Grouping
20	4	0.8	A
0	4	0.8	A
30	4	0.7	A
10	4	0.5	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak2_day 14

Starch	Rare Sugar	N	Mean	Grouping
11	20	2	1.0	A
9	0	2	0.8	A B
11	30	2	0.8	A B
11	0	2	0.8	A B
9	30	2	0.7	A B C
9	20	2	0.6	B C
11	10	2	0.5	B C
9	10	2	0.4	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak3_day 14

Starch	N	Mean	Grouping
11	8	3.0	A
9	8	2.4	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak3_day 14

Rare Sugar	N	Mean	Grouping
0	4	3.7	A
20	4	3.0	B
30	4	2.7	B
10	4	1.3	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak3_day 14

Starch	Rare Sugar	N	Mean	Grouping
11	0	2	4.4	A
11	20	2	3.8	A B
9	0	2	3.1	B C
11	30	2	2.7	C
9	30	2	2.7	C
9	20	2	2.3	C D

9	10	2	1.5	D E
11	10	2	1.2	E

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak 4_day 14

Starch	N	Mean	Grouping
11	8	5.1	A
9	8	0.0	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak 4_day 14

Rare Sugar	N	Mean	Grouping
30	4	8.0	A
10	4	2.3	B
20	4	0.0	C
0	4	0.0	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak 4_day 14

Starch	Rare Sugar	N	Mean	Grouping
11	30	2	16.0	A
11	10	2	4.5	B
9	20	2	0.0	C
9	0	2	0.0	C
11	20	2	0.0	C
9	10	2	-0.0	C
11	0	2	-0.0	C
9	30	2	-0.0	C

Means that do not share a letter are significantly different.

Table A. 15. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on T2 (spin-spin) relaxation times of each compartment (peaks) obtained by NNLS using adjusted SS for Tests; day 21*

General Linear Model: Peak 1, Peak 2, Peak 3, Peak 4 versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for Peak1_day 21, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.0030250	0.0030250	0.0030250	8.64	0.019
Rare Sugar	3	0.0006750	0.0006750	0.0002250	0.64	0.609
Starch*Rare Sugar	3	0.0018750	0.0018750	0.0006250	1.79	0.228
Error	8	0.0028000	0.0028000	0.0003500		
Total	15	0.0083750				

S = 0.0187083   R-Sq = 66.57%   R-Sq(adj) = 37.31%

Analysis of Variance for peak2_day 21, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.00006	0.00006	0.00006	0.00	0.951
Rare Sugar	3	0.31262	0.31262	0.10421	7.40	0.011
Starch*Rare Sugar	3	0.07287	0.07287	0.02429	1.72	0.239
Error	8	0.11265	0.11265	0.01408		
Total	15	0.49819				

S = 0.118664   R-Sq = 77.39%   R-Sq(adj) = 57.60%

Analysis of Variance for peak3_day 21, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.6006	0.6006	0.6006	6.20	0.038
Rare Sugar	3	6.2019	6.2019	2.0673	21.34	0.000
Starch*Rare Sugar	3	1.5719	1.5719	0.5240	5.41	0.025
Error	8	0.7750	0.7750	0.0969		
Total	15	9.1494				

S = 0.311247   R-Sq = 91.53%   R-Sq(adj) = 84.12%

Grouping Information Using Tukey Method and 95.0% Confidence for Peak1_day 21

Starch	N	Mean	Grouping
11	8	0.2	A
9	8	0.2	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak1_day 21

Rare Sugar	N	Mean	Grouping
0	4	0.2	A
30	4	0.2	A
20	4	0.2	A
10	4	0.2	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for Peak1_day 21

Starch	Rare Sugar	N	Mean	Grouping
11	10	2	0.2	A
11	0	2	0.2	A
9	30	2	0.2	A
11	30	2	0.2	A
11	20	2	0.2	A
9	0	2	0.2	A
9	20	2	0.2	A
9	10	2	0.1	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for peak2_day 21

Starch	N	Mean	Grouping
9	8	0.8	A
11	8	0.8	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for peak2_day 21

Rare Sugar	N	Mean	Grouping
10	4	1.0	A
0	4	0.7	A B
20	4	0.7	B
30	4	0.6	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for peak2_day 21

Starch	Rare Sugar	N	Mean	Grouping

9	10	2	1.1	A
11	10	2	0.9	A B
11	0	2	0.8	A B
11	20	2	0.7	A B
9	0	2	0.7	A B
11	30	2	0.6	B
9	20	2	0.6	B
9	30	2	0.6	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for peak3_day 21

Starch	N	Mean	Grouping
11	8	3.0	A
9	8	2.6	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for peak3_day 21

Rare Sugar	N	Mean	Grouping
10	4	3.5	A
0	4	3.2	A
20	4	2.5	B
30	4	2.0	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for peak3_day 21

Starch	Rare Sugar	N	Mean	Grouping
11	10	2	3.7	A
11	0	2	3.7	A
9	10	2	3.4	A B
11	20	2	2.9	A B C
9	0	2	2.7	A B C D
9	30	2	2.3	B C D
9	20	2	2.0	C D
11	30	2	1.7	D

Means that do not share a letter are significantly different.

Table A. 16. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on T2 (spin-spin) relaxation times of each compartment (peaks) obtained by NNLS using adjusted SS for Tests; day 28*

General Linear Model: Peak 1, Peak 2, Peak 3, Peak 4 versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for peak1_day 28, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.0039062	0.0039062	0.0039062	27.17	0.001
Rare Sugar	3	0.0008187	0.0008187	0.0002729	1.90	0.208
Starch*Rare Sugar	3	0.0018687	0.0018687	0.0006229	4.33	0.043
Error	8	0.0011500	0.0011500	0.0001437		
Total	15	0.0077437				

S = 0.0119896   R-Sq = 85.15%   R-Sq(adj) = 72.15%

Unusual Observations for peak1_day 28

Obs	peak1_day 28	Fit	SE Fit	Residual	St Resid
7	0.190000	0.210000	0.008478	-0.020000	-2.36 R
8	0.230000	0.210000	0.008478	0.020000	2.36 R

R denotes an observation with a large standardized residual.

Analysis of Variance for peak2_day 28, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.348100	0.348100	0.348100	79.57	0.000
Rare Sugar	3	0.132600	0.132600	0.044200	10.10	0.004
Starch*Rare Sugar	3	0.096300	0.096300	0.032100	7.34	0.011
Error	8	0.035000	0.035000	0.004375		
Total	15	0.612000				

S = 0.0661438   R-Sq = 94.28%   R-Sq(adj) = 89.28%

Analysis of Variance for peak3_day 28, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	12.7806	12.7806	12.7806	161.02	0.000
Rare Sugar	3	3.2869	3.2869	1.0956	13.80	0.002
Starch*Rare Sugar	3	2.2069	2.2069	0.7356	9.27	0.006
Error	8	0.6350	0.6350	0.0794		
Total	15	18.9094				

S = 0.281736   R-Sq = 96.64%   R-Sq(adj) = 93.70%

Grouping Information Using Tukey Method and 95.0% Confidence for peak1_day 28

Starch	N	Mean	Grouping
11	8	0.2	A
9	8	0.2	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for peak1_day 28

Rare Sugar	N	Mean	Grouping
0	4	0.2	A
30	4	0.2	A
10	4	0.2	A
20	4	0.2	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for peak1_day 28

Starch	Rare Sugar	N	Mean	Grouping
11	30	2	0.2	A
11	10	2	0.2	A
11	0	2	0.2	A B
9	0	2	0.2	A B
11	20	2	0.2	A B
9	20	2	0.2	A B
9	30	2	0.2	B
9	10	2	0.2	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for peak2_day 28

Starch	N	Mean	Grouping
11	8	0.9	A
9	8	0.6	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for peak2_day 28

Rare Sugar	N	Mean	Grouping
30	4	0.9	A
10	4	0.7	B

0	4	0.7	B
20	4	0.7	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for peak2_day 28

Starch	Rare Sugar	N	Mean	Grouping
11	30	2	1.2	A
11	10	2	0.9	A B
11	20	2	0.8	B C
11	0	2	0.7	B C
9	30	2	0.6	C
9	0	2	0.6	C
9	10	2	0.6	C
9	20	2	0.6	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for peak3_day 28

Starch	N	Mean	Grouping
11	8	4.3	A
9	8	2.5	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for peak3_day 28

Rare Sugar	N	Mean	Grouping
0	4	3.9	A
30	4	3.8	A
10	4	3.1	B
20	4	2.8	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for peak3_day 28

Starch	Rare Sugar	N	Mean	Grouping
11	30	2	5.0	A
11	10	2	4.4	A B
11	0	2	4.4	A B
11	20	2	3.4	B C
9	0	2	3.3	B C
9	30	2	2.6	C D
9	20	2	2.3	C D
9	10	2	1.8	D

Means that do not share a letter are significantly different.

Table A. 17. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on relative area of each compartment (peaks) obtained by NNLS using adjusted SS for Tests; day 0*

General Linear Model: RA1, RA2, RA3, RA4 versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for RA1, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	724.55	724.55	724.55	75.48	0.000
Rare Sugar	3	470.00	470.00	156.67	16.32	0.001
Starch*Rare Sugar	3	22.60	22.60	7.53	0.78	0.535
Error	8	76.80	76.80	9.60		
Total	15	1293.94				

S = 3.09829   R-Sq = 94.07%   R-Sq(adj) = 88.87%

Analysis of Variance for RA2, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	91.15	91.15	91.15	12.83	0.007
Rare Sugar	3	562.28	562.28	187.43	26.37	0.000
Starch*Rare Sugar	3	210.16	210.16	70.05	9.86	0.005
Error	8	56.85	56.85	7.11		
Total	15	920.45				

S = 2.66583   R-Sq = 93.82%   R-Sq(adj) = 88.42%

Analysis of Variance for RA3, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	11.408	11.408	11.408	1.41	0.269
Rare Sugar	3	22.479	22.479	7.493	0.93	0.471
Starch*Rare Sugar	3	71.452	71.452	23.817	2.95	0.098
Error	8	64.658	64.658	8.082		
Total	15	169.997				

S = 2.84293   R-Sq = 61.97%   R-Sq(adj) = 28.68%

Analysis of Variance for RA4, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	1552.75	1552.75	1552.75	657.58	0.000
Rare Sugar	3	519.34	519.34	173.11	73.31	0.000
Starch*Rare Sugar	3	519.34	519.34	173.11	73.31	0.000
Error	8	18.89	18.89	2.36		

```
Total              15  2610.32


S = 1.53666   R-Sq = 99.28%   R-Sq(adj) = 98.64%

Grouping Information Using Tukey Method and 95.0% Confidence for RA1

Starch  N  Mean  Grouping
 9      8  47.4  A
11      8  34.0    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for RA1

Rare
Sugar  N  Mean  Grouping
10     4  45.4  A
 0     4  43.2  A
20     4  42.8  A
30     4  31.5    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for RA1

        Rare
Starch  Sugar  N  Mean  Grouping
 9      10     2  53.3  A
 9       0     2  50.2  A B
 9      20     2  47.6  A B C
 9      30     2  38.7    B C
11      20     2  38.0    B C
11      10     2  37.5      C
11       0     2  36.2      C D
11      30     2  24.2        D

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for RA2

Starch  N  Mean  Grouping
 9      8  25.2  A
11      8  20.4    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for RA2

Rare
Sugar  N  Mean  Grouping
20     4  29.7  A
30     4  27.6  A
 0     4  18.1    B
10     4  15.9    B
```

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA2

Starch	Rare Sugar	N	Mean	Grouping
9	30	2	34.4	A
11	20	2	32.9	A
9	20	2	26.4	A B
9	0	2	21.7	B C
11	30	2	20.8	B C
9	10	2	18.3	B C
11	0	2	14.4	C
11	10	2	13.6	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA3

Starch	N	Mean	Grouping
9	8	27.4	A
11	8	25.7	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA3

Rare Sugar	N	Mean	Grouping
30	4	27.8	A
20	4	27.5	A
0	4	25.5	A
10	4	25.2	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA3

Starch	Rare Sugar	N	Mean	Grouping
11	20	2	29.1	A
11	30	2	28.8	A
9	10	2	28.4	A
9	0	2	28.1	A
9	30	2	26.9	A
9	20	2	26.0	A
11	0	2	22.9	A
11	10	2	21.9	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA4

Starch	N	Mean	Grouping
11	8	19.7	A

9	8	0.0	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA4

Rare Sugar	N	Mean	Grouping
10	4	13.5	A
0	4	13.3	A
30	4	12.6	A
20	4	0.0	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA4

Starch	Rare Sugar	N	Mean	Grouping
11	10	2	27.1	A
11	0	2	26.5	A
11	30	2	25.2	A
9	20	2	0.0	B
9	30	2	0.0	B
9	0	2	0.0	B
9	10	2	0.0	B
11	20	2	-0.0	B

Means that do not share a letter are significantly different.

Table A. 18. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on relative area of each compartment (peaks) obtained by NNLS using adjusted SS for Tests; day 7*

General Linear Model: RA1_day 7, RA2_day 7, ... versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for RA1_day 7, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	930.56	930.56	930.56	685.83	0.000
Rare Sugar	3	460.17	460.17	153.39	113.05	0.000
Starch*Rare Sugar	3	235.19	235.19	78.40	57.78	0.000
Error	8	10.85	10.85	1.36		
Total	15	1636.77				

S = 1.16483   R-Sq = 99.34%   R-Sq(adj) = 98.76%

Analysis of Variance for RA2_day 7, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	181.64	181.64	181.64	17.53	0.003
Rare Sugar	3	208.10	208.10	69.37	6.69	0.014
Starch*Rare Sugar	3	337.81	337.81	112.60	10.87	0.003
Error	8	82.90	82.90	10.36		
Total	15	810.45				

S = 3.21909   R-Sq = 89.77%   R-Sq(adj) = 80.82%

Analysis of Variance for RA3_day 7, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.562	0.562	0.562	0.97	0.355
Rare Sugar	3	104.589	104.589	34.863	59.82	0.000
Starch*Rare Sugar	3	133.867	133.867	44.622	76.57	0.000
Error	8	4.662	4.662	0.583		
Total	15	243.681				

S = 0.763389   R-Sq = 98.09%   R-Sq(adj) = 96.41%

Analysis of Variance for RA4_day 7, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	414.53	414.53	414.53	42.31	0.000
Rare Sugar	3	496.32	496.32	165.44	16.89	0.001
Starch*Rare Sugar	3	496.32	496.32	165.44	16.89	0.001
Error	8	78.38	78.38	9.80		

```
Total              15  1485.55


S = 3.13006   R-Sq = 94.72%   R-Sq(adj) = 90.11%


Grouping Information Using Tukey Method and 95.0% Confidence for
RA1_day 7

Starch  N  Mean  Grouping
 9      8  49.3  A
11      8  34.0    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for
RA1_day 7

Rare
Sugar  N  Mean  Grouping
 0     4  46.3  A
10     4  44.8  A B
20     4  42.8    B
30     4  32.6      C

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for
RA1_day 7

        Rare
Starch  Sugar  N  Mean  Grouping
 9      10     2  58.5  A
 9       0     2  52.5    B
 9      20     2  46.1      C
11       0     2  40.1        D
 9      30     2  39.9        D
11      20     2  39.6        D
11      10     2  31.0          E
11      30     2  25.3            F

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for
RA2_day 7

Starch  N  Mean  Grouping
11      8  30.2  A
 9      8  23.5    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for
RA2_day 7

Rare
```

Sugar	N	Mean	Grouping
20	4	30.5	A
30	4	30.2	A
0	4	24.4	A B
10	4	22.3	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA2_day 7

Starch	Rare Sugar	N	Mean	Grouping
9	30	2	33.7	A
11	20	2	32.6	A
11	10	2	31.0	A
11	0	2	30.5	A B
9	20	2	28.5	A B
11	30	2	26.8	A B
9	0	2	18.2	B C
9	10	2	13.6	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA3_day 7

Starch	N	Mean	Grouping
11	8	27.6	A
9	8	27.3	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA3_day 7

Rare Sugar	N	Mean	Grouping
30	4	30.2	A
0	4	29.3	A
20	4	26.6	B
10	4	23.6	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA3_day 7

Starch	Rare Sugar	N	Mean	Grouping
11	30	2	33.9	A
11	0	2	29.4	B
9	0	2	29.2	B
9	10	2	27.9	B C
11	20	2	27.9	B C
9	30	2	26.5	B C

9	20	2	25.4	C
11	10	2	19.4	D

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA4_day 7

Starch	N	Mean	Grouping
11	8	10.2	A
9	8	0.0	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA4_day 7

Rare Sugar	N	Mean	Grouping
10	4	13.4	A
30	4	7.0	A B
0	4	0.0	B
20	4	-0.0	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA4_day 7

Starch	Rare Sugar	N	Mean	Grouping
11	10	2	26.8	A
11	30	2	14.0	B
9	0	2	0.0	C
9	10	2	0.0	C
9	20	2	0.0	C
11	20	2	-0.0	C
11	0	2	-0.0	C
9	30	2	-0.0	C

Means that do not share a letter are significantly different.

Table A. 19. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on relative area of each compartment (peaks) obtained by NNLS using adjusted SS for Tests; day 0*

General Linear Model: RA1_day 14, RA2_day 14, ... versus Starch, Rare Sugar

```
Factor      Type   Levels  Values
Starch      fixed       2  9, 11
Rare Sugar  fixed       4  0, 10, 20, 30


Analysis of Variance for RA1_day 14, using Adjusted SS for Tests

Source             DF   Seq SS  Adj SS  Adj MS       F      P
Starch              1   791.16  791.16  791.16  278.91  0.000
Rare Sugar          3   747.61  747.61  249.20   87.85  0.000
Starch*Rare Sugar   3   150.62  150.62   50.21   17.70  0.001
Error               8    22.69   22.69    2.84
Total              15  1712.08


S = 1.68422   R-Sq = 98.67%   R-Sq(adj) = 97.51%


Analysis of Variance for RA2_day 14, using Adjusted SS for Tests

Source             DF   Seq SS  Adj SS  Adj MS      F      P
Starch              1    14.18   14.18   14.18   1.75  0.223
Rare Sugar          3   880.94  880.94  293.65  36.18  0.000
Starch*Rare Sugar   3   176.32  176.32   58.77   7.24  0.011
Error               8    64.93   64.93    8.12
Total              15  1136.37


S = 2.84901   R-Sq = 94.29%   R-Sq(adj) = 89.29%


Analysis of Variance for RA3_day 14, using Adjusted SS for Tests

Source             DF   Seq SS   Adj SS  Adj MS      F      P
Starch              1   22.515   22.515  22.515   7.51  0.025
Rare Sugar          3   44.023   44.023  14.674   4.89  0.032
Starch*Rare Sugar   3  145.707  145.707  48.569  16.19  0.001
Error               8   23.999   23.999   3.000
Total              15  236.244


S = 1.73201   R-Sq = 89.84%   R-Sq(adj) = 80.95%

Analysis of Variance for RA4_day 14, using Adjusted SS for Tests

Source             DF   Seq SS  Adj SS  Adj MS       F      P
Starch              1   386.32  386.32  386.32  436.71  0.000
Rare Sugar          3   499.12  499.12  166.37  188.07  0.000
Starch*Rare Sugar   3   499.12  499.12  166.37  188.07  0.000
Error               8     7.08    7.08    0.88
Total              15  1391.63
```

```
S = 0.940538   R-Sq = 99.49%   R-Sq(adj) = 99.05%


Grouping Information Using Tukey Method and 95.0% Confidence for
RA1_day 14

Starch  N  Mean  Grouping
 9      8  50.5  A
11      8  36.4    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for
RA1_day 14

Rare
Sugar  N  Mean  Grouping
 0     4  50.0  A
10     4  47.8  A
20     4  43.9    B
30     4  32.2      C

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for
RA1_day 14

        Rare
Starch  Sugar  N  Mean  Grouping
 9      10     2  59.7  A
 9       0     2  54.2  A B
 9      20     2  48.4    B C
11       0     2  45.7      C D
 9      30     2  39.7        D E
11      20     2  39.4        D E
11      10     2  35.9          E
11      30     2  24.8            F

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for
RA2_day 14

Starch  N  Mean  Grouping
11      8  24.8  A
 9      8  22.9  A

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence for
RA2_day 14

Rare
Sugar  N  Mean  Grouping
```

30	4	31.3	A
20	4	29.5	A
0	4	22.0	B
10	4	12.5	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA2_day 14

Starch	Rare Sugar	N	Mean	Grouping
9	30	2	35.8	A
11	20	2	33.0	A
11	30	2	26.9	A B
9	20	2	26.1	A B
11	0	2	26.0	A B
9	0	2	18.1	B C
11	10	2	13.4	C
9	10	2	11.7	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA3_day 14

Starch	N	Mean	Grouping
11	8	28.9	A
9	8	26.5	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA3_day 14

Rare Sugar	N	Mean	Grouping
30	4	30.3	A
0	4	28.0	A B
20	4	26.6	A B
10	4	26.1	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA3_day 14

Starch	Rare Sugar	N	Mean	Grouping
11	30	2	36.2	A
9	10	2	28.6	B
11	0	2	28.3	B
11	20	2	27.6	B
9	0	2	27.6	B
9	20	2	25.5	B
9	30	2	24.5	B

```
11      10     2  23.5    B
```

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA4_day 14

```
Starch  N  Mean  Grouping
11      8   9.8  A
 9      8   0.0    B
```

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA4_day 14

```
Rare
Sugar  N  Mean  Grouping
10     4  13.6  A
30     4   6.1    B
 0     4   0.0      C
20     4  -0.0      C
```

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA4_day 14

```
        Rare
Starch  Sugar  N  Mean  Grouping
11      10     2  27.2  A
11      30     2  12.1    B
 9       0     2   0.0      C
 9      10     2   0.0      C
 9      20     2  -0.0      C
11      20     2  -0.0      C
 9      30     2  -0.0      C
11       0     2  -0.0      C
```

Means that do not share a letter are significantly different.

Table A. 20. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on relative area of each compartment (peaks) obtained by NNLS using adjusted SS for Tests; day 21*

General Linear Model: RA1_day 21, RA2_day 21, ... versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for RA1_day 21, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	889.38	889.38	889.38	133.43	0.000
Rare Sugar	3	802.16	802.16	267.39	40.11	0.000
Starch*Rare Sugar	3	86.87	86.87	28.96	4.34	0.043
Error	8	53.33	53.33	6.67		
Total	15	1831.74				

S = 2.58180   R-Sq = 97.09%   R-Sq(adj) = 94.54%

Analysis of Variance for RA2_day 21, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	0.198	0.198	0.198	0.04	0.851
Rare Sugar	3	211.489	211.489	70.496	13.39	0.002
Starch*Rare Sugar	3	263.151	263.151	87.717	16.66	0.001
Error	8	42.122	42.122	5.265		
Total	15	516.960				

S = 2.29461   R-Sq = 91.85%   R-Sq(adj) = 84.72%

Analysis of Variance for RA3_day 21, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	370.66	370.66	370.66	197.08	0.000
Rare Sugar	3	408.03	408.03	136.01	72.32	0.000
Starch*Rare Sugar	3	332.08	332.08	110.69	58.86	0.000
Error	8	15.05	15.05	1.88		
Total	15	1125.81				

S = 1.37140   R-Sq = 98.66%   R-Sq(adj) = 97.49%

Analysis of Variance for RA4_day 21, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	100.80	100.80	100.80	3487.94	0.000
Rare Sugar	3	302.40	302.40	100.80	3487.94	0.000
Starch*Rare Sugar	3	302.40	302.40	100.80	3487.94	0.000
Error	8	0.23	0.23	0.03		
Total	15	705.84				

S = 0.17   R-Sq = 99.97%   R-Sq(adj) = 99.94%

Grouping Information Using Tukey Method and 95.0% Confidence for RA1_day 21

Starch	N	Mean	Grouping
9	8	55.2	A
11	8	40.3	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA1_day 21

Rare Sugar	N	Mean	Grouping
10	4	54.0	A
0	4	51.9	A
20	4	49.1	A
30	4	35.8	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA1_day 21

Starch	Rare Sugar	N	Mean	Grouping
9	10	2	64.2	A
9	20	2	56.1	A B
9	0	2	55.8	A B
11	0	2	48.0	B C
9	30	2	44.6	C
11	10	2	43.8	C
11	20	2	42.1	C
11	30	2	27.1	D

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA2_day 21

Starch	N	Mean	Grouping
11	8	25.5	A
9	8	25.3	A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA2_day 21

Rare Sugar	N	Mean	Grouping

10	4	29.8	A
20	4	26.4	A
30	4	25.6	A
0	4	19.7	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA2_day 21

Starch	Rare Sugar	N	Mean	Grouping
9	10	2	32.0	A
9	30	2	31.0	A B
11	20	2	30.4	A B
11	10	2	27.7	A B C
11	0	2	23.7	A B C D
9	20	2	22.4	B C D
11	30	2	20.2	C D
9	0	2	15.7	D

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA3_day 21

Starch	N	Mean	Grouping
11	8	29.2	A
9	8	19.6	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA3_day 21

Rare Sugar	N	Mean	Grouping
30	4	28.6	A
0	4	28.4	A
20	4	24.5	B
10	4	16.1	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA3_day 21

Starch	Rare Sugar	N	Mean	Grouping
11	30	2	32.7	A
9	0	2	28.5	A B
11	10	2	28.4	A B
11	0	2	28.3	A B
11	20	2	27.5	A B
9	30	2	24.5	B C
9	20	2	21.5	C

9	10	2	3.9	D

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA4_day 21

Starch	N	Mean	Grouping
11	8	5.0	A
9	8	0.0	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA4_day 21

Rare Sugar	N	Mean	Grouping
30	4	10.0	A
20	4	0.0	B
10	4	-0.0	B
0	4	-0.0	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA4_day 21

Starch	Rare Sugar	N	Mean	Grouping
11	30	2	20.1	A
9	20	2	0.0	B
9	0	2	0.0	B
11	20	2	0.0	B
9	30	2	0.0	B
11	10	2	-0.0	B
9	10	2	-0.0	B
11	0	2	-0.0	B

Means that do not share a letter are significantly different.

Table A. 21. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on relative area of each compartment (peaks) obtained by NNLS using adjusted SS for Tests; day 28*

General Linear Model: RA1_day 28, RA2_day 28, ... versus Starch, Rare Sugar

Factor	Type	Levels	Values
Starch	fixed	2	9, 11
Rare Sugar	fixed	4	0, 10, 20, 30

Analysis of Variance for RA1_day 28, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	395.31	395.31	395.31	161.91	0.000
Rare Sugar	3	784.91	784.91	261.64	107.16	0.000
Starch*Rare Sugar	3	272.16	272.16	90.72	37.16	0.000
Error	8	19.53	19.53	2.44		
Total	15	1471.91				

S = 1.56253   R-Sq = 98.67%   R-Sq(adj) = 97.51%

Analysis of Variance for RA2_day 28, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	230.20	230.20	230.20	146.61	0.000
Rare Sugar	3	521.54	521.54	173.85	110.72	0.000
Starch*Rare Sugar	3	265.39	265.39	88.46	56.34	0.000
Error	8	12.56	12.56	1.57		
Total	15	1029.70				

S = 1.25306   R-Sq = 98.78%   R-Sq(adj) = 97.71%

Analysis of Variance for RA3_day 28, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Starch	1	22.208	22.208	22.208	12.31	0.008
Rare Sugar	3	47.325	47.325	15.775	8.74	0.007
Starch*Rare Sugar	3	29.869	29.869	9.956	5.52	0.024
Error	8	14.433	14.433	1.804		
Total	15	113.835				

S = 1.34320   R-Sq = 87.32%   R-Sq(adj) = 76.23%

Grouping Information Using Tukey Method and 95.0% Confidence for RA1_day 28

Starch	N	Mean	Grouping
9	8	44.0	A
11	8	34.1	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA1_day 28

Rare Sugar	N	Mean	Grouping
10	4	48.9	A
20	4	39.4	B
0	4	38.8	B
30	4	29.1	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA1_day 28

Starch	Rare Sugar	N	Mean	Grouping
9	10	2	61.0	A
9	20	2	42.2	B
9	0	2	40.5	B
11	0	2	37.1	B C
11	10	2	36.9	B C
11	20	2	36.5	B C
9	30	2	32.4	C
11	30	2	25.8	D

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA2_day 28

Starch	N	Mean	Grouping
11	8	34.2	A
9	8	26.6	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA2_day 28

Rare Sugar	N	Mean	Grouping
30	4	37.5	A
20	4	31.8	B
0	4	30.7	B
10	4	21.6	C

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA2_day 28

Starch	Rare Sugar	N	Mean	Grouping
11	30	2	37.6	A

9	30	2	37.4	A
11	20	2	33.8	A B
11	0	2	33.1	A B C
11	10	2	32.3	B C
9	20	2	29.7	B C
9	0	2	28.4	C
9	10	2	10.9	D

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA3_day 28

Starch	N	Mean	Grouping
11	8	31.7	A
9	8	29.4	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA3_day 28

Rare Sugar	N	Mean	Grouping
30	4	33.4	A
0	4	30.5	A B
10	4	29.5	B
20	4	28.9	B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence for RA3_day 28

Starch	Rare Sugar	N	Mean	Grouping
11	30	2	36.5	A
9	0	2	31.1	B
11	10	2	30.8	B
9	30	2	30.2	B
11	0	2	29.8	B
11	20	2	29.7	B
9	10	2	28.1	B
9	20	2	28.0	B

Means that do not share a letter are significantly different.

Table A. 22. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on peak temperature of TGA curves using adjusted SS for Tests*

General Linear Model: Peak Temp versus RareSugar ; SPI

```
Factor  Type   Levels  Values
Rare    fixed       4  0; 10; 20; 30
soy     fixed       2  0; 2


Analysis of Variance for Peak Temp, using Adjusted SS for Tests

Source    DF   Seq SS   Adj SS   Adj MS      F      P
Rare       3  531.923  531.923  177.308  31.18  0.000
soy        1    2.512    2.512    2.512   0.44  0.525
Rare*soy   3   71.006   71.006   23.669   4.16  0.047
Error      8   45.486   45.486    5.686
Total     15  650.927


S = 2.38449   R-Sq = 93.01%   R-Sq(adj) = 86.90%


Grouping Information Using Tukey Method and 95.0% Confidence

Rare  N   Mean  Grouping
30    4  137.4  A
20    4  132.3  A B
10    4  129.6    B
 0    4  121.4      C

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

soy  N   Mean  Grouping
0    8  130.6  A
2    8  129.8  A

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

Rare  soy  N   Mean  Grouping
30    0    2  141.1  A
30    2    2  133.7  A B
20    2    2  133.5  A B
20    0    2  131.2    B C
10    0    2  130.4    B C
10    2    2  128.9    B C D
 0    2    2  123.1      C D
 0    0    2  119.7        D

Means that do not share a letter are significantly different.
```

Table A. 23. *Analysis of variance of starch based confectionery. Effect of starch and rare sugar concentration on calculated crystallinity based on X-ray diffraction results of formulation using adjusted SS for Tests*

General Linear Model: Crystallinity versus Rare, starch

```
Factor  Type   Levels  Values
Rare    fixed       2  0, 30
starch  fixed       2  9, 11


Analysis of Variance for Crystallinity, using Adjusted SS for Tests

Source       DF   Seq SS   Adj SS   Adj MS      F      P
Rare          1  112.500  112.500  112.500  50.00  0.002
starch        1    4.500    4.500    4.500   2.00  0.230
Rare*starch   1   50.000   50.000   50.000  22.22  0.009
Error         4    9.000    9.000    2.250
Total         7  176.000


S = 1.5   R-Sq = 94.89%   R-Sq(adj) = 91.05%


Grouping Information Using Tukey Method and 95.0% Confidence

Rare  N  Mean  Grouping
 0    4  18.3  A
30    4  10.8    B

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

starch  N  Mean  Grouping
 9      4  15.3  A
11      4  13.8  A

Means that do not share a letter are significantly different.


Grouping Information Using Tukey Method and 95.0% Confidence

Rare  starch  N  Mean  Grouping
 0     9      2  21.5  A
 0    11      2  15.0    B
30    11      2  12.5    B
30     9      2   9.0    B

Means that do not share a letter are significantly different.
```

B. One way analysis of variance for effect of storage

Table B. 1. *One way analysis of variance (ANOVA) for effect of storage on (1) water activity (aw); (2) moisture content (MC %); (3) T1; (4) T2 of each formulation using adjusted SS for Tests*

(1.1) One-way ANOVA: Water activity of 11_R0 versus Day

```
Source  DF         SS         MS     F      P
Day      4  0,0034012  0,0008503  8,78  0,017
Error    5  0,0004841  0,0000968
Total    9  0.0038853

S = 0.009840   R-Sq = 87.54%   R-Sq(adj) = 77.57%


                            Individual 95% CIs For Mean Based on
                            Pooled StDev
Level  N     Mean    StDev  -+---------+---------+---------+--------
 0     2  0.69065  0.00233                      (------*------)
 7     2  0.65120  0.00750      (------*-------)
14     2  0.64350  0.00537   (------*-------)
21     2  0.66340  0.01980          (------*-------)
28     2  0.63930  0.00127  (------*------)
                            -+---------+---------+---------+--------
                            0.625     0.650     0.675     0.700

Pooled StDev = 0.00984


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 0   2  0.69065  A
21   2  0.66340  A B
 7   2  0.65120  A B
14   2  0.64350    B
28   2  0.63930    B

Means that do not share a letter are significantly different.
```

(1.2) One-way ANOVA: Water activity of 11_R10 versus Day

```
Source  DF         SS         MS      F      P
Day      4  0.0082542  0.0020635  94.41  0.000
Error    5  0.0001093  0.0000219
Total    9  0.0083635

S = 0.004675   R-Sq = 98.69%   R-Sq(adj) = 97.65%


                            Individual 95% CIs For Mean Based on
                            Pooled StDev
Level  N     Mean    StDev  -+---------+---------+---------+--------
 0     2  0.65930  0.00255                              (--*--)
```

```
 7     2  0.60265  0.00233            (--*--)
14     2  0.63045  0.00544                     (--*--)
21     2  0.57460  0.00269   (--*-)
28     2  0.60290  0.00778            (--*--)
                            -+---------+---------+---------+--------
                            0.570     0.600     0.630     0.660

Pooled StDev = 0.00468


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 0   2  0.65930  A
14   2  0.63045    B
28   2  0.60290      C
 7   2  0.60265      C
21   2  0.57460        D

Means that do not share a letter are significantly different.
```

(1.3) One-way ANOVA: Water activity of 11_R20 versus Day

```
Source  DF        SS        MS      F      P
Day      4  0.004589  0.001147  10.65  0.012
Error    5  0.000538  0.000108
Total    9  0.005127

S = 0.01038   R-Sq = 89.50%   R-Sq(adj) = 81.10%


                            Individual 95% CIs For Mean Based on
                            Pooled StDev
Level  N     Mean    StDev  --+---------+---------+---------+-------
 0     2  0.62150  0.01018                        (-------*------)
 7     2  0.58165  0.00785         (-------*------)
14     2  0.61060  0.01428                     (------*-------)
21     2  0.56270  0.01216  (------*-------)
28     2  0.58135  0.00460         (-------*------)
                            --+---------+---------+---------+-------
                            0.550     0.575     0.600     0.625

Pooled StDev = 0.01038


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 0   2  0.62150  A
14   2  0.61060  A
 7   2  0.58165  A B
28   2  0.58135  A B
21   2  0.56270    B

Means that do not share a letter are significantly different.
```

(1.4) One-way ANOVA: Water activity of 11_R30 versus Day

```
Source  DF        SS        MS      F      P
Day      4  0.004010  0.001002  10.01  0.013
Error    5  0.000501  0.000100
Total    9  0.004510

S = 0.01001   R-Sq = 88.90%   R-Sq(adj) = 80.02%


                            Individual 95% CIs For Mean Based on
                            Pooled StDev
Level  N     Mean    StDev  ------+---------+---------+---------+---
 0     2  0.61495  0.00955                           (------*------)
 7     2  0.57305  0.00092          (------*------)
14     2  0.57565  0.01831           (------*-------)
21     2  0.55330  0.00735  (------*-------)
28     2  0.57660  0.00438           (-------*------)
                            ------+---------+---------+---------+---
                                0.550     0.575     0.600     0.625

Pooled StDev = 0.01001


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 0   2  0.61495  A
28   2  0.57660  A B
14   2  0.57565  A B
 7   2  0.57305    B
21   2  0.55330    B

Means that do not share a letter are significantly different.
```

(1.5) One-way ANOVA: Water activity of 9_R0 versus Day

```
Source  DF        SS        MS     F      P
Day      4  0.003715  0.000929  6.63  0.031
Error    5  0.000701  0.000140
Total    9  0.004416

S = 0.01184   R-Sq = 84.13%   R-Sq(adj) = 71.44%


                            Individual 95% CIs For Mean Based on
                            Pooled StDev
Level  N     Mean    StDev  -------+---------+---------+---------+--
 0     2  0.66075  0.00007                      (------*------)
 7     2  0.62395  0.01209          (------*------)
14     2  0.62425  0.01266          (------*------)
21     2  0.60080  0.01725  (------*------)
28     2  0.62295  0.00983         (-------*------)
                            -------+---------+---------+---------+--
                                 0.600     0.630     0.660     0.690
```

```
Pooled StDev = 0.01184


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 0   2  0.66075  A
14   2  0.62425  A B
 7   2  0.62395  A B
28   2  0.62295  A B
21   2  0.60080    B

Means that do not share a letter are significantly different.
```

(1.6) One-way ANOVA: Water activity of 9_R10 versus Day

```
Source  DF         SS         MS     F      P
Day      4  0.0023226  0.0005806  6.21  0.035
Error    5  0.0004672  0.0000934
Total    9  0.0027898

S = 0.009667   R-Sq = 83.25%   R-Sq(adj) = 69.85%


                            Individual 95% CIs For Mean Based on
                            Pooled StDev
Level  N     Mean    StDev  -------+---------+---------+---------+--
 0     2  0.56625  0.00205                      (--------*--------)
 7     2  0.54510  0.00212            (--------*-------)
14     2  0.54510  0.00834            (--------*-------)
21     2  0.52380  0.01937  (--------*--------)
28     2  0.56310  0.00368                     (--------*-------)
                            -------+---------+---------+---------+--
                                 0.520     0.540     0.560     0.580

Pooled StDev = 0.00967


Grouping Information Using Tukey Method

Day  N      Mean  Grouping
 0   2  0.566250  A
28   2  0.563100  A
14   2  0.545100  A B
 7   2  0.545100  A B
21   2  0.523800    B

Means that do not share a letter are significantly different.
```

(1.7) One-way ANOVA: Water activity of 9_R20 versus Day

```
Source  DF        SS        MS     F      P
Day      4  0.002150  0.000538  4.75  0.059
Error    5  0.000566  0.000113
```

```
Total    9  0.002716

S = 0.01064   R-Sq = 79.17%   R-Sq(adj) = 62.50%


                                Individual 95% CIs For Mean Based on
                                Pooled StDev
Level  N     Mean    StDev  -------+---------+---------+---------+--
 0     2  0.56550  0.00127                    (---------*--------)
 7     2  0.54865  0.00290            (--------*---------)
14     2  0.56600  0.02319                    (---------*---------)
21     2  0.52630  0.00000  (---------*---------)
28     2  0.55730  0.00424                (---------*--------)
                            -------+---------+---------+---------+--
                                 0.520     0.540     0.560     0.580

Pooled StDev = 0.01064


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
14   2  0.56600  A
 0   2  0.56550  A
28   2  0.55730  A
 7   2  0.54865  A
21   2  0.52630  A

Means that do not share a letter are significantly different.
```

(1.8) One-way ANOVA: Water activity of 9_R30 versus Day

```
Source  DF         SS         MS     F      P
Day      4  0.0022423  0.0005606  9.27  0.016
Error    5  0.0003024  0.0000605
Total    9  0.0025447

S = 0.007777   R-Sq = 88.12%   R-Sq(adj) = 78.61%


                                Individual 95% CIs For Mean Based on
                                Pooled StDev
Level  N     Mean    StDev  ---+---------+---------+---------+------
 0     2  0.54385  0.00474                  (------*------)
 7     2  0.52850  0.00382          (------*------)
14     2  0.51345  0.00714   (------*------)
21     2  0.50780  0.01457  (------*------)
28     2  0.54385  0.00148                  (------*------)
                            ---+---------+---------+---------+------
                             0.500     0.520     0.540     0.560

Pooled StDev = 0.00778


Grouping Information Using Tukey Method

Day  N      Mean  Grouping
28   2  0.543850  A
```

```
 0   2  0.543850  A
 7   2  0.528500  A B
14   2  0.513450  A B
21   2  0.507800    B
```

Means that do not share a letter are significantly different.

(2.1) One-way ANOVA: Moisture Content (MC%) of 11_R0 versus Day

```
Source  DF     SS    MS     F      P
Day      4   8.36  2.09  1.81  0.265
Error    5   5.78  1.16
Total    9  14.14

S = 1.075   R-Sq = 59.12%   R-Sq(adj) = 26.42%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  --------+---------+---------+---------+-
 0     2  14.945  0.007              (---------*--------)
 7     2  13.014  2.201     (---------*---------)
14     2  13.236  0.320      (---------*---------)
21     2  12.629  0.618   (---------*---------)
28     2  12.319  0.670  (---------*--------)
                         --------+---------+---------+---------+-
                              12.0      14.0      16.0      18.0

Pooled StDev = 1.075


Grouping Information Using Tukey Method

Day  N    Mean  Grouping
 0   2  14.945  A
14   2  13.236  A
 7   2  13.014  A
21   2  12.629  A
28   2  12.319  A
```

Means that do not share a letter are significantly different.

(2.2) One-way ANOVA: Moisture Content (MC%) of 11_R10 versus Day

```
Source  DF      SS     MS      F      P
Day      4  24.932  6.233  35.25  0.001
Error    5   0.884  0.177
Total    9  25.817

S = 0.4205   R-Sq = 96.58%   R-Sq(adj) = 93.84%


                         Individual 95% CIs For Mean Based on Pooled
StDev
Level  N    Mean  StDev     +---------+---------+---------+---------
 0     2  15.204  0.199                             (----*----)
 7     2  14.668  0.030                          (----*----)
```

```
14     2  11.823  0.899         (----*----)
21     2  12.219  0.163           (----*-----)
28     2  11.314  0.092     (----*-----)
                            +---------+---------+---------+---------
                         10.5      12.0      13.5      15.0

Pooled StDev = 0.421


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 0   2  15.2041  A
 7   2  14.6681  A
21   2  12.2186    B
14   2  11.8234    B
28   2  11.3144    B

Means that do not share a letter are significantly different.
```

(2.3) One-way ANOVA: Moisture Content (MC%) of 11_R20 versus Day

```
Source  DF      SS     MS     F      P
Day      4  15.415  3.854  4.41  0.068
Error    5   4.371  0.874
Total    9  19.786

S = 0.9350   R-Sq = 77.91%   R-Sq(adj) = 60.23%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ---------+---------+---------+---------+
 0     2  15.444  1.832                   (-------*--------)
 7     2  13.696  0.904           (-------*--------)
14     2  12.534  0.288     (--------*-------)
21     2  11.965  0.045  (--------*-------)
28     2  12.520  0.336     (--------*-------)
                         ---------+---------+---------+---------+
                               12.0      14.0      16.0      18.0

Pooled StDev = 0.935


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 0   2  15.4439  A
 7   2  13.6956  A
14   2  12.5335  A
28   2  12.5196  A
21   2  11.9653  A

Means that do not share a letter are significantly different.
```

(2.4) One-way ANOVA: Moisture Content (MC%) of 11_R30 versus Day

```
Source  DF      SS      MS      F      P
Day      4  5.7400  1.4350  17.57  0.004
Error    5  0.4084  0.0817
Total    9  6.1484

S = 0.2858   R-Sq = 93.36%   R-Sq(adj) = 88.04%


                         Individual 95% CIs For Mean Based on Pooled
StDev
Level  N    Mean  StDev    -+---------+---------+---------+--------
 0     2  13.847  0.069                       (-----*------)
 7     2  14.428  0.147                              (-----*------)
14     2  12.523  0.040     (------*-----)
21     2  12.479  0.410    (------*-----)
28     2  13.149  0.461             (-----*------)
                           -+---------+---------+---------+--------
                         12.00     12.80     13.60     14.40

Pooled StDev = 0.286


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 7   2  14.4277  A
 0   2  13.8473  A B
28   2  13.1494    B C
14   2  12.5235      C
21   2  12.4789      C

Means that do not share a letter are significantly different.
```

(2.5) One-way ANOVA: Moisture Content (MC%) of 9_R0 versus Day

```
Source  DF      SS     MS     F      P
Day      4   9.192  2.298  6.30  0.034
Error    5   1.825  0.365
Total    9  11.016

S = 0.6041   R-Sq = 83.44%   R-Sq(adj) = 70.19%


                         Individual 95% CIs For Mean Based on Pooled
StDev
Level  N    Mean  StDev     +---------+---------+---------+---------
 0     2  14.092  0.011                      (------*-------)
 7     2  14.366  0.616                       (-------*------)
14     2  12.954  0.895              (------*-------)
21     2  13.239  0.499                (------*-------)
28     2  11.652  0.628     (-------*------)
                            +---------+---------+---------+---------
                         10.5      12.0      13.5      15.0
```

```
Pooled StDev = 0.604


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 7   2  14.3659  A
 0   2  14.0924  A
21   2  13.2386  A B
14   2  12.9543  A B
28   2  11.6519    B

Means that do not share a letter are significantly different.
```

(2.6) One-way ANOVA: Moisture Content (MC%) of 9_R10 versus Day

```
Source  DF      SS     MS     F      P
Day      4  17.591  4.398  5.16  0.051
Error    5   4.259  0.852
Total    9  21.849

S = 0.9229   R-Sq = 80.51%   R-Sq(adj) = 64.91%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ---+---------+---------+---------+------
 0     2  12.436  0.116         (-------*--------)
 7     2  14.864  1.818                     (-------*--------)
14     2  12.234  0.718        (-------*--------)
21     2  11.107  0.626  (--------*-------)
28     2  11.386  0.184    (-------*-------)
                         ---+---------+---------+---------+------
                          10.0      12.0      14.0      16.0

Pooled StDev = 0.923


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 7   2  14.8635  A
 0   2  12.4362  A B
14   2  12.2343  A B
28   2  11.3865  A B
21   2  11.1075    B

Means that do not share a letter are significantly different.
```

(2.7) One-way ANOVA: Moisture Content (MC%) of 9_R20 versus Day

```
Source  DF     SS     MS      F      P
Day      4  4.536  1.134  10.98  0.011
Error    5  0.517  0.103
Total    9  5.052
```

```
S = 0.3214   R-Sq = 89.78%   R-Sq(adj) = 81.60%


                              Individual 95% CIs For Mean Based on Pooled
StDev
Level  N    Mean  StDev   -+---------+---------+---------+--------
 0     2  12.414  0.058            (------*------)
 7     2  13.685  0.488                            (------*------)
14     2  12.157  0.042         (------*------)
21     2  11.720  0.242   (------*-------)
28     2  12.090  0.464        (------*------)
                          -+---------+---------+---------+--------
                        11.20     12.00     12.80     13.60

Pooled StDev = 0.321


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 7   2  13.6845  A
 0   2  12.4138  A B
14   2  12.1569    B
28   2  12.0895    B
21   2  11.7195    B

Means that do not share a letter are significantly different.
```

(2.8) One-way ANOVA: Moisture Content (MC%) of 9_R30 versus Day

```
Source  DF     SS     MS     F      P
Day      4  2.140  0.535  0.85  0.551
Error    5  3.153  0.631
Total    9  5.293

S = 0.7941   R-Sq = 40.44%   R-Sq(adj) = 0.00%


                              Individual 95% CIs For Mean Based on
                              Pooled StDev
Level  N    Mean  StDev  ------+---------+---------+---------+---
 0     2  12.187  0.193        (-----------*-----------)
 7     2  12.725  0.286            (-----------*-----------)
14     2  11.481  0.057  (-----------*-----------)
21     2  11.592  0.254   (-----------*-----------)
28     2  12.303  1.722        (------------*-----------)
                         ------+---------+---------+---------+---
                            10.8      12.0      13.2      14.4

Pooled StDev = 0.794


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 7   2  12.7247  A
28   2  12.3028  A
```

```
 0   2  12.1868  A
21   2  11.5925  A
14   2  11.4814  A

Means that do not share a letter are significantly different.
```

(3.1) One-way ANOVA: T1 of 11_R0 versus Day

```
Source  DF     SS     MS     F      P
Day      4  5.288  1.322  3.00  0.129
Error    5  2.201  0.440
Total    9  7.490

S = 0.6635   R-Sq = 70.61%   R-Sq(adj) = 47.10%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  --------+---------+---------+---------+-
 0     2  49.677  0.754    (---------*---------)
 7     2  51.020  1.092              (---------*---------)
14     2  51.070  0.165               (---------*---------)
21     2  49.458  0.096  (---------*---------)
28     2  49.566  0.634   (---------*---------)
                         --------+---------+---------+---------+-
                              49.2      50.4      51.6      52.8

Pooled StDev = 0.664


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
14   2  51.0695  A
 7   2  51.0195  A
 0   2  49.6775  A
28   2  49.5661  A
21   2  49.4580  A

Means that do not share a letter are significantly different.
```

(3.2) One-way ANOVA: T1 of 11_R10 versus Day

```
Source  DF     SS     MS     F      P
Day      4  2.157  0.539  2.56  0.165
Error    5  1.053  0.211
Total    9  3.210

S = 0.4588   R-Sq = 67.20%   R-Sq(adj) = 40.97%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ---+---------+---------+---------+------
 0     2  48.201  0.716                (----------*---------)
 7     2  47.485  0.000        (----------*---------)
14     2  47.916  0.016              (---------*---------)
21     2  47.048  0.451   (---------*----------)
```

```
28     2  47.034  0.579  (----------*---------)
                         ---+---------+---------+---------+------
                         46.40     47.20     48.00     48.80

Pooled StDev = 0.459


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 0   2  48.2005  A
14   2  47.9155  A
 7   2  47.4850  A
21   2  47.0480  A
28   2  47.0339  A

Means that do not share a letter are significantly different.
```

(3.3) One-way ANOVA: T1 of 11_R20 versus Day

```
Source  DF     SS     MS     F      P
Day      4  6.440  1.610  4.18  0.074
Error    5  1.928  0.386
Total    9  8.368

S = 0.6209   R-Sq = 76.96%   R-Sq(adj) = 58.53%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  -----+---------+---------+---------+----
 0     2  45.963  0.480           (---------*--------)
 7     2  44.873  0.351  (---------*--------)
14     2  45.200  0.490    (---------*--------)
21     2  46.875  1.154                 (---------*--------)
28     2  46.752  0.048                (---------*--------)
                         -----+---------+---------+---------+----
                           44.4      45.6      46.8      48.0

Pooled StDev = 0.621


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
21   2  46.8750  A
28   2  46.7517  A
 0   2  45.9635  A
14   2  45.1995  A
 7   2  44.8730  A

Means that do not share a letter are significantly different.
```

(3.4) One-way ANOVA: T1 of 11_R30 versus Day

```
Source  DF     SS     MS     F      P
Day      4  0.564  0.141  0.19  0.931
```

```
Error    5  3.620  0.724
Total    9  4.184

S = 0.8509   R-Sq = 13.48%   R-Sq(adj) = 0.00%


                             Individual 95% CIs For Mean Based on
                             Pooled StDev
Level  N    Mean  StDev   --+---------+---------+---------+-------
 0     2  41.300  0.309   (--------------*--------------)
 7     2  41.738  0.218       (---------------*---------------)
14     2  41.475  1.022    (---------------*--------------)
21     2  41.985  1.420         (---------------*---------------)
28     2  41.506  0.645     (--------------*---------------)
                          --+---------+---------+---------+-------
                         40.0      41.0      42.0      43.0

Pooled StDev = 0.851


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
21   2  41.9850  A
 7   2  41.7380  A
28   2  41.5063  A
14   2  41.4750  A
 0   2  41.2995  A

Means that do not share a letter are significantly different.
```

(3.5) One-way ANOVA: T1 of 9_R0 versus Day

```
Source  DF     SS     MS     F      P
Day      4  0.922  0.231  0.93  0.516
Error    5  1.246  0.249
Total    9  2.169

S = 0.4992   R-Sq = 42.54%   R-Sq(adj) = 0.00%


                             Individual 95% CIs For Mean Based on
                             Pooled StDev
Level  N    Mean  StDev  -----+---------+---------+---------+----
 0     2  50.948  0.780  (------------*------------)
 7     2  51.569  0.424           (------------*------------)
14     2  51.566  0.206           (------------*------------)
21     2  51.883  0.542               (------------*------------)
28     2  51.530  0.348          (------------*------------)
                         -----+---------+---------+---------+----
                            50.40     51.10     51.80     52.50

Pooled StDev = 0.499


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
```

```
21   2  51.8835  A
 7   2  51.5690  A
14   2  51.5660  A
28   2  51.5297  A
 0   2  50.9485  A

Means that do not share a letter are significantly different.
```

(3.6) One-way ANOVA: T1 of 9_R10 versus Day

```
Source  DF      SS     MS     F      P
Day      4  10.235  2.559  5.85  0.040
Error    5   2.187  0.437
Total    9  12.422

S = 0.6614   R-Sq = 82.39%   R-Sq(adj) = 68.31%


                               Individual 95% CIs For Mean Based on
                               Pooled StDev
Level  N    Mean  StDev   --+---------+---------+---------+-------
 0     2  54.884  0.686   (-------*-------)
 7     2  56.099  0.042          (-------*-------)
14     2  57.204  0.845                (-------*-------)
21     2  57.295  0.557                 (-------*-------)
28     2  55.104  0.831    (-------*-------)
                          --+---------+---------+---------+-------
                          54.0      55.5      57.0      58.5

Pooled StDev = 0.661


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
21   2  57.2950  A
14   2  57.2045  A
 7   2  56.0990  A
28   2  55.1038  A
 0   2  54.8840  A

Means that do not share a letter are significantly different.
```

(3.7) One-way ANOVA: T1 of 9_R20 versus Day

```
Source  DF     SS    MS     F      P
Day      4  14.17  3.54  2.63  0.159
Error    5   6.74  1.35
Total    9  20.90

S = 1.161   R-Sq = 67.77%   R-Sq(adj) = 41.99%


                               Individual 95% CIs For Mean Based on
                               Pooled StDev
Level  N    Mean  StDev  ------+---------+---------+---------+---
 0     2  49.785  1.425      (----------*---------)
 7     2  48.954  0.487  (----------*---------)
```

```
14     2  50.019  1.164        (---------*----------)
21     2  52.437  1.698                    (---------*----------)
28     2  49.628  0.480      (---------*----------)
                          ------+---------+---------+---------+---
                             48.0      50.0      52.0      54.0

Pooled StDev = 1.161


Grouping Information Using Tukey Method

Day  N    Mean  Grouping
21   2  52.437  A
14   2  50.019  A
 0   2  49.785  A
28   2  49.628  A
 7   2  48.954  A

Means that do not share a letter are significantly different.
```

(3.8) One-way ANOVA: T1 of 9_R30 versus Day

```
Source  DF      SS     MS     F      P
Day      4   7.336  1.834  2.13  0.215
Error    5   4.313  0.863
Total    9  11.650

S = 0.9288   R-Sq = 62.98%   R-Sq(adj) = 33.36%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ----+---------+---------+---------+-----
 0     2  46.340  0.132    (----------*----------)
 7     2  46.980  0.950        (----------*----------)
14     2  47.474  1.507           (----------*-----------)
21     2  48.489  0.982                  (----------*-----------)
28     2  46.094  0.398  (----------*-----------)
                         ----+---------+---------+---------+-----
                          45.0      46.5      48.0      49.5

Pooled StDev = 0.929


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
21   2  48.4885  A
14   2  47.4745  A
 7   2  46.9805  A
 0   2  46.3405  A
28   2  46.0941  A

Means that do not share a letter are significantly different.
```

(4.1) One-way ANOVA: T2 of 11_R0 versus Day

```
Source  DF      SS      MS      F      P
Day      4  0.8126  0.2032  12.73  0.008
Error    5  0.0798  0.0160
Total    9  0.8924

S = 0.1263   R-Sq = 91.06%   R-Sq(adj) = 83.91%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  -------+---------+---------+---------+--
 0     2  1.9630  0.1344         (-----*------)
 7     2  2.5325  0.0983                         (-----*------)
14     2  1.7605  0.1294   (-----*------)
21     2  1.7500  0.1188  (------*------)
28     2  2.0454  0.1456           (-----*------)
                          -------+---------+---------+---------+--
                               1.75      2.10      2.45      2.80

Pooled StDev = 0.1263


Grouping Information Using Tukey Method

Day  N    Mean  Grouping
 7   2  2.5325  A
28   2  2.0454  A B
 0   2  1.9630    B
14   2  1.7605    B
21   2  1.7500    B

Means that do not share a letter are significantly different.
```

(4.2) One-way ANOVA: T2 of 11_R10 versus Day

```
Source  DF       SS       MS       F      P
Day      4  0.69738  0.17434  129.19  0.000
Error    5  0.00675  0.00135
Total    9  0.70413

S = 0.03674   R-Sq = 99.04%   R-Sq(adj) = 98.28%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  -----+---------+---------+---------+----
 0     2  1.9525  0.0007          (--*--)
 7     2  2.4140  0.0325                            (--*-)
14     2  1.7030  0.0113  (--*--)
21     2  1.7090  0.0325   (-*--)
28     2  2.0789  0.0671               (--*--)
                          -----+---------+---------+---------+----
                             1.75      2.00      2.25      2.50

Pooled StDev = 0.0367


Grouping Information Using Tukey Method
```

```
Day  N     Mean  Grouping
 7   2  2.41400  A
28   2  2.07885    B
 0   2  1.95250    B
21   2  1.70900      C
14   2  1.70300      C

Means that do not share a letter are significantly different.
```

(4.3) One-way ANOVA: T2 of 11_R20 versus Day

```
Source  DF       SS       MS      F      P
Day      4  0.61080  0.15270  16.90  0.004
Error    5  0.04518  0.00904
Total    9  0.65598

S = 0.09506   R-Sq = 93.11%   R-Sq(adj) = 87.60%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  -----+---------+---------+---------+----
 0     2  1.7835  0.0955                   (----*-----)
 7     2  1.9495  0.1195                        (-----*-----)
14     2  1.5740  0.1032            (----*-----)
21     2  1.2150  0.0933  (----*-----)
28     2  1.5564  0.0491           (-----*-----)
                          -----+---------+---------+---------+----
                             1.20      1.50      1.80      2.10

Pooled StDev = 0.0951


Grouping Information Using Tukey Method

Day  N    Mean  Grouping
 7   2  1.9495  A
 0   2  1.7835  A B
14   2  1.5740  A B C
28   2  1.5564    B C
21   2  1.2150      C

Means that do not share a letter are significantly different.
```

(4.4) One-way ANOVA: T2 of 11_R30 versus Day

```
Source  DF      SS      MS      F      P
Day      4  1.4364  0.3591  10.78  0.011
Error    5  0.1665  0.0333
Total    9  1.6029

S = 0.1825   R-Sq = 89.61%   R-Sq(adj) = 81.30%


                          Individual 95% CIs For Mean Based on Pooled
StDev
```

```
Level  N    Mean   StDev     +---------+---------+---------+---------
 0     2  2.1610  0.1513            (-----*------)
 7     2  2.6515  0.0785                     (------*------)
14     2  2.0285  0.1761         (------*-----)
21     2  1.8440  0.2079     (------*------)
28     2  2.8421  0.2515                         (------*-----)
                             +---------+---------+---------+---------
                           1.50      2.00      2.50      3.00

Pooled StDev = 0.1825


Grouping Information Using Tukey Method

Day  N    Mean  Grouping
28   2  2.8421  A
 7   2  2.6515  A B
 0   2  2.1610  A B C
14   2  2.0285    B C
21   2  1.8440      C

Means that do not share a letter are significantly different.
```

(4.5) One-way ANOVA: T2 of 9_R0 versus Day

```
Source  DF       SS       MS      F      P
Day      4  0.46366  0.11591  76.81  0.000
Error    5  0.00755  0.00151
Total    9  0.47120

S = 0.03885   R-Sq = 98.40%   R-Sq(adj) = 97.12%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  ------+---------+---------+---------+---
 0     2  1.5190  0.0863                              (---*--)
 7     2  1.5420  0.0071                                (--*---)
14     2  1.3955  0.0049                        (---*--)
21     2  1.2445  0.0049                 (--*---)
28     2  0.9564  0.0020  (---*--)
                          ------+---------+---------+---------+---
                              1.00      1.20      1.40      1.60

Pooled StDev = 0.0388


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 7   2  1.54200  A
 0   2  1.51900  A
14   2  1.39550  A B
21   2  1.24450    B
28   2  0.95640      C

Means that do not share a letter are significantly different.
```

(4.6) One-way ANOVA: T2 of 9_R10 versus Day

```
Source  DF        SS        MS       F      P
Day      4  0.061444  0.015361  108.37  0.000
Error    5  0.000709  0.000142
Total    9  0.062153

S = 0.01191   R-Sq = 98.86%   R-Sq(adj) = 97.95%


                            Individual 95% CIs For Mean Based on
                            Pooled StDev
Level  N     Mean    StDev  --------+---------+---------+---------+-
 0     2  0.81600  0.00849                               (---*--)
 7     2  0.76450  0.00636                        (--*--)
14     2  0.75450  0.01768                       (--*--)
21     2  0.59850  0.00778  (--*---)
28     2  0.80659  0.01494                              (--*--)
                            --------+---------+---------+---------+-
                                0.630     0.700     0.770     0.840

Pooled StDev = 0.01191


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 0   2  0.81600  A
28   2  0.80659  A B
 7   2  0.76450    B C
14   2  0.75450      C
21   2  0.59850        D

Means that do not share a letter are significantly different.
```

(4.7) One-way ANOVA: T2 of 9_R20 versus Day

```
Source  DF       SS       MS      F      P
Day      4  0.18838  0.04710  12.22  0.009
Error    5  0.01927  0.00385
Total    9  0.20765

S = 0.06208   R-Sq = 90.72%   R-Sq(adj) = 83.30%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  ------+---------+---------+---------+---
 0     2  1.0075  0.0757                       (------*------)
 7     2  1.0470  0.0679                         (------*------)
14     2  0.9055  0.0643                 (------*------)
21     2  0.6605  0.0686  (------*------)
28     2  0.9735  0.0097                     (------*------)
                          ------+---------+---------+---------+---
                              0.64      0.80      0.96      1.12
```

```
Pooled StDev = 0.0621


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 7   2  1.04700  A
 0   2  1.00750  A
28   2  0.97350  A
14   2  0.90550  A B
21   2  0.66050    B

Means that do not share a letter are significantly different.
```

(4.8) One-way ANOVA: T2 of 9_R30 versus Day

```
Source  DF       SS       MS     F      P
Day      4  0.10198  0.02550  4.64  0.062
Error    5  0.02746  0.00549
Total    9  0.12944

S = 0.07410   R-Sq = 78.79%   R-Sq(adj) = 61.82%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev   -+---------+---------+---------+--------
 0     2  1.0750  0.0834                 (--------*--------)
 7     2  1.1600  0.0014                      (--------*--------)
14     2  1.0085  0.1039            (--------*--------)
21     2  0.8715  0.0573   (--------*--------)
28     2  1.1188  0.0800                    (--------*--------)
                           -+---------+---------+---------+--------
                          0.75      0.90      1.05      1.20

Pooled StDev = 0.0741


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 7   2  1.16000  A
28   2  1.11880  A
 0   2  1.07500  A
14   2  1.00850  A
21   2  0.87150  A

Means that do not share a letter are significantly different.
```

Table B. 2. *Analysis of variance of starch based confectionery. Effect of storage on hardness of each formulations using adjusted SS for Tests*

(1) One-way ANOVA: Hardness of 11_R0 versus Day

```
Source  DF       SS      MS       F      P
Day      3  1897.61  632.54  468.56  0.000
Error    4     5.40    1.35
Total    7  1903.01

S = 1.162   R-Sq = 99.72%   R-Sq(adj) = 99.50%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  -------+---------+---------+---------+--
 0     2   6,078  0,106  (-*-)
10     2  19,543  0,735             (-*-)
20     2  35,904  2,142                           (-*-)
30     2  46,395  0,511                                    (-*-)
                         -------+---------+---------+---------+--
                               12        24        36        48

Pooled StDev = 1,162


Grouping Information Using Tukey Method

Day   N    Mean  Grouping
30    2  46.395  A
20    2  35.904    B
10    2  19.543      C
 0    2   6.078        D

Means that do not share a letter are significantly different.
```

(2) One-way ANOVA: Hardness of 11_R10 versus Day

```
Source  DF       SS      MS      F      P
Day      3  1139.67  379.89  47.80  0.001
Error    4    31.79    7.95
Total    7  1171.45

S = 2.819   R-Sq = 97.29%   R-Sq(adj) = 95.25%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ---------+---------+---------+---------+
 0     2   7.287  0.527  (----*----)
10     2  25.317  1.326                (----*----)
20     2  32.986  4.099                       (---*----)
30     2  39.057  3.598                            (----*---)
                         ---------+---------+---------+---------+
```

```
                                 12        24        36        48

Pooled StDev = 2.819
Grouping Information Using Tukey Method

Day   N    Mean  Grouping
30    2  39.057  A
20    2  32.986  A B
10    2  25.317    B
 0    2   7.287      C

Means that do not share a letter are significantly different.
```

(3) One-way ANOVA: Hardness of 11_R20 versus Day

```
Source  DF       SS      MS      F      P
Day      3  118.073  39.358  56.28  0.001
Error    4    2.797   0.699
Total    7  120.871

S = 0.8363   R-Sq = 97.69%   R-Sq(adj) = 95.95%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean  StDev  ---+---------+---------+---------+------
 0     2   4.140  0.728  (----*----)
10     2   9.918  0.867                  (---*----)
20     2  13.226  1.032                           (----*---)
30     2  13.819  0.671                             (---*----)
                         ---+---------+---------+---------+------
                          3.5       7.0      10.5      14.0

Pooled StDev = 0.836


Grouping Information Using Tukey Method

Day  N    Mean  Grouping
30    2  13.819  A
20    2  13.226  A B
10    2   9.918    B
 0    2   4.140      C

Means that do not share a letter are significantly different.
```

(4) One-way ANOVA: Hardness of 11_R30 versus Day

```
Source  DF       SS      MS       F      P
Day      3  17.3461  5.7820  175.70  0.000
Error    4   0.1316  0.0329
Total    7  17.4777

S = 0.1814   R-Sq = 99.25%   R-Sq(adj) = 98.68%


                           Individual 95% CIs For Mean Based on
```

```
                            Pooled StDev
Level  N    Mean   StDev   -+---------+---------+---------+--------
 0     2  2.5826  0.2391   (--*-)
10     2  4.5394  0.1717                   (--*--)
20     2  5.8262  0.0742                              (--*--)
30     2  6.4256  0.1986                                   (--*--)
                           -+---------+---------+---------+--------
                          2.4       3.6       4.8       6.0

Pooled StDev = 0.1814


Grouping Information Using Tukey Method

Day   N    Mean  Grouping
30    2  6.4256  A
20    2  5.8262  A
10    2  4.5394    B
 0    2  2.5826      C

Means that do not share a letter are significantly different.
```

(5) One-way ANOVA: Hardness of 9_R0 versus Day

```
Source  DF       SS      MS       F      P
Day      3  1937.19  645.73  114.33  0.000
Error    4    22.59    5.65
Total    7  1959.78

S = 2.377   R-Sq = 98.85%   R-Sq(adj) = 97.98%


                           Individual 95% CIs For Mean Based on
                           Pooled StDev
Level  N    Mean  StDev  +---------+---------+---------+---------
 0     2  23.919  0.811                   (---*---)
10     2   5.200  0.513  (---*---)
20     2  41.893  4.588                                  (---*---)
30     2  43.513  0.789                                   (---*---)
                         +---------+---------+---------+---------
                         0        12        24        36

Pooled StDev = 2.377


Grouping Information Using Tukey Method

Day   N    Mean  Grouping
30    2  43.513  A
20    2  41.893  A
 0    2  23.919    B
10    2   5.200      C

Means that do not share a letter are significantly different.
```

(6) One-way ANOVA: Hardness of 9_R10 versus Day

```
Source  DF     SS    MS     F      P
Day      3  269.0  89.7  8.15  0.035
Error    4   44.0  11.0
Total    7  313.1

S = 3.318   R-Sq = 85.94%   R-Sq(adj) = 75.39%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ---------+---------+---------+---------+
 0     2  17.453  2.819              (-------*-------)
10     2   7.352  0.204  (-------*-------)
20     2  22.567  5.715                    (-------*-------)
30     2  20.206  1.838                 (-------*-------)
                         ---------+---------+---------+---------+
                               8.0      16.0      24.0      32.0

Pooled StDev = 3.318


Grouping Information Using Tukey Method

Day  N    Mean  Grouping
20   2  22.567  A
30   2  20.206  A B
 0   2  17.453  A B
10   2   7.352    B

Means that do not share a letter are significantly different.
```

(7) One-way ANOVA: Hardness of 9_R20 versus Day

```
Source  DF      SS     MS      F      P
Day      3  25.193  8.398  17.69  0.009
Error    4   1.899  0.475
Total    7  27.092

S = 0.6890   R-Sq = 92.99%   R-Sq(adj) = 87.73%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  ------+---------+---------+---------+---
 0     2  6.9436  0.1524               (------*-----)
10     2  4.1668  0.1184  (------*------)
20     2  8.4867  0.8881                       (-----*------)
30     2  8.5363  1.0360                       (------*-----)
                          ------+---------+---------+---------+---
                              4.0       6.0       8.0      10.0

Pooled StDev = 0.6890
```

```
Grouping Information Using Tukey Method

Day   N    Mean  Grouping
30    2  8.5363  A
20    2  8.4867  A
 0    2  6.9436  A B
10    2  4.1668    B

Means that do not share a letter are significantly different.
```

(8) One-way ANOVA: Hardness of 9_R30 versus Day

```
Source  DF      SS     MS      F      P
Day      3  15.254  5.085  12.23  0.018
Error    4   1.664  0.416
Total    7  16.918

S = 0.6449   R-Sq = 90.17%   R-Sq(adj) = 82.79%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  -----+---------+---------+---------+----
 0     2  6.0728  0.5724                 (-------*-------)
10     2  3.7265  0.0827  (-------*-------)
20     2  7.3683  0.5075                         (-------*-------)
30     2  6.7629  1.0351                     (-------*-------)
                          -----+---------+---------+---------+----
                             3.2       4.8       6.4       8.0

Pooled StDev = 0.6449


Grouping Information Using Tukey Method

Day   N    Mean  Grouping
20    2  7.3683  A
30    2  6.7629  A
 0    2  6.0728  A B
10    2  3.7265    B

Means that do not share a letter are significantly different.
```

Table B. 3. *Analysis of variance of starch based confectionery. Effect of storage on glass transition temperature (T_g) of each formulations using adjusted SS for Tests*

(1) One-way ANOVA: Tg of 11_R0 versus Day

```
Source  DF    SS    MS     F      P
Day_tg   1   2.2   2.2  0.19  0.708
Error    2  23.9  12.0
Total    3  26.2

S = 3.458   R-Sq = 8.55%   R-Sq(adj) = 0.00%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N     Mean  StDev  ---------+---------+---------+---------+
 0     2  -36.680  1.344  (-----------------*----------------)
28     2  -35.185  4.702     (----------------*-----------------)
                          ---------+---------+---------+---------+
                               -42.0     -36.0     -30.0     -24.0

Pooled StDev = 3.458


Grouping Information Using Tukey Method

Day_tg  N     Mean  Grouping
28      2  -35.185  A
 0      2  -36.680  A

Means that do not share a letter are significantly different.
```

(2) One-way ANOVA: Tg_11_R10 versus Day_tg

```
Source  DF     SS     MS     F      P
Day_tg   1  0.265  0.265  0.34  0.617
Error    2  1.539  0.769
Total    3  1.804

S = 0.8771   R-Sq = 14.70%   R-Sq(adj) = 0.00%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N     Mean  StDev  ----+---------+---------+---------+-----
 0     2  -39.905  0.728  (-----------------*-----------------)
28     2  -39.390  1.004      (----------------*-----------------)
                          ----+---------+---------+---------+-----
                          -42.0     -40.5     -39.0     -37.5

Pooled StDev = 0.877
```

```
Grouping Information Using Tukey Method

Day_tg  N     Mean  Grouping
28      2  -39.3900  A
 0      2  -39.9050  A

Means that do not share a letter are significantly different.
```

(3) One-way ANOVA: Tg_11_R20 versus Day_tg

```
Source  DF     SS     MS      F      P
Day_tg   1  4.537  4.537  18.77  0.049
Error    2  0.483  0.242
Total    3  5.020

S = 0.4916   R-Sq = 90.37%   R-Sq(adj) = 85.56%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean  StDev  ------+---------+---------+---------+---
 0     2  -37.830  0.057              (---------*---------)
28     2  -39.960  0.693  (---------*---------)
                          ------+---------+---------+---------+---
                            -40.5     -39.0     -37.5     -36.0

Pooled StDev = 0.492


Grouping Information Using Tukey Method

Day_tg  N     Mean  Grouping
 0      2  -37.8300  A
28      2  -39.9600    B

Means that do not share a letter are significantly different.
```

(4) One-way ANOVA: Tg_11_R30 versus Day_tg

```
Source  DF    SS    MS     F      P
Day_tg   1  0.40  0.40  0.38  0.601
Error    2  2.13  1.07
Total    3  2.54

S = 1.033   R-Sq = 15.89%   R-Sq(adj) = 0.00%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean  StDev  -----+---------+---------+---------+----
 0     2  -39.240  1.400     (---------------*---------------)
28     2  -39.875  0.417  (---------------*--------------)
                          -----+---------+---------+---------+----
                           -42.0     -40.0     -38.0     -36.0
```

```
Pooled StDev = 1.033


Grouping Information Using Tukey Method

Day_tg  N     Mean  Grouping
 0      2  -39.240  A
28      2  -39.875  A

Means that do not share a letter are significantly different.
```

(5) One-way ANOVA: Tg_9_R0 versus Day_tg

```
Source  DF     SS    MS     F      P
Day_tg   1   7.87  7.87  2.18  0.277
Error    2   7.20  3.60
Total    3  15.07

S = 1.898   R-Sq = 52.21%   R-Sq(adj) = 28.31%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N     Mean  StDev  ---------+---------+---------+---------+
 0     2  -35.120  0.141         (-------------*--------------)
28     2  -37.925  2.680  (-------------*--------------)
                          ---------+---------+---------+---------+
                               -40.0     -36.0     -32.0     -28.0

Pooled StDev = 1.898


Grouping Information Using Tukey Method

Day_tg  N     Mean  Grouping
 0      2  -35.120  A
28      2  -37.925  A

Means that do not share a letter are significantly different.
```

(6) One-way ANOVA: Tg_9_R10 versus Day_tg

```
Source  DF     SS     MS     F      P
Day_tg   1  0.990  0.990  1.47  0.349
Error    2  1.345  0.673
Total    3  2.335

S = 0.8201   R-Sq = 42.39%   R-Sq(adj) = 13.59%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N     Mean  StDev  -----+---------+---------+---------+----
 0     2  -39.300  1.160        (----------------*----------------)
28     2  -40.295  0.021  (---------------*----------------)
                          -----+---------+---------+---------+----
```

```
                          -42.0     -40.5     -39.0     -37.5

Pooled StDev = 0.820


Grouping Information Using Tukey Method

Day_tg  N     Mean  Grouping
 0      2  -39.3000  A
28      2  -40.2950  A

Means that do not share a letter are significantly different.
```

(7) One-way ANOVA: Tg_9_R20 versus Day_tg

```
Source  DF      SS      MS      F      P
Day_tg   1  6.3756  6.3756  77.44  0.013
Error    2  0.1647  0.0823
Total    3  6.5403

S = 0.2869   R-Sq = 97.48%   R-Sq(adj) = 96.22%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean  StDev  -----+---------+---------+---------+----
 0     2  -37.995  0.375                     (------*-------)
28     2  -40.520  0.156  (------*-------)
                          -----+---------+---------+---------+----
                           -40.8     -39.6     -38.4     -37.2

Pooled StDev = 0.287


Grouping Information Using Tukey Method

Day_tg  N     Mean  Grouping
 0      2  -37.9950  A
28      2  -40.5200    B

Means that do not share a letter are significantly different.
```

(8) One-way ANOVA: Tg_9_R30 versus Day_tg

```
Source  DF     SS     MS     F      P
Day_tg   1  0.384  0.384  0.70  0.491
Error    2  1.097  0.549
Total    3  1.482

S = 0.7407   R-Sq = 25.94%   R-Sq(adj) = 0.00%


                          Individual 95% CIs For Mean Based on Pooled
StDev
```

```
Level  N     Mean  StDev      +---------+---------+---------+--------
-
 0     2  -39.065  0.955           (--------------*--------------)
28     2  -39.685  0.431      (--------------*--------------)
                              +---------+---------+---------+--------
-
                          -42.0     -40.5     -39.0     -37.5

Pooled StDev = 0.741


Grouping Information Using Tukey Method

Day_tg  N      Mean  Grouping
 0      2  -39.0650  A
28      2  -39.6850  A

Means that do not share a letter are significantly different.
```

Table B. 4. *Analysis of variance of starch based confectionery. Effect of storage on Peak1 for each formulation using adjusted SS for Tests*

(1) One-way ANOVA: 11_R0 versus day

```
Source  DF        SS        MS     F      P
day      4  0.000160  0.000040  0.09  0.982
Error    5  0.002250  0.000450
Total    9  0.002410

S = 0.02121   R-Sq = 6.64%   R-Sq(adj) = 0.00%


                            Individual 95% CIs For Mean Based on
Pooled StDev
Level  N     Mean    StDev  ---------+---------+---------+---------+
 0     2  0.19000  0.00000  (--------------*--------------)
 7     2  0.20000  0.01414      (--------------*--------------)
14     2  0.20000  0.01414      (--------------*--------------)
21     2  0.20000  0.04243      (--------------*--------------)
28     2  0.19500  0.00707    (--------------*--------------)
                            ---------+---------+---------+---------+
                                 0.175     0.200     0.225
0.250

Pooled StDev = 0.02121


Grouping Information Using Tukey Method

day  N     Mean  Grouping
21   2  0.20000  A
14   2  0.20000  A
 7   2  0.20000  A
28   2  0.19500  A
 0   2  0.19000  A

Means that do not share a letter are significantly different.
```

(2) One-way ANOVA: 11_R10 versus day

```
Source  DF         SS         MS     F      P
day      4  0.0002600  0.0000650  2.17  0.209
Error    5  0.0001500  0.0000300
Total    9  0.0004100

S = 0.005477   R-Sq = 63.41%   R-Sq(adj) = 34.15%


                            Individual 95% CIs For Mean Based on
                            Pooled StDev
Level  N     Mean    StDev  -----+---------+---------+---------+----
 0     2  0.20500  0.00707            (---------*---------)
 7     2  0.19500  0.00707  (---------*---------)
14     2  0.20500  0.00707            (---------*---------)
21     2  0.20000  0.00000       (---------*---------)
```

```
28     2  0.21000  0.00000                 (---------*---------)
                               -----+---------+---------+---------+----
                                  0.190     0.200     0.210     0.220

Pooled StDev = 0.00548


Grouping Information Using Tukey Method

day  N      Mean  Grouping
28   2  0.210000  A
14   2  0.205000  A
 0   2  0.205000  A
21   2  0.200000  A
 7   2  0.195000  A

Means that do not share a letter are significantly different.
```

(3) One-way ANOVA: 11_R20_Peak 1 versus day

```
Source  DF        SS        MS     F      P
day      4  0.001440  0.000360  3.00  0.130
Error    5  0.000600  0.000120
Total    9  0.002040

S = 0.01095   R-Sq = 70.59%   R-Sq(adj) = 47.06%


                            Individual 95% CIs For Mean Based on
Pooled StDev
Level  N     Mean    StDev    +---------+---------+---------+--------
-
 0     2  0.20000  0.00000              (---------*---------)
 7     2  0.21000  0.00000                   (---------*---------)
14     2  0.20000  0.01414              (---------*---------)
21     2  0.18000  0.01414    (---------*---------)
28     2  0.18000  0.01414    (---------*---------)
                              +---------+---------+---------+--------
-
                            0.160     0.180     0.200     0.220

Pooled StDev = 0.01095


Grouping Information Using Tukey Method

day  N     Mean  Grouping
 7   2  0.21000  A
14   2  0.20000  A
 0   2  0.20000  A
28   2  0.18000  A
21   2  0.18000  A

Means that do not share a letter are significantly different.
```

(4) One-way ANOVA: 11_R30 versus day

```
Source  DF        SS        MS     F      P
day      4  0.001040  0.000260  0.90  0.529
Error    5  0.001450  0.000290
Total    9  0.002490

S = 0.01703   R-Sq = 41.77%   R-Sq(adj) = 0.00%


                            Individual 95% CIs For Mean Based on
Pooled StDev
Level  N     Mean    StDev    +---------+---------+---------+--------
-
 0     2  0.19000  0.00000        (-----------*-----------)
 7     2  0.19000  0.00000        (-----------*-----------)
14     2  0.18500  0.02121      (-----------*-----------)
21     2  0.18000  0.01414    (-----------*-----------)
28     2  0.21000  0.02828                (-----------*-----------)
                              +---------+---------+---------+--------
-
                            0.150     0.175     0.200     0.225

Pooled StDev = 0.01703


Grouping Information Using Tukey Method

day  N     Mean  Grouping
28   2  0.21000  A
 7   2  0.19000  A
 0   2  0.19000  A
14   2  0.18500  A
21   2  0.18000  A

Means that do not share a letter are significantly different.
```

(5) One-way ANOVA: 9_R0_Peak 1 versus day

```
Source  DF         SS         MS     F      P
day      4  0.0008000  0.0002000  4.00  0.080
Error    5  0.0002500  0.0000500
Total    9  0.0010500

S = 0.007071   R-Sq = 76.19%   R-Sq(adj) = 57.14%


                            Individual 95% CIs For Mean Based on
                            Pooled StDev
Level  N     Mean    StDev  -----+---------+---------+---------+----
 0     2  0.18000  0.01414        (--------*--------)
 7     2  0.19000  0.00000               (--------*-------)
14     2  0.19500  0.00707                  (--------*--------)
21     2  0.17000  0.00000  (-------*--------)
28     2  0.19000  0.00000               (--------*-------)
                            -----+---------+---------+---------+----
                               0.165     0.180     0.195     0.210
```

```
Pooled StDev = 0.00707

Grouping Information Using Tukey Method

day  N      Mean  Grouping
14   2  0.195000  A
28   2  0.190000  A
 7   2  0.190000  A
 0   2  0.180000  A
21   2  0.170000  A

Means that do not share a letter are significantly different.
```

(6) One-way ANOVA: 9_R10_Peak 1 versus day

```
Source  DF         SS         MS     F      P
day      4  0.0007400  0.0001850  2.64  0.158
Error    5  0.0003500  0.0000700
Total    9  0.0010900

S = 0.008367   R-Sq = 67.89%   R-Sq(adj) = 42.20%


                            Individual 95% CIs For Mean Based on
                            Pooled StDev
Level  N     Mean    StDev  ---+---------+---------+---------+------
 0     2  0.13500  0.00707     (---------*---------)
 7     2  0.13000  0.00000  (---------*---------)
14     2  0.13500  0.00707     (---------*---------)
21     2  0.14000  0.01414        (---------*---------)
28     2  0.15500  0.00707                  (---------*---------)
                            ---+---------+---------+---------+------
                             0.120     0.135     0.150     0.165

Pooled StDev = 0.00837


Grouping Information Using Tukey Method

day  N      Mean  Grouping
28   2  0.155000  A
21   2  0.140000  A
14   2  0.135000  A
 0   2  0.135000  A
 7   2  0.130000  A

Means that do not share a letter are significantly different.
```

(7) One-way ANOVA: 9_R20_Peak 1 versus day

```
Source  DF        SS        MS     F      P
day      4  0.000460  0.000115  1.05  0.468
Error    5  0.000550  0.000110
Total    9  0.001010

S = 0.01049   R-Sq = 45.54%   R-Sq(adj) = 1.98%
```

```
                                 Individual 95% CIs For Mean Based on
                                 Pooled StDev
Level  N     Mean    StDev  ------+---------+---------+---------+---
 0     2  0.18000  0.01414              (------------*------------)
 7     2  0.16500  0.00707     (------------*------------)
14     2  0.16500  0.00707     (------------*------------)
21     2  0.16000  0.01414  (------------*-----------)
28     2  0.16500  0.00707     (------------*------------)
                            ------+---------+---------+---------+---
                                0.150     0.165     0.180     0.195

Pooled StDev = 0.01049


Grouping Information Using Tukey Method

day  N     Mean  Grouping
 0   2  0.18000  A
28   2  0.16500  A
14   2  0.16500  A
 7   2  0.16500  A
21   2  0.16000  A

Means that do not share a letter are significantly different.
```

(8) One-way ANOVA: 9_R30_Peak 1 versus day

```
Source  DF        SS        MS     F      P
day      4  0.001660  0.000415  2.77  0.147
Error    5  0.000750  0.000150
Total    9  0.002410

S = 0.01225   R-Sq = 68.88%   R-Sq(adj) = 43.98%


                            Individual 95% CIs For Mean Based on
Pooled StDev
Level  N     Mean    StDev   -+---------+---------+---------+--------
 0     2  0.19500  0.00707                  (-----------*----------)
 7     2  0.19500  0.00707                  (-----------*----------)
14     2  0.18500  0.02121             (-----------*----------)
21     2  0.18000  0.01414           (----------*----------)
28     2  0.16000  0.00000   (----------*----------)
                             -+---------+---------+---------+--------
                            0.140     0.160     0.180     0.200

Pooled StDev = 0.01225


Grouping Information Using Tukey Method

day  N     Mean  Grouping
 7   2  0.19500  A
 0   2  0.19500  A
14   2  0.18500  A
21   2  0.18000  A
28   2  0.16000  A
```

```
Means that do not share a letter are significantly different.
```

Table B. 5. *Analysis of variance of starch based confectionery. Effect of storage on Peak 2 for each formulation using adjusted SS for Tests*

(1) One-way ANOVA: 11_R0_Peak 2 versus day

```
Source  DF      SS      MS     F      P
day      4  0.1392  0.0348  0.83  0.561
Error    5  0.2108  0.0422
Total    9  0.3500

S = 0.2053   R-Sq = 39.78%   R-Sq(adj) = 0.00%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  ------+---------+---------+---------+---
 0     2  0.4850  0.1344  (-----------*------------)
 7     2  0.8150  0.2616             (-----------*------------)
14     2  0.7700  0.0707           (------------*-----------)
21     2  0.7750  0.3182           (------------*-----------)
28     2  0.7250  0.1344          (-----------*------------)
                          ------+---------+---------+---------+---
                              0.30      0.60      0.90      1.20

Pooled StDev = 0.2053


Grouping Information Using Tukey Method

day  N    Mean  Grouping
 7   2  0.8150  A
21   2  0.7750  A
14   2  0.7700  A
28   2  0.7250  A
 0   2  0.4850  A

Means that do not share a letter are significantly different.
```

(2) One-way ANOVA: 11_R10_Peak 2 versus day

```
Source  DF       SS       MS      F      P
day      4  0.32190  0.08048  31.56  0.001
Error    5  0.01275  0.00255
Total    9  0.33465

S = 0.05050   R-Sq = 96.19%   R-Sq(adj) = 93.14%


                            Individual 95% CIs For Mean Based on
                            Pooled StDev
Level  N     Mean    StDev  -------+---------+---------+---------+--
 0     2  0.60500  0.03536           (-----*-----)
 7     2  0.46500  0.06364  (-----*-----)
14     2  0.53000  0.07071      (-----*-----)
```

```
21     2  0.87000  0.00000                             (----*-----)
28     2  0.90500  0.04950                               (-----*----)
                            --------+---------+---------+---------+--
                                 0.48      0.64      0.80      0.96

Pooled StDev = 0.05050


Grouping Information Using Tukey Method

day  N     Mean  Grouping
28   2  0.90500  A
21   2  0.87000  A
 0   2  0.60500    B
14   2  0.53000    B
 7   2  0.46500    B

Means that do not share a letter are significantly different.
```

(3) One-way ANOVA: 11_R20_Peak 2 versus day

```
Source  DF       SS       MS     F      P
day      4  0.13796  0.03449  3.68  0.093
Error    5  0.04685  0.00937
Total    9  0.18481

S = 0.09680   R-Sq = 74.65%   R-Sq(adj) = 54.37%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  -----+---------+---------+---------+----
 0     2  0.9700  0.0424               (----------*----------)
 7     2  1.0200  0.1131                  (----------*----------)
14     2  0.9850  0.1626                (----------*----------)
21     2  0.7400  0.0283  (----------*----------)
28     2  0.7700  0.0707    (----------*----------)
                          -----+---------+---------+---------+----
                             0.64      0.80      0.96      1.12

Pooled StDev = 0.0968


Grouping Information Using Tukey Method

day  N     Mean  Grouping
 7   2  1.02000  A
14   2  0.98500  A
 0   2  0.97000  A
28   2  0.77000  A
21   2  0.74000  A

Means that do not share a letter are significantly different.
```

(4) One-way ANOVA: 11_R30_Peak 2 versus day

```
Source  DF       SS       MS      F      P
day      4  0.35436  0.08859  10.10  0.013
Error    5  0.04385  0.00877
Total    9  0.39821

S = 0.09365   R-Sq = 88.99%   R-Sq(adj) = 80.18%


                           Individual 95% CIs For Mean Based on
                           Pooled StDev
Level  N    Mean   StDev   --+---------+---------+---------+-------
 0     2  0.6500  0.0990    (------*------)
 7     2  0.7700  0.1414         (------*------)
14     2  0.7700  0.0707         (------*------)
21     2  0.6250  0.0636   (------*------)
28     2  1.1500  0.0707                        (------*------)
                           --+---------+---------+---------+-------
                           0.50      0.75      1.00      1.25

Pooled StDev = 0.0936


Grouping Information Using Tukey Method

day  N    Mean  Grouping
28   2  1.1500  A
14   2  0.7700    B
 7   2  0.7700    B
 0   2  0.6500    B
21   2  0.6250    B

Means that do not share a letter are significantly different.
```

(5) One-way ANOVA: 9_R0_Peak 2 versus day

```
Source  DF       SS       MS     F      P
day      4  0.02994  0.00749  4.09  0.077
Error    5  0.00915  0.00183
Total    9  0.03909

S = 0.04278   R-Sq = 76.59%   R-Sq(adj) = 57.87%


                             Individual 95% CIs For Mean Based on
                             Pooled StDev
Level  N     Mean    StDev   -----+---------+---------+---------+----
 0     2  0.74000  0.02828              (-------*-------)
 7     2  0.69500  0.03536          (-------*------)
14     2  0.79000  0.04243                   (-------*-------)
21     2  0.69500  0.03536          (-------*------)
28     2  0.62500  0.06364   (-------*------)
                             -----+---------+---------+---------+----
                                0.60      0.70      0.80      0.90
```

```
Pooled StDev = 0.04278


Grouping Information Using Tukey Method

day  N     Mean  Grouping
14   2  0.79000  A
 0   2  0.74000  A
21   2  0.69500  A
 7   2  0.69500  A
28   2  0.62500  A

Means that do not share a letter are significantly different.
```

(6) One-way ANOVA: 9_R10_Peak 2 versus day

```
Source  DF       SS       MS      F      P
day      4  0.70936  0.17734  70.37  0.000
Error    5  0.01260  0.00252
Total    9  0.72196

S = 0.05020   R-Sq = 98.25%   R-Sq(adj) = 96.86%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  ---------+---------+---------+---------+
 0     2  0.3750  0.1061  (---*---)
 7     2  0.4350  0.0212     (--*---)
14     2  0.4350  0.0212     (--*---)
21     2  1.1000  0.0000                             (---*---)
28     2  0.5650  0.0212          (---*--)
                          ---------+---------+---------+---------+
                                0.50      0.75      1.00      1.25

Pooled StDev = 0.0502


Grouping Information Using Tukey Method

day  N    Mean  Grouping
21   2  1.1000  A
28   2  0.5650    B
14   2  0.4350    B
 7   2  0.4350    B
 0   2  0.3750    B

Means that do not share a letter are significantly different.
```

(7) One-way ANOVA: 9_R20_Peak 2 versus day

```
Source  DF       SS       MS     F      P
day      4  0.00906  0.00226  0.45  0.767
Error    5  0.02490  0.00498
Total    9  0.03396

S = 0.07057   R-Sq = 26.68%   R-Sq(adj) = 0.00%
```

```
                                 Individual 95% CIs For Mean Based on
                                 Pooled StDev
Level  N     Mean    StDev  --------+---------+---------+---------+-
 0     2  0.63500  0.12021           (------------*-----------)
 7     2  0.59000  0.05657      (------------*------------)
14     2  0.59000  0.05657      (------------*------------)
21     2  0.62500  0.06364          (------------*-----------)
28     2  0.55000  0.00000  (------------*------------)
                            --------+---------+---------+---------+-
                                 0.50      0.60      0.70      0.80

Pooled StDev = 0.07057


Grouping Information Using Tukey Method

day  N     Mean  Grouping
 0   2  0.63500  A
21   2  0.62500  A
14   2  0.59000  A
 7   2  0.59000  A
28   2  0.55000  A

Means that do not share a letter are significantly different.
```

(8) One-way ANOVA: 9_R30_Peak 2 versus day

```
Source  DF       SS       MS     F      P
day      4  0.01320  0.00330  1.10  0.448
Error    5  0.01500  0.00300
Total    9  0.02820

S = 0.05477   R-Sq = 46.81%   R-Sq(adj) = 4.26%


                                 Individual 95% CIs For Mean Based on
                                 Pooled StDev
Level  N     Mean    StDev  -------+---------+---------+---------+--
 0     2  0.69500  0.03536             (------------*-----------)
 7     2  0.67500  0.06364           (-----------*------------)
14     2  0.69500  0.09192             (------------*-----------)
21     2  0.60500  0.03536  (------------*-----------)
28     2  0.63000  0.00000     (------------*-----------)
                            -------+---------+---------+---------+--
                                 0.560     0.640     0.720     0.800

Pooled StDev = 0.05477

Grouping Information Using Tukey Method

day  N     Mean  Grouping
14   2  0.69500  A
 0   2  0.69500  A
 7   2  0.67500  A
28   2  0.63000  A
21   2  0.60500  A
```

```
Means that do not share a letter are significantly different.
```

Table B. 6. *Analysis of variance of starch based confectionery. Effect of storage on Peak 3 for each formulation using adjusted SS for Tests*

(1) One-way ANOVA: 11_R0_Peak 3 versus day

```
Source  DF      SS     MS      F      P
day      4  14.004  3.501  21.75  0.002
Error    5   0.805  0.161
Total    9  14.809

S = 0.4012   R-Sq = 94.56%   R-Sq(adj) = 90.22%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  -----+---------+---------+---------+----
 0     2  1.3000  0.2828  (-----*-----)
 7     2  4.2500  0.2121                        (-----*-----)
14     2  4.4000  0.4243                          (-----*-----)
21     2  3.7000  0.5657                    (-----*-----)
28     2  4.4000  0.4243                          (-----*-----)
                          -----+---------+---------+---------+----
                             1.2       2.4       3.6       4.8

Pooled StDev = 0.4012


Grouping Information Using Tukey Method

day  N    Mean  Grouping
28   2  4.4000  A
14   2  4.4000  A
 7   2  4.2500  A
21   2  3.7000  A
 0   2  1.3000    B

Means that do not share a letter are significantly different.
```

(2) One-way ANOVA: 11_R10_Peak 3 versus day

```
Source  DF       SS      MS       F      P
day      4  19.1060  4.7765  265.36  0.000
Error    5   0.0900  0.0180
Total    9  19.1960

S = 0.1342   R-Sq = 99.53%   R-Sq(adj) = 99.16%


                          Individual 95% CIs For Mean Based on Pooled
StDev
Level  N    Mean   StDev    +---------+---------+---------+---------
 0     2  1.3500  0.0707     (--*-)
 7     2  1.2500  0.2121    (--*-)
14     2  1.2000  0.1414    (-*-)
```

```
21      2  3.7000  0.1414                             (-*-)
28      2  4.4000  0.0000                                    (-*-)
                            +---------+---------+---------+---------
                          1.0       2.0       3.0       4.0

Pooled StDev = 0.1342


Grouping Information Using Tukey Method

day  N    Mean  Grouping
28   2  4.4000  A
21   2  3.7000    B
 0   2  1.3500      C
 7   2  1.2500      C
14   2  1.2000      C

Means that do not share a letter are significantly different.
```

(3) One-way ANOVA: 11_R20_Peak 3 versus day

```
Source  DF      SS      MS     F      P
day      4  2.7760  0.6940  8.26  0.020
Error    5  0.4200  0.0840
Total    9  3.1960

S = 0.2898   R-Sq = 86.86%   R-Sq(adj) = 76.35%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  ------+---------+---------+---------+---
 0     2  4.2500  0.2121                     (-------*------)
 7     2  4.2500  0.2121                     (-------*------)
14     2  3.8500  0.3536               (-------*-------)
21     2  2.9000  0.2828  (------*-------)
28     2  3.3500  0.3536        (-------*------)
                          ------+---------+---------+---------+---
                              2.80      3.50      4.20      4.90

Pooled StDev = 0.2898


Grouping Information Using Tukey Method

day  N    Mean  Grouping
 7   2  4.2500  A
 0   2  4.2500  A
14   2  3.8500  A B
28   2  3.3500  A B
21   2  2.9000    B

Means that do not share a letter are significantly different.
```

(4) One-way ANOVA: 11_R30_Peak 3 versus day

```
Source   DF      SS      MS       F      P
```

```
day       4  13.970  3.493  16.32  0.004
Error     5   1.070  0.214
Total     9  15.040

S = 0.4626   R-Sq = 92.89%   R-Sq(adj) = 87.19%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  -----+---------+---------+---------+----
 0     2  1.9000  0.2828    (-----*----)
 7     2  2.7000  0.8485         (-----*-----)
14     2  2.7500  0.2121          (----*-----)
21     2  1.6500  0.2121  (-----*-----)
28     2  5.0000  0.4243                         (----*-----)
                          -----+---------+---------+---------+----
                             1.5       3.0       4.5       6.0

Pooled StDev = 0.4626


Grouping Information Using Tukey Method

day  N    Mean  Grouping
28   2  5.0000  A
14   2  2.7500    B
 7   2  2.7000    B
 0   2  1.9000    B
21   2  1.6500    B

Means that do not share a letter are significantly different.
```

(5) One-way ANOVA: 9_R0_Peak 3 versus day

```
Source  DF      SS      MS     F      P
day      4  0.5360  0.1340  4.62  0.062
Error    5  0.1450  0.0290
Total    9  0.6810

S = 0.1703   R-Sq = 78.71%   R-Sq(adj) = 61.67%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  --+---------+---------+---------+-------
 0     2  3.3000  0.0000                   (--------*--------)
 7     2  3.2000  0.1414                 (-------*--------)
14     2  3.1000  0.0000              (--------*-------)
21     2  2.7000  0.0000  (--------*--------)
28     2  3.3500  0.3536                     (--------*--------)
                          --+---------+---------+---------+-------
                          2.45      2.80      3.15      3.50

Pooled StDev = 0.1703


Grouping Information Using Tukey Method
```

```
day  N    Mean  Grouping
28   2  3.3500  A
 0   2  3.3000  A
 7   2  3.2000  A
14   2  3.1000  A
21   2  2.7000  A

Means that do not share a letter are significantly different.
```

(6) One-way ANOVA: 9_R10_Peak 3 versus day

```
Source  DF      SS      MS      F      P
day      4  5.2540  1.3135  93.82  0.000
Error    5  0.0700  0.0140
Total    9  5.3240

S = 0.1183   R-Sq = 98.69%   R-Sq(adj) = 97.63%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  ---------+---------+---------+---------+
 0     2  1.5500  0.2121   (---*--)
 7     2  1.6000  0.0000    (---*--)
14     2  1.5000  0.0000  (---*---)
21     2  3.4000  0.1414                                (---*--)
28     2  1.7500  0.0707       (--*---)
                          ---------+---------+---------+---------+
                                1.80      2.40      3.00      3.60

Pooled StDev = 0.1183


Grouping Information Using Tukey Method

day  N    Mean  Grouping
21   2  3.4000  A
28   2  1.7500    B
 7   2  1.6000    B
 0   2  1.5500    B
14   2  1.5000    B

Means that do not share a letter are significantly different.
```

(7) One-way ANOVA: 9_R20_Peak 3 versus day

```
Source  DF      SS      MS     F      P
day      4  0.1660  0.0415  0.44  0.776
Error    5  0.4700  0.0940
Total    9  0.6360

S = 0.3066   R-Sq = 26.10%   R-Sq(adj) = 0.00%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
```

```
Level  N    Mean   StDev  ---+---------+---------+---------+------
 0     2  2.4000  0.2828          (-------------*-------------)
 7     2  2.4000  0.2828          (-------------*-------------)
14     2  2.2500  0.2121      (-------------*-------------)
21     2  2.0500  0.4950  (-------------*-------------)
28     2  2.3000  0.1414        (------------*-------------)
                          ---+---------+---------+---------+------
                           1.60      2.00      2.40      2.80

Pooled StDev = 0.3066


Grouping Information Using Tukey Method

day  N    Mean  Grouping
 7   2  2.4000  A
 0   2  2.4000  A
28   2  2.3000  A
14   2  2.2500  A
21   2  2.0500  A

Means that do not share a letter are significantly different.
```

(8) One-way ANOVA: 9_R30_Peak 3 versus day

```
Source  DF      SS      MS     F      P
day      4  0.2240  0.0560  1.27  0.391
Error    5  0.2200  0.0440
Total    9  0.4440

S = 0.2098   R-Sq = 50.45%   R-Sq(adj) = 10.81%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  --------+---------+---------+---------+-
 0     2  2.6500  0.0707               (------------*------------)
 7     2  2.5500  0.2121           (-------------*------------)
14     2  2.6500  0.3536               (------------*------------)
21     2  2.2500  0.2121  (------------*------------)
28     2  2.6000  0.0000             (-------------*-----------)
                          --------+---------+---------+---------+-
                                2.10      2.40      2.70      3.00

Pooled StDev = 0.2098


Grouping Information Using Tukey Method

day  N    Mean  Grouping
 0   2  2.6500  A
14   2  2.6500  A
28   2  2.6000  A
 7   2  2.5500  A
21   2  2.2500  A

Means that do not share a letter are significantly different.
```

Table B. 7. *Analysis of variance of starch based confectionery. Effect of storage on Peak 4 for each formulation using adjusted SS for Tests*

(2) One-way ANOVA: 11_R0_Peak 4 versus day

```
Source  DF        SS        MS  F  P
day      4  51.98400  12.99600  *  *
Error    5   0.00000   0.00000
Total    9  51.98400

S = 0   R-Sq = 100.00%   R-Sq(adj) = 100.00%


                            Individual 95% CIs For Mean Based on
Pooled StDev
Level  N     Mean    StDev    +---------+---------+---------+--------
-
 0     2  5.70000  0.00000                                          *
 7     2  0.00000  0.00000    *
14     2  0.00000  0.00000    *
21     2  0.00000  0.00000    *
28     2  0.00000  0.00000    *
                              +---------+---------+---------+--------
-
                            0.0       1.5       3.0       4.5

Pooled StDev = 0.00000


Grouping Information Using Tukey Method

day  N     Mean  Grouping
 0   2  5.70000  A
28   2  0.00000    B
21   2  0.00000      C
14   2  0.00000        D
 7   2  0.00000          E

Means that do not share a letter are significantly different.
```

(3) One-way ANOVA: 11_R10_Peak 4 versus day

```
Source  DF       SS       MS       F      P
day      4  60.6300  15.1575  842.08  0.000
Error    5   0.0900   0.0180
Total    9  60.7200

S = 0.1342   R-Sq = 99.85%   R-Sq(adj) = 99.73%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
```

```
Level  N    Mean   StDev  --+---------+---------+---------+-------
 0     2  5.3000  0.0000                                    (*-)
 7     2  5.1500  0.2121                                   (*-)
14     2  4.5500  0.2121                              (*-)
21     2  0.0000  0.0000  (-*-)
28     2  0.0000  0.0000  (-*-)
                          --+---------+---------+---------+-------
                          0.0       1.5       3.0       4.5

Pooled StDev = 0.1342


Grouping Information Using Tukey Method

day  N    Mean  Grouping
 0   2  5.3000  A
 7   2  5.1500  A
14   2  4.5500    B
28   2  0.0000      C
21   2  0.0000      C

Means that do not share a letter are significantly different.
```

(4) One-way ANOVA: 11_R20_Peak 4 versus day

```
Source  DF         SS         MS  F  P
day      4  0.0000000  0.0000000  *  *
Error    5  0.0000000  0.0000000
Total    9  0.0000000

S = 0   R-Sq = *%   R-Sq(adj) = *%



Level  N         Mean        StDev
 0     2  0.000000000  0.000000000
 7     2  0.000000000  0.000000000
14     2  0.000000000  0.000000000
21     2  0.000000000  0.000000000
28     2  0.000000000  0.000000000

       Individual 95% CIs For Mean Based on Pooled StDev
Level    +---------+---------+---------+---------
 0       *
 7       *
14       *
21       *
28       *
         +---------+---------+---------+---------
       0.000000  0.000010  0.000020  0.000030

Pooled StDev = 0.000000000


Grouping Information Using Tukey Method

day  N         Mean  Grouping
28   2  0.000000000  A
```

```
21   2  0.000000000    B
14   2  0.000000000      C
 7   2  0.000000000        D
 0   2  0.000000000          E

Means that do not share a letter are significantly different.
```

(5) One-way ANOVA: 11_R30_Peak 4 versus day

```
Source  DF     SS     MS     F      P
day      4  487.0  121.7  4.75  0.059
Error    5  128.1   25.6
Total    9  615.1

S = 5.061   R-Sq = 79.18%   R-Sq(adj) = 62.52%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  ---------+---------+---------+---------+
 0     2   5.900   0.283        (---------*---------)
 7     2  15.000  11.314                 (---------*---------)
14     2  16.000   0.000                  (---------*---------)
21     2   0.000   0.000  (---------*---------)
28     2   0.000   0.000  (---------*---------)
                          ---------+---------+---------+---------+
                                   0        10        20        30

Pooled StDev = 5.061


Grouping Information Using Tukey Method

day  N    Mean  Grouping
14   2  16.000  A
 7   2  15.000  A
 0   2   5.900  A
28   2   0.000  A
21   2   0.000  A

Means that do not share a letter are significantly different.
```

Table B. 8. *Analysis of variance of starch based confectionery. Effect of storage on Relative Area 1 (RA1) for each formulation using adjusted SS for Tests*

(13) One-way ANOVA: 11_R0_RA1 versus day

```
Source  DF     SS    MS     F      P
day      4  217.8  54.5  3.63  0.095
Error    5   75.0  15.0
Total    9  292.8

S = 3.873   R-Sq = 74.38%   R-Sq(adj) = 53.89%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  --------+---------+---------+---------+-
 0     2  36.210  5.360  (---------*---------)
 7     2  40.105  1.648       (---------*---------)
14     2  45.705  2.468               (---------*---------)
21     2  47.995  5.565                   (---------*---------)
28     2  37.125  2.553   (---------*---------)
                         --------+---------+---------+---------+-
                              35.0      42.0      49.0      56.0

Pooled StDev = 3.873


Grouping Information Using Tukey Method

day  N    Mean  Grouping
21   2  47.995  A
14   2  45.705  A
 7   2  40.105  A
28   2  37.125  A
 0   2  36.210  A

Means that do not share a letter are significantly different.
```

(14) One-way ANOVA: 11_R10_RA1 versus day

```
Source  DF      SS     MS      F      P
day      4  167.43  41.86  13.85  0.006
Error    5   15.11   3.02
Total    9  182.54

S = 1.738   R-Sq = 91.72%   R-Sq(adj) = 85.10%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ----+---------+---------+---------+-----
 0     2  37.455  1.393              (-----*-----)
 7     2  31.025  0.417  (-----*-----)
14     2  35.930  3.154           (-----*-----)
```

```
21     2  43.830  0.778                            (------*-----)
28     2  36.875  1.563              (------*-----)
                         ----+---------+---------+---------+-----
                          30.0      35.0      40.0      45.0

Pooled StDev = 1.738


Grouping Information Using Tukey Method

day  N    Mean  Grouping
21   2  43.830  A
 0   2  37.455  A B
28   2  36.875  A B
14   2  35.930    B
 7   2  31.025    B

Means that do not share a letter are significantly different.
```

(15) One-way ANOVA: 11_R20_RA1 versus day

```
Source  DF     SS    MS     F      P
day      4  35.04  8.76  4.73  0.060
Error    5   9.27  1.85
Total    9  44.31

S = 1.361   R-Sq = 79.09%   R-Sq(adj) = 62.36%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  -------+---------+---------+---------+--
 0     2  38.030  1.541        (-------*-------)
 7     2  39.570  0.721             (-------*-------)
14     2  39.380  0.976            (-------*--------)
21     2  42.140  2.022                     (-------*--------)
28     2  36.485  1.153  (--------*-------)
                         -------+---------+---------+---------+--
                             36.0      39.0      42.0      45.0

Pooled StDev = 1.361


Grouping Information Using Tukey Method

day  N    Mean  Grouping
21   2  42.140  A
 7   2  39.570  A B
14   2  39.380  A B
 0   2  38.030  A B
28   2  36.485    B

Means that do not share a letter are significantly different.
```

(16) One-way ANOVA: 11_R30_RA1 versus day

```
Source  DF     SS    MS     F      P
day      4   9.48  2.37  1.34  0.370
Error    5   8.82  1.76
Total    9  18.29

S = 1.328   R-Sq = 51.81%   R-Sq(adj) = 13.25%


                         Individual 95% CIs For Mean Based on Pooled
StDev
Level  N    Mean  StDev   -+---------+---------+---------+--------
 0     2  24.235  1.365   (-----------*-----------)
 7     2  25.300  1.838        (------------*-----------)
14     2  24.770  1.570      (-----------*-----------)
21     2  27.075  1.039                 (-----------*-----------)
28     2  25.820  0.170           (-----------*-----------)
                          -+---------+---------+---------+--------
                         22.0      24.0      26.0      28.0

Pooled StDev = 1.328


Grouping Information Using Tukey Method

day  N    Mean  Grouping
21   2  27.075  A
28   2  25.820  A
 7   2  25.300  A
14   2  24.770  A
 0   2  24.235  A

Means that do not share a letter are significantly different.
```

(17) One-way ANOVA: 9_R0_RA1 versus day

```
Source  DF      SS     MS      F      P
day      4  293.28  73.32  40.79  0.001
Error    5    8.99   1.80
Total    9  302.27

S = 1.341   R-Sq = 97.03%   R-Sq(adj) = 94.65%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  -------+---------+---------+---------+--
 0     2  50.155  1.266                   (---*---)
 7     2  52.520  0.057                      (----*---)
14     2  54.205  1.450                         (---*---)
21     2  55.830  1.754                            (---*---)
28     2  40.480  1.485  (---*----)
                         -------+---------+---------+---------+--
                             42.0      48.0      54.0      60.0
```

```
Pooled StDev = 1.341


Grouping Information Using Tukey Method

day  N    Mean  Grouping
21   2  55.830  A
14   2  54.205  A B
 7   2  52.520  A B
 0   2  50.155    B
28   2  40.480      C

Means that do not share a letter are significantly different.
```

(18) One-way ANOVA: 9_R10_RA1 versus day

```
Source  DF      SS     MS     F      P
day      4  125.46  31.37  3.66  0.094
Error    5   42.84   8.57
Total    9  168.30

S = 2.927   R-Sq = 74.55%   R-Sq(adj) = 54.18%


                         Individual 95% CIs For Mean Based on Pooled
StDev
Level  N    Mean  StDev     +---------+---------+---------+---------
 0     2  53.325  6.131     (---------*---------)
 7     2  58.535  1.563              (---------*--------)
14     2  59.675  0.757                (--------*---------)
21     2  64.155  1.266                       (---------*---------)
28     2  60.955  0.799                  (---------*--------)
                            +---------+---------+---------+---------
                         48.0      54.0      60.0      66.0

Pooled StDev = 2.927


Grouping Information Using Tukey Method

day  N    Mean  Grouping
21   2  64.155  A
28   2  60.955  A
14   2  59.675  A
 7   2  58.535  A
 0   2  53.325  A

Means that do not share a letter are significantly different.
```

(19) One-way ANOVA: 9_R20_RA1 versus day

```
Source  DF      SS     MS      F      P
day      4  207.01  51.75  20.44  0.003
Error    5   12.66   2.53
Total    9  219.67
```

```
S = 1.591   R-Sq = 94.24%   R-Sq(adj) = 89.63%


                             Individual 95% CIs For Mean Based on Pooled
StDev
Level  N    Mean  StDev    -+---------+---------+---------+--------
 0     2  47.555  0.813              (-----*-----)
 7     2  46.080  1.259           (-----*-----)
14     2  48.430  0.354                (-----*-----)
21     2  56.135  2.906                               (-----*-----)
28     2  42.230  1.358     (----*-----)
                           -+---------+---------+---------+--------
                         40.0      45.0      50.0      55.0

Pooled StDev = 1.591


Grouping Information Using Tukey Method

day  N    Mean  Grouping
21   2  56.135  A
14   2  48.430    B
 0   2  47.555    B
 7   2  46.080    B
28   2  42.230    B

Means that do not share a letter are significantly different.
```

(20) One-way ANOVA: 9_R30_RA1 versus day

```
Source  DF      SS     MS      F      P
day      4  151.63  37.91  18.04  0.004
Error    5   10.51   2.10
Total    9  162.14

S = 1.450   R-Sq = 93.52%   R-Sq(adj) = 88.34%


                             Individual 95% CIs For Mean Based on Pooled
StDev
Level  N    Mean  StDev     +---------+---------+---------+---------
 0     2  38.730  1.428                 (----*-----)
 7     2  39.875  0.191                   (-----*----)
14     2  39.730  0.665                   (----*-----)
21     2  44.565  1.860                             (----*----)
28     2  32.405  2.128     (----*----)
                            +---------+---------+---------+---------
                         30.0      35.0      40.0      45.0

Pooled StDev = 1.450

Grouping Information Using Tukey Method

day  N    Mean  Grouping
21   2  44.565  A
 7   2  39.875  A B
14   2  39.730  A B
 0   2  38.730    B
```

```
28   2  32.405      C

Means that do not share a letter are significantly different.
```

Table B. 9. *Analysis of variance of starch based confectionery. Effect of storage on Relative Area 2 (RA2) for each formulation using adjusted SS for Tests*

(2) One-way ANOVA: 11_R0_RA2 versus day

```
Source  DF      SS      MS      F      P
day      4  417.21  104.30  12.25  0.009
Error    5   42.59    8.52
Total    9  459.80

S = 2.919   R-Sq = 90.74%   R-Sq(adj) = 83.33%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ---------+---------+---------+---------+
 0     2  14.420  4.087  (------*------)
 7     2  30.535  1.732                      (-----*------)
14     2  25.960  1.697                (-----*------)
21     2  23.730  4.172             (------*-----)
28     2  33.060  1.612                         (-----*------)
                         ---------+---------+---------+---------+
                              16.0      24.0      32.0      40.0

Pooled StDev = 2.919


Grouping Information Using Tukey Method

day  N    Mean  Grouping
28   2  33.060  A
 7   2  30.535  A
14   2  25.960  A B
21   2  23.730  A B
 0   2  14.420    B

Means that do not share a letter are significantly different.
```

(3) One-way ANOVA: 11_R10_RA2 versus day

```
Source  DF      SS      MS      F      P
day      4  705.15  176.29  25.65  0.002
Error    5   34.37    6.87
Total    9  739.52

S = 2.622   R-Sq = 95.35%   R-Sq(adj) = 91.63%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ---------+---------+---------+---------+
 0     2  13.550  1.315  (-----*-----)
```

```
 7     2  31.025  0.417                      (-----*-----)
14     2  13.380  5.572  (-----*-----)
21     2  27.670  0.580                  (-----*-----)
28     2  32.285  1.039                       (-----*-----)
                         ---------+---------+---------+---------+
                              16.0      24.0      32.0      40.0

Pooled StDev = 2.622


Grouping Information Using Tukey Method

day  N    Mean  Grouping
28   2  32.285  A
 7   2  31.025  A
21   2  27.670  A
 0   2  13.550    B
14   2  13.380    B

Means that do not share a letter are significantly different.
```

(4) One-way ANOVA: 11_R20_RA2 versus day

```
Source  DF      SS      MS      F      P
day      4  51.135  12.784  14.50  0.006
Error    5   4.409   0.882
Total    9  55.544

S = 0.9390   R-Sq = 92.06%   R-Sq(adj) = 85.71%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  -------+---------+---------+---------+--
 0     2  32.925  1.195                      (------*------)
 7     2  32.575  0.870                    (------*------)
14     2  32.980  1.146                      (------*------)
21     2  27.515  0.686  (------*------)
28     2  33.820  0.665                         (------*------)
                         -------+---------+---------+---------+--
                              27.5      30.0      32.5      35.0

Pooled StDev = 0.939


Grouping Information Using Tukey Method

day  N    Mean  Grouping
28   2  33.820  A
14   2  32.980  A
 0   2  32.925  A
 7   2  32.575  A
21   2  27.515    B

Means that do not share a letter are significantly different.
```

(5) One-way ANOVA: 11_R30_RA2 versus day

```
Source  DF     SS    MS     F      P
day      4  328.4  82.1  3.03  0.128
Error    5  135.5  27.1
Total    9  463.9

S = 5.205   R-Sq = 70.80%   R-Sq(adj) = 47.44%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ---------+---------+---------+---------+
 0     2  20.835  4.561  (---------*--------)
 7     2  26.820  8.754        (---------*--------)
14     2  26.900  5.035        (---------*--------)
21     2  32.695  3.359              (---------*--------)
28     2  37.645  1.181                   (---------*--------)
                         ---------+---------+---------+---------+
                                 20        30        40        50

Pooled StDev = 5.205


Grouping Information Using Tukey Method

day  N    Mean  Grouping
28   2  37.645  A
21   2  32.695  A
14   2  26.900  A
 7   2  26.820  A
 0   2  20.835  A

Means that do not share a letter are significantly different.
```

(6) One-way ANOVA: 9_R0_RA2 versus day

```
Source  DF      SS     MS      F      P
day      4  196.06  49.02  23.25  0.002
Error    5   10.54   2.11
Total    9  206.60

S = 1.452   R-Sq = 94.90%   R-Sq(adj) = 90.82%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ----+---------+---------+---------+-----
 0     2  21.710  1.711              (----*-----)
 7     2  18.240  0.071       (----*-----)
14     2  18.130  1.386       (----*-----)
21     2  15.690  1.428  (----*-----)
28     2  28.420  1.909                            (----*----)
```

```
                          ----+---------+---------+---------+-----
                           15.0      20.0      25.0      30.0

Pooled StDev = 1.452


Grouping Information Using Tukey Method

day  N    Mean  Grouping
28   2  28.420  A
 0   2  21.710    B
 7   2  18.240    B C
14   2  18.130    B C
21   2  15.690      C

Means that do not share a letter are significantly different.
```

(7) One-way ANOVA: 9_R10_RA2 versus day

```
Source  DF      SS     MS      F      P
day      4  216.72  54.18  17.21  0.004
Error    5   15.75   3.15
Total    9  232.47

S = 1.775   R-Sq = 93.23%   R-Sq(adj) = 87.81%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean  StDev  ---------+---------+---------+---------+
 0     2  18.265  3.528                         (----*-----)
 7     2  13.565  1.110                 (-----*----)
14     2  11.660  0.665              (----*-----)
21     2   3.880  0.962  (----*-----)
28     2  10.900  0.834             (----*-----)
                         ---------+---------+---------+---------+
                                6.0      12.0      18.0      24.0

Pooled StDev = 1.775


Grouping Information Using Tukey Method

day  N    Mean  Grouping
 0   2  18.265  A
 7   2  13.565  A B
14   2  11.660  A B
28   2  10.900    B C
21   2   3.880      C

Means that do not share a letter are significantly different.
```

(8) One-way ANOVA: 9_R20_RA2 versus day

```
Source  DF     SS     MS     F      P
day      4  62.99  15.75  6.38  0.034
Error    5  12.33   2.47
```

```
Total    9  75.32

S = 1.570   R-Sq = 83.63%   R-Sq(adj) = 70.53%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ----+---------+---------+---------+-----
 0     2  26.450  0.665             (--------*-------)
 7     2  28.520  0.962                   (-------*--------)
14     2  26.110  1.103            (--------*-------)
21     2  22.390  2.758  (-------*-------)
28     2  29.735  1.464                       (-------*-------)
                         ----+---------+---------+---------+-----
                          21.0      24.5      28.0      31.5

Pooled StDev = 1.570

Grouping Information Using Tukey Method

day  N    Mean  Grouping
28   2  29.735  A
 7   2  28.520  A B
 0   2  26.450  A B
14   2  26.110  A B
21   2  22.390    B

Means that do not share a letter are significantly different.
```

(9) One-way ANOVA: 9_R30_RA2 versus day

```
Source  DF     SS     MS     F      P
day      4  46.68  11.67  8.50  0.019
Error    5   6.87   1.37
Total    9  53.55

S = 1.172   R-Sq = 87.18%   R-Sq(adj) = 76.92%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ----+---------+---------+---------+-----
 0     2  34.400  0.608             (------*------)
 7     2  33.675  0.417          (------*------)
14     2  35.790  0.877                 (------*------)
21     2  30.960  2.234  (------*------)
28     2  37.410  0.750                       (------*------)
                         ----+---------+---------+---------+-----
                          30.0      33.0      36.0      39.0

Pooled StDev = 1.172

Grouping Information Using Tukey Method

day  N    Mean  Grouping
28   2  37.410  A
14   2  35.790  A
 0   2  34.400  A B
```

```
 7   2  33.675  A B
21   2  30.960    B

Means that do not share a letter are significantly different.
```

Table B. 10. *Analysis of variance of starch based confectionery. Effect of storage on Relative Area 3 (RA3) for each formulation using adjusted SS for Tests*

(2) One-way ANOVA: 11_R0_RA3 versus day

```
Source  DF     SS    MS     F      P
day      4   62.8  15.7  1.51  0.327
Error    5   52.0  10.4
Total    9  114.8

S = 3.225   R-Sq = 54.69%   R-Sq(adj) = 18.45%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ------+---------+---------+---------+---
 0     2  22.860  6.972  (-----------*----------)
 7     2  29.365  0.078              (-----------*----------)
14     2  28.335  0.771            (-----------*----------)
21     2  28.270  1.386            (-----------*----------)
28     2  29.815  0.940               (-----------*----------)
                         ------+---------+---------+---------+---
                            20.0      25.0      30.0      35.0

Pooled StDev = 3.225


Grouping Information Using Tukey Method

day  N    Mean  Grouping
28   2  29.815  A
 7   2  29.365  A
14   2  28.335  A
21   2  28.270  A
 0   2  22.860  A

Means that do not share a letter are significantly different.
```

(3) One-way ANOVA: 11_R10_RA3 versus day

```
Source  DF       SS      MS       F      P
day      4  177.009  44.252  120.22  0.000
Error    5    1.840   0.368
Total    9  178.850

S = 0.6067   R-Sq = 98.97%   R-Sq(adj) = 98.15%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  --------+---------+---------+---------+-
 0     2  21.930  0.212          (--*--)
```

```
 7     2  19.370  0.806  (--*--)
14     2  23.520  0.834              (--*--)
21     2  28.350  0.410                            (--*--)
28     2  30.845  0.530                                   (--*--)
                         --------+---------+---------+---------+-
                              21.0      24.5      28.0      31.5

Pooled StDev = 0.607


Grouping Information Using Tukey Method

day  N    Mean  Grouping
28   2  30.845  A
21   2  28.350    B
14   2  23.520      C
 0   2  21.930      C
 7   2  19.370        D

Means that do not share a letter are significantly different.
```

(4) One-way ANOVA: 11_R20_RA3 versus day

```
Source  DF     SS     MS      F      P
day      4  7.491  1.873  10.71  0.011
Error    5  0.875  0.175
Total    9  8.365

S = 0.4182   R-Sq = 89.55%   R-Sq(adj) = 81.18%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev   --+---------+---------+---------+-------
 0     2  29.050  0.339                 (------*-------)
 7     2  27.855  0.148       (-------*-------)
14     2  27.640  0.170     (------*-------)
21     2  27.515  0.686    (------*-------)
28     2  29.695  0.488                       (-------*-------)
                          --+---------+---------+---------+-------
                         27.0      28.0      29.0      30.0

Pooled StDev = 0.418


Grouping Information Using Tukey Method

day  N     Mean  Grouping
28   2  29.6950  A
 0   2  29.0500  A B
 7   2  27.8550    B
14   2  27.6400    B
21   2  27.5150    B

Means that do not share a letter are significantly different.
```

(5) One-way ANOVA: 11_R30_RA3 versus day

```
Source  DF      SS     MS     F      P
day      4   78.36  19.59  2.30  0.193
Error    5   42.62   8.52
Total    9  120.98

S = 2.920   R-Sq = 64.77%   R-Sq(adj) = 36.58%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ---+---------+---------+---------+------
 0     2  28.810  2.461  (----------*---------)
 7     2  33.915  1.902            (----------*---------)
14     2  36.190  4.455                 (---------*----------)
21     2  32.695  3.359          (---------*----------)
28     2  36.535  1.351                 (----------*----------)
                         ---+---------+---------+---------+------
                         25.0      30.0      35.0      40.0

Pooled StDev = 2.920


Grouping Information Using Tukey Method

day  N    Mean  Grouping
28   2  36.535  A
14   2  36.190  A
 7   2  33.915  A
21   2  32.695  A
 0   2  28.810  A

Means that do not share a letter are significantly different.
```

(6) One-way ANOVA: 9_R0_RA3 versus day

```
Source  DF      SS     MS      F      P
day      4  14.801  3.700  31.58  0.001
Error    5   0.586  0.117
Total    9  15.386

S = 0.3423   R-Sq = 96.19%   R-Sq(adj) = 93.15%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  -----+---------+---------+---------+----
 0     2  28.130  0.453      (----*-----)
 7     2  29.245  0.120            (----*----)
14     2  27.605  0.276  (----*----)
21     2  28.485  0.332        (----*-----)
28     2  31.100  0.424                              (----*----)
                         -----+---------+---------+---------+----
```

```
                          27.6      28.8      30.0      31.2

Pooled StDev = 0.342


Grouping Information Using Tukey Method

day  N     Mean  Grouping
28   2  31.1000  A
 7   2  29.2450    B
21   2  28.4850    B C
 0   2  28.1300    B C
14   2  27.6050      C

Means that do not share a letter are significantly different.
```

(7) One-way ANOVA: 9_R10_RA3 versus day

```
Source  DF      SS      MS      F      P
day      4  952.51  238.13  93.50  0.000
Error    5   12.73    2.55
Total    9  965.24

S = 1.596   R-Sq = 98.68%   R-Sq(adj) = 97.63%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ---------+---------+---------+---------+
 0     2  28.410  2.602                                 (---*--)
 7     2  27.900  0.453                                (---*---)
14     2  28.635  1.464                                 (---*--)
21     2   3.880  0.962  (---*--)
28     2  28.140  1.640                                 (--*---)
                         ---------+---------+---------+---------+
                               8.0      16.0      24.0      32.0

Pooled StDev = 1.596


Grouping Information Using Tukey Method

day  N    Mean  Grouping
14   2  28.635  A
 0   2  28.410  A
28   2  28.140  A
 7   2  27.900  A
21   2   3.880    B

Means that do not share a letter are significantly different.
```

(8) One-way ANOVA: 9_R20_RA3 versus day

```
Source  DF      SS      MS      F      P
day      4  45.289  11.322  19.70  0.003
Error    5   2.874   0.575
Total    9  48.163
```

```
S = 0.7581   R-Sq = 94.03%   R-Sq(adj) = 89.26%


                         Individual 95% CIs For Mean Based on Pooled
StDev
Level  N    Mean  StDev     +---------+---------+---------+---------
 0     2  25.995  1.478                     (-----*----)
 7     2  25.405  0.304                   (-----*----)
14     2  25.460  0.750                   (-----*----)
21     2  21.480  0.156     (-----*----)
28     2  28.045  0.106                              (----*-----)
                            +---------+---------+---------+---------
                         20.0      22.5      25.0      27.5

Pooled StDev = 0.758


Grouping Information Using Tukey Method

day  N    Mean  Grouping
28   2  28.045  A
 0   2  25.995  A
14   2  25.460  A
 7   2  25.405  A
21   2  21.480    B

Means that do not share a letter are significantly different.
```

(9) One-way ANOVA: 9_R30_RA3 versus day

```
Source  DF     SS     MS     F      P
day      4  43.56  10.89  5.89  0.039
Error    5   9.25   1.85
Total    9  52.81

S = 1.360   R-Sq = 82.48%   R-Sq(adj) = 68.47%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  -------+---------+---------+---------+--
 0     2  26.870  0.820          (--------*-------)
 7     2  26.455  0.233         (-------*-------)
14     2  24.495  0.233  (--------*-------)
21     2  24.480  0.382  (--------*-------)
28     2  30.180  2.885                   (--------*-------)
                         -------+---------+---------+---------+--
                             24.0      27.0      30.0      33.0

Pooled StDev = 1.360

Grouping Information Using Tukey Method

day  N    Mean  Grouping
28   2  30.180  A
 0   2  26.870  A B
 7   2  26.455  A B
```

```
14   2  24.495    B
21   2  24.480    B

Means that do not share a letter are significantly different.
```

Table B. 11. *Analysis of variance of starch based confectionery. Effect of storage on Relative Area 4 (RA4) for each formulation using adjusted SS for Tests*

(13) One-way ANOVA: 11_R0_RA4 versus day

```
Source  DF       SS      MS       F      P
day      4  1124.87  281.22  228.26  0.000
Error    5     6.16    1.23
Total    9  1131.03

S = 1.110   R-Sq = 99.46%   R-Sq(adj) = 99.02%

                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ---+---------+---------+---------+------
 0     2  26.515  2.482                                   (-*--)
 7     2   0.000  0.000  (--*--)
14     2   0.000  0.000  (--*--)
21     2   0.000  0.000  (--*--)
28     2   0.000  0.000  (--*--)
                         ---+---------+---------+---------+------
                          0.0       8.0      16.0      24.0

Pooled StDev = 1.110


Grouping Information Using Tukey Method

day  N    Mean  Grouping
 0   2  26.515  A
28   2   0.000    B
21   2   0.000    B
14   2   0.000    B
 7   2   0.000    B

Means that do not share a letter are significantly different.
```

(14) One-way ANOVA: 11_R10_RA4 versus day

```
Source  DF       SS      MS       F      P
day      4  1748.92  437.23  403.16  0.000
Error    5     5.42    1.08
Total    9  1754.34

S = 1.041   R-Sq = 99.69%   R-Sq(adj) = 99.44%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  --+---------+---------+---------+-------
 0     2  27.060  0.283                                 (--*-)
 7     2  26.755  1.690                                 (-*--)
```

```
14     2  27.165  1.577                                    (-*-)
21     2   0.000  0.000  (-*-)
28     2   0.000  0.000  (-*-)
                         --+---------+---------+---------+-------
                         0.0       8.0      16.0      24.0

Pooled StDev = 1.041


Grouping Information Using Tukey Method

day  N    Mean  Grouping
14   2  27.165  A
 0   2  27.060  A
 7   2  26.755  A
28   2   0.000    B
21   2   0.000    B

Means that do not share a letter are significantly different.
```

(15) One-way ANOVA: 11_R20_RA4 versus day

```
Source  DF         SS         MS  F  P
day      4  0.0000000  0.0000000  *  *
Error    5  0.0000000  0.0000000
Total    9  0.0000000

S = 0   R-Sq = *%   R-Sq(adj) = *%



Level  N         Mean        StDev
 0     2  0.000000000  0.000000000
 7     2  0.000000000  0.000000000
14     2  0.000000000  0.000000000
21     2  0.000000000  0.000000000
28     2  0.000000000  0.000000000

       Individual 95% CIs For Mean Based on Pooled StDev
Level    +---------+---------+---------+---------
 0       *
 7       *
14       *
21       *
28       *
         +---------+---------+---------+---------
       0.000000  0.000010  0.000020  0.000030

Pooled StDev = 0.000000000

Grouping Information Using Tukey Method

day  N         Mean  Grouping
28   2  0.000000000  A
21   2  0.000000000    B
14   2  0.000000000      C
 7   2  0.000000000        D
```

```
 0   2  0.000000000          E

Means that do not share a letter are significantly different.
```

(16) One-way ANOVA: 11_R30_RA4 versus day

```
Source  DF     SS     MS     F      P
day      4  724.5  181.1  9.74  0.014
Error    5   93.0   18.6
Total    9  817.4

S = 4.313   R-Sq = 88.62%   R-Sq(adj) = 79.52%


                             Individual 95% CIs For Mean Based on
                             Pooled StDev
Level  N    Mean  StDev  -------+---------+---------+---------+--
 0     2  25.235  3.557                      (------*------)
 7     2  13.965  8.690           (------*-----)
14     2  12.145  2.143          (-----*------)
21     2  20.080  0.481                (------*-----)
28     2   0.000  0.000  (------*------)
                         -------+---------+---------+---------+--
                                0        12        24        36

Pooled StDev = 4.313


Grouping Information Using Tukey Method

day  N    Mean  Grouping
 0   2  25.235  A
21   2  20.080  A
 7   2  13.965  A B
14   2  12.145  A B
28   2   0.000    B

Means that do not share a letter are significantly different.
```

.

Table B. 12**.** *Analysis of variance of starch based confectionery. Effect of storage on Moisture loss % on obtained from TGA curves using adjusted SS for Tests*

(1) One-way ANOVA: 11_R0 versus Day

```
Source  DF     SS     MS     F      P
Day      1  1.823  1.823  2.14  0.281
Error    2  1.704  0.852
Total    3  3.527

S = 0.9231   R-Sq = 51.68%   R-Sq(adj) = 27.52%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ---+---------+---------+---------+------
 0     2  11.620  1.202         (-------------*-------------)
28     2  10.270  0.509  (-------------*-------------)
                         ---+---------+---------+---------+------
                          8.0      10.0      12.0      14.0

Pooled StDev = 0.923


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 0   2  11.6200  A
28   2  10.2700  A

Means that do not share a letter are significantly different.
```

(2) One-way ANOVA: 11_R10 versus Day

```
Source  DF       SS       MS     F      P
Day      1  0.03803  0.03803  4.03  0.182
Error    2  0.01885  0.00942
Total    3  0.05687

S = 0.09708   R-Sq = 66.86%   R-Sq(adj) = 50.29%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  ---------+---------+---------+---------+
 0     2  9.1100  0.0283  (-------------*--------------)
28     2  9.3050  0.1344           (--------------*--------------)
                          ---------+---------+---------+---------+
                                9.00      9.20      9.40      9.60

Pooled StDev = 0.0971
```

```
Grouping Information Using Tukey Method

Day  N     Mean  Grouping
28   2  9.30500  A
 0   2  9.11000  A

Means that do not share a letter are significantly different.
```

(3) One-way ANOVA: 11_R20 versus Day

```
Source  DF    SS    MS     F      P
Day      1  0.34  0.34  0.34  0.618
Error    2  2.01  1.00
Total    3  2.35

S = 1.002   R-Sq = 14.56%   R-Sq(adj) = 0.00%


                        Individual 95% CIs For Mean Based on
                        Pooled StDev
Level  N   Mean  StDev  -------+---------+---------+---------+--
 0     2  7.560  0.665  (---------------*---------------)
28     2  8.145  1.252    (---------------*---------------)
                        -------+---------+---------+---------+--
                             6.0       8.0      10.0      12.0

Pooled StDev = 1.002


Grouping Information Using Tukey Method

Day  N   Mean  Grouping
28   2  8.145  A
 0   2  7.560  A

Means that do not share a letter are significantly different.
```

(4) One-way ANOVA: 11_R30 versus Day

```
Source  DF      SS      MS     F      P
Day      1  0.1600  0.1600  1.90  0.302
Error    2  0.1681  0.0840
Total    3  0.3281

S = 0.2899   R-Sq = 48.77%   R-Sq(adj) = 23.15%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  -----+---------+---------+---------+----
 0     2  10.195  0.219  (--------------*--------------)
28     2  10.595  0.346         (--------------*-------------)
                         -----+---------+---------+---------+----
                            9.60     10.20     10.80     11.40
```

```
Pooled StDev = 0.290


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
28   2  10.5950  A
 0   2  10.1950  A

Means that do not share a letter are significantly different.
```

(5) One-way ANOVA: 9_R0 versus Day

```
Source  DF     SS     MS     F      P
Day      1  0.563  0.563  0.92  0.439
Error    2  1.226  0.613
Total    3  1.788

S = 0.7829   R-Sq = 31.45%   R-Sq(adj) = 0.00%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  -+---------+---------+---------+--------
 0     2  10.410  0.523       (--------------*---------------)
28     2   9.660  0.976  (--------------*---------------)
                          -+---------+---------+---------+--------
                         7.5       9.0      10.5      12.0

Pooled StDev = 0.783


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
 0   2  10.4100  A
28   2   9.6600  A

Means that do not share a letter are significantly different.
```

(6) One-way ANOVA: 9_R10 versus Day

```
Source  DF       SS       MS       F      P
Day      1  2.67322  2.67322  483.84  0.002
Error    2  0.01105  0.00553
Total    3  2.68427

S = 0.07433   R-Sq = 99.59%   R-Sq(adj) = 99.38%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  -+---------+---------+---------+--------
 0     2  7.9750  0.0354  (---*---)
28     2  9.6100  0.0990                            (---*---)
                          -+---------+---------+---------+--------
```

```
                           7.80      8.40      9.00      9.60

Pooled StDev = 0.0743


Grouping Information Using Tukey Method

Day  N    Mean  Grouping
28   2  9.6100  A
 0   2  7.9750    B

Means that do not share a letter are significantly different.
```

(7) One-way ANOVA: 9_R20 versus Day

```
Source  DF     SS     MS      F      P
Day      1  6.656  6.656  27.59  0.034
Error    2  0.483  0.241
Total    3  7.139

S = 0.4912   R-Sq = 93.24%   R-Sq(adj) = 89.86%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ---------+---------+---------+---------+
 0     2   7.635  0.643  (---------*---------)
28     2  10.215  0.262                  (---------*---------)
                         ---------+---------+---------+---------+
                               7.5       9.0      10.5      12.0

Pooled StDev = 0.491


Grouping Information Using Tukey Method

Day  N     Mean  Grouping
28   2  10.2150  A
 0   2   7.6350    B

Means that do not share a letter are significantly different.
```

(8) One-way ANOVA: 9_R30 versus Day

```
Source  DF     SS     MS     F      P
Day      1  5.570  5.570  6.36  0.128
Error    2  1.751  0.875
Total    3  7.321

S = 0.9357   R-Sq = 76.08%   R-Sq(adj) = 64.12%


                        Individual 95% CIs For Mean Based on
                        Pooled StDev
Level  N   Mean  StDev   -+---------+---------+---------+--------
 0     2  7.585  1.322   (----------*-----------)
28     2  9.945  0.049            (-----------*----------)
```

```
                  -+---------+---------+---------+--------
                 5.0       7.5      10.0      12.5

Pooled StDev = 0.936


Grouping Information Using Tukey Method

Day  N    Mean  Grouping
28   2  9.9450  A
 0   2  7.5850  A

Means that do not share a letter are significantly different.
```

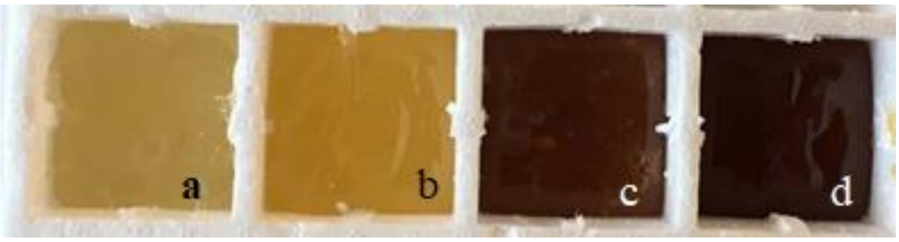

Figure A. 1. Color of starch based confections immediately after cooking (a) 11_S0_R0 (b) 11_S0_R30 (c) 9_S2_R0 (d) 9_S2_R30