



Study and Characterization of Microstructural and
Physio-chemical properties of potato products for 3D
Food Printing.

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SEPTEMBER 25, 2018

PHD THESIS

Universitat Politecnica de Catalunya (UPC) and Lebanese University (LU)



UNIVERSITAT POLITÈCNICA
DE CATALUNYA
BARCELONATECH

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Universitat Politècnica de Catalunya BarcelonaTech (UPC)

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Cotutelle Doctoral Thesis

Study and Characterization of Microstructural and Physio-chemical properties of potato products for 3D Food Printing.

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Dr. Monserrat Pujola

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Acknowledgements

First of all, I would like to thank myself for being my ultimate friend all along this journey, for enduring all these responsibilities, ups and downs and for persisting to carry on the path till the end...and Thanks God for always providing me with this strength to continue, Thanks for your guidance, for your pure kindness and protectiveness when I was lonely, for facilitating all my ways when I really felt it is over, Thanks for everything....

I would like also to thank my advisors in Spain Dr. Francesc Sepulcre and Dr. Montserrat Pujola, for being wonderfully supportive and for sharing their immense knowledge. For always believing in me starting from the first year, for teaching me different things in Life as well, that life is not always perfect, you couldn't expect to succeed every time, as I was not used to the term of failure, but failure itself is a normal methodology that you use its outcome every time to push your borders, strengthen your strategies, unlock your fears and widen up your mind. Thanks for teaching me that PhD is not only a project where you should come up with a result at the end, but a chapter of life that covers all these aspects...

Much gratitude is extended to Dr. Amira Haddarah, my Lebanese advisor, for her insightful comments and encouragement, for her willingness and openness to share her experience, but also for inciting me to widen my research from various perspectives.

My sincere thanks goes to my family, Dad, Mom, sisters, brothers, Grandpa and my friend and cousin Hanane, your motivation during the years of my research has provided me with the confidence and the desire to persevere and have turned my difficult times in to joy.

Last but not least, I would like to direct this thesis to my grandma's soul, who was my best friend and first supporter to go through this journey. Yet, she left us suddenly during my first PhD year when I was abroad. I still feel distracted for not being able to say goodbye, but I know you are up there proud and happy for me.

Summary-English

3D food printing is a precise digitalized process that is based on monitoring the characteristics of the printed substrate in accordance with the process parameters. In this thesis mashed potatoes were first mixed with different food additives (agar, alginate, lecithin and glycerol) at different concentrations (0.5, 1 and 1.5%) in order to compare how each additive would affect the yield stress, viscosity, thixotropy, mechanical properties as well as the internal microstructure of potato puree. It was observed that agar and alginate enhanced the rheological and mechanical properties of puree by forming a stronger internetwork structure thus providing better printing with many build up shapes and that are stable post deposition. On the other hand, lecithin and glycerol decreases the rheological and mechanical properties of puree and thus although the extrusion was smooth, end printed products were unstable and collapsed instantly. Additionally, to inspect the reason behind obtaining those rheological and mechanical values, a further investigation at the molecular level (applying FTIR and XRD) was done. It was revealed that additives such as glycerol and lecithin can penetrate the starch granules and induce a more intense effect on the structure as their respective concentrations increase by either suppressing (ex, glycerol) or enhancing (ex lecithin) the starch structure. In contrast, long polymeric molecules such as agar and alginate interact partially via the surface of the starch granules modifying partially the conformation of starch structure, which confirms the previous deductions from the rheological properties part. Furthermore, FTIR spectra showed that the skeleton formed by the amylose/amylopectin is somehow hidden in the dehydrated potato flakes, but was covered almost completely upon the addition of water such as to complement that of an original raw potato FTIR spectra, proving that water molecules have a central role in the maintenance of the starch structure conformation. To verify this hypothesis, task 4 was developed in order to make sure after what time of water reduction is the starch conformation altered (using this time potato tubers) and to identify whether the starch structure is modified more by the effect of the water removal or the heat treatment (microwaved and boiling). Findings showed that microwaved (MP) and boiled (BP) potato were more susceptible for water evaporation by freeze drying expressed via the following microstructural changes only after 6 hours of lyophilization; 1- obtaining an IR spectrum with much lower intensities (dried spectrum) compared to the initial spectrum, 2- undergoing a major transformation from gelatinized swollen starch to some recoiling towards a dried starch granule (SEM figures), 3- exhibiting an increase in the intensity of their respective XRD patterns. Moreover, RP took around 24 hours to reach a dried stage that was characterized by some ruptured granules embedded within leached starch matrix, an FTIR spectra that resembles in intensity that of BP and MP, possessing two peaks at 485 cm⁻¹ and 620 cm⁻¹ and that were assigned as a distinctive for a dried potato starch spectrum. Concluding that water removal sublimates the effect of the heat processing treatment, being the major contributor in the modifications of the starch structure. MP and BP were then used as basic samples for 3D printing trials while adding to each different food substrates at 1% concentration with respect to the weight (butter, olive oil, alginate and agar) except for carrots which were added at a ratio of 1/3 of the respective potato weight. All MP samples showed higher rheological and mechanical properties that lead to more stable printed products. Best printability was accounted with butter insertion which elevated the yield stress and thixotropy, thus increasing structural integrity and maintaining higher retaining shape property while preserving smooth extrusion and creamy surface structure.

Resumen- Español

La impresión 3D de alimentos es un proceso digitalizado preciso que se basa en el monitoreo de las características del sustrato impreso de acuerdo con los parámetros del proceso. En esta tesis, se ha utilizado como sustrato el puré de patatas mezclado con diferentes aditivos alimentarios (agar, alginato, lecitina y glicerol) a diferentes concentraciones (0,5, 1 y 1,5%) para poder comparar el efecto de cada aditivo sobre las propiedades reológicas (límite elástico, viscosidad, tixotropía), mecánicas y la microestructura interna del puré de patata. Los resultados han permitido observar que el agar y el alginato mejoraron las propiedades reológicas y mecánicas del puré al formar una estructura de interconexión más fuerte, proporcionando una mejor impresión con diversidad de formas y estables después de la deposición. Por otro lado, el uso de lecitina y glicerol disminuyeron las propiedades reológicas y mecánicas del puré y, por lo tanto, aunque la extrusión fue posible, los productos finales impresos fueron inestables y se colapsaron al instante. Adicionalmente, para validar la obtención de esos valores reológicos y mecánicos, se realizó una investigación adicional a nivel molecular aplicando FTIR y XRD. Los resultados indicaron que los aditivos glicerol y lecitina pueden penetrar en los gránulos de almidón e inducir un efecto más intenso sobre la estructura a medida que aumentan la concentración, suprimiendo (glicerol) o potenciando (lecitina) la estructura del almidón. Por el contrario, moléculas poliméricas largas como agar y alginato interactúan parcialmente a través de la superficie de los gránulos de almidón modificando parcialmente la conformación de su estructura, lo que confirmó los resultados previos de las propiedades reológicas. Además, los espectros FTIR mostraron que el esqueleto formado por la amilosa / amilopectina que esta " oculto" en las escamas de patata deshidratada, con la adición de agua vuelve a tener prácticamente el espectro original de FTIR de la patata cruda, lo que demuestra que las moléculas de agua tienen un papel central en el mantenimiento de la conformación de la estructura del almidón. Para verificar la hipótesis, de que " la reducción del agua puede alterar la conformación y estructura del almidón del tubérculo de patata" se procedió a comprobar el efecto de la eliminación de agua (liofilización) o el efecto del tratamiento térmico (cocción en microondas o hervido). Los resultados mostraron que la evaporación del agua por liofilización presentaba cambios micro-estructurales superiores a las cocinadas en microondas (MP) o hervida (BP) ya que con solo 6 horas de liofilización se obtuvo; un espectro FTIR con intensidades mucho más bajas (espectro seco) en comparación con el espectro inicial; se observó mediante SEM una transformación importante del almidón hinchado (gelatinizado) hacia un gránulo de almidón seco y se incrementó la intensidad de sus respectivos patrones de X-RD. Además, en la patata cruda (RP) se tardó alrededor de 24 horas en alcanzar la deshidratación, que se caracterizó por algunos gránulos rotos incrustados dentro de la matriz del almidón lixiviado, un espectro FTIR que se asemeja en intensidad al de BP y MP, (picos a 485 cm⁻¹ y 620 cm⁻¹) que fueron asignados como un distintivo para un espectro de almidón de patata deshidratada. Concluyendo que la eliminación del agua por sublimación produce efectos micro-estructurales superiores al del procesamiento térmico, siendo el agua el principal contribuyente de las modificaciones de la estructura del almidón. Para finalizar, se usaron estos dos tratamientos: cocción al microondas (MP) y hervido (BP) para las pruebas de impresión 3D. Los resultados obtenidos indicaron que todas las muestras MP mostraron mejores propiedades reológicas y mecánicas lo que nos permitió obtener productos impresos más estables

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- **Chapter 1: Introduction**

1. Potato starch microstructure

Purees made from mixture of vegetables are, in general, widely welcomed high-quality products, especially in ready-meals markets. Newly, potato purees have made the transition of vegetables from traditional non-printable materials into available ingredients to be used in 3D printing technology. In fact, starch is the major component of potato tubers, accounting around 70% of the dry matter content (Bordoloi, Kaur, & Singh, 2012) and it is the textural properties of the native starches that marks them to be easily modified by different chemical, enzymatic and physical methods, making starch also a preferred polymer for many technological manipulations in the food industry, such as thickening, coating, gelling, and encapsulating agent (native starches do not generally have ideal properties for food products in which most often they are chemically modified to improve their tolerance to processing) (Hermansson and Svegmarm 1996; Singh et al. 2007). Generally, the raw starch found in potato tubers is organized into structurally void granules consisting of two types of α -glucans: amylopectin (a heavily branched α -glucan polymer of high average molecular weight with an α (1 \rightarrow 4)-linked backbone and α (1 \rightarrow 6)-linked branches) and amylose (a linear and relatively long α -glucan polymer linked by α (1 \rightarrow 4)-linkages). Raw starch granules show a crystalline/amorphous structure that can be recognized at both the short- (nm) and long-range (several μ m) scales. In particular, short-range ordering corresponds to double and single helical amylose or amylopectin, embedded in amorphous or crystalline lamellar regions, as well as amylose-amylopectin helices complexes (Tester, Karkalas, & Qi, 2004). The arrangement and ordering of double helices into concentric alternating stacks of microcrystalline and amorphous lamellar structures are associated with long-range ordering (Fig. 1).

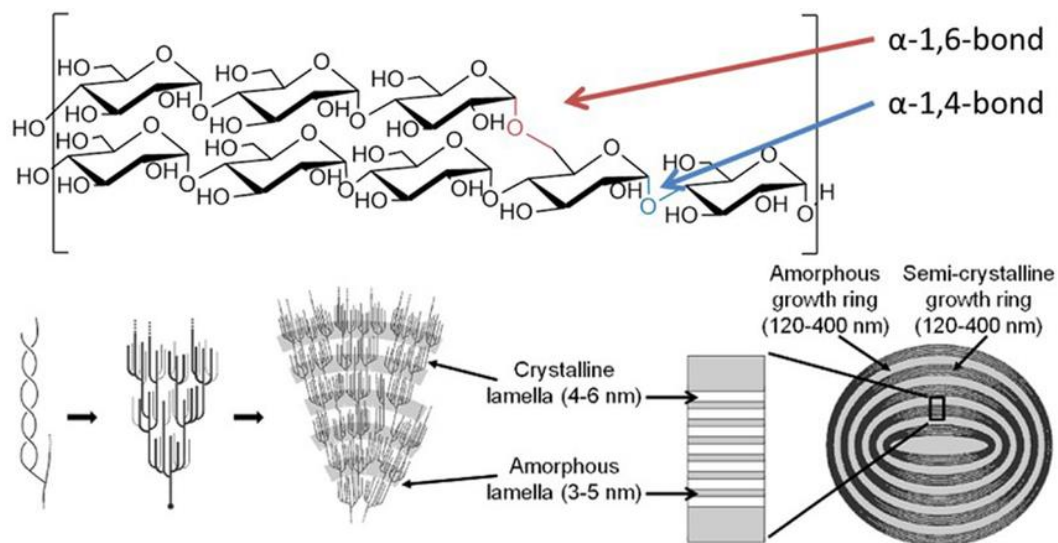


Figure. 1 Structure of the starch granule (O'Neill & Field, 2015)

2. Starch response to different technological processes

Potato starch is unique among other starches in having large size granules and high swelling power due to the presence of high level of phosphate groups that are covalently linked to the C6 and C3 positions of the glucose monomers. In combination with swelling, breakdown and retro-gradation of starch are the three processes that determine the texture of starch based food during processing. For instance, upon applying additional water and high temperature to starch, water is absorbed to the amorphous region and starch granule swell. The elevated temperature will cause the double helical structure of amylopectin to diffuse and the amylose to leach out from starch granules. Granules now containing mostly amylopectin collapse and are held in a matrix of amylose forming gel, this response refers to starch gelatinization. The process of pasting or retro-gradation usually follows gelatinization, which involves the formation of starch gel or paste due to amylopectin recrystallization after system cooling or subsequent storage. Also, pressure or shear application, for example during extrusion as well as some additives insertion may cause starch fragmentation and solubilization due to the breakdown of the main and secondary hydrogen bonds between neighboring starch polymers in starch structure and the formation of a new network complex with the applied additives. In fact, these different responses of starch to processing methods offer its unique characteristics and determine its textural and rheological properties. However, starch pastes in general are strongly thixotropic and shear thinning (BeMiller, 2011; Lai & Kokini, 1991; Ramos & Ibarz, 1998; N. Singh, Singh, Kaur, Sodhi, & Gill, 2003).

Moreover, Potato tubers are commonly cooked before consumption using various methods, such as boiling, frying, baking or microwaving, which produces potatoes with different mechanical and sensorial characteristics according to the type of cooking method used. For instance, it was reported that microwaving potatoes induced more a firmer texture than boiling and baking and that the individual sugar content increased during baking and microwaving compared to that during boiling (Yang, Achaerandio, & Pujolà, 2016). The major changes induced during cooking can be summarized as follows: softening of the potato tissue due to heating, which causes a loss of integrity of the cell membranes; weakening of binding between intact cells, leading to their separation and resulting in a loss of turgor. Moreover, cooking promotes starch swelling by modifying the percentage of available water and inducing gelatinization (Fedec, Ooraikul, & Hadziyev, 1977; Ormerod, Ralfs, Jobling, & Gidley, 2002; N. Singh, Kaur, Ezekiel, & Guraya, 2005).

3. Most widely used techniques for determining starch microstructure and texture

Accordingly, a good understanding of potato texture upon application of physical pressure (extrusion while 3D printing) or chemical (food additive while mixing) requires sufficient knowledge of microstructural features such as cell shape, size and media characteristics. Advanced microscopic techniques, such as confocal scanning laser microscopy and electron microscopy (SEM) have been used by various researchers to study the microstructure properties of food including potatoes (Bordoloi et al., 2012; Kaur, Singh, & Singh, 2004). Moreover, the texture and rheological properties of raw, cooked or mashed potatoes have been studied using a texture analyzer, rotational

viscometer, cone-cylinder viscometer by various researchers (Dankar, Haddarah, El Omar, Sepulcre, & Pujolà, 2018; Huang, Kennedy, Li, Xu, & Xie, 2007;; N. Singh, Kaur, Ezekiel, & Guraya, 2005; N. Singh et al., 2003; Svegmarm & Hermansson, 1993, Hughes, Faulks, & Grant, 1975). Furthermore, in order to investigate the reason behind such a cellular shape that appear by a SEM or such a rheological or textural behavior, a deeper investigation at the molecular level is required and which could be hold on by several techniques, such as Fourier-transform infrared spectroscopy (FTIR). Using FTIR, it would be possible to identify the most characteristic vibrational bands of several starches, provide information on amylose and amylopectin chain folding (Ramazan Kizil et al., 2002) and the crystalline/amorphous ratio (Ispas-Szabo, Ravenelle, Hassan, Preda, & Mateescu, 1999). Also, to study the retro-gradation of potato starch (Flores-Molares et al., 2012; Van Soest et al.,1994) under the conclusion that the spectral region 800-1100 cm^{-1} contains bands that are sensitive to the starch polymer conformation (α (1 \rightarrow 4)-linked backbone, $-\text{CH}_2$ backbone, etc.) and that can be used to follow crystallite melting and the multi-stage processes of retro-gradation (Zhang et al., 2013; Flores-Molares et al., 2012)). Nuclear magnetic resonance (NMR), X-ray diffraction (XRD) and differential scanning calorimetry (DSC) are other important chemical analyses that have been used to characterize starch structures and detect any changes in the starch pattern crystallinity due to different processing techniques. DSC has been greatly used to detect the loss of crystalline order during gelatinization (first order melting thermal transition) and the reordering of starch systems during aging (second order thermal glass transition). For instance, NMR and XRD were used by Cooke & Gidley (1992) to identify that the enthalpy transition is primarily due to the loss of the double helical order rather than crystallinity. Moreover, Ribotta et al. (2004) found that amylopectin retro-gradation and B-type crystalline structure were augmented during ageing using DCS and XRD.

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▪ **Chapter 2: Bibliography**
**3D printing technology: The new era for food
customization and elaboration**

- *This chapter has been published as:*

Dankar, I., Haddarah, A., Omar, F. E. L., Sepulcre, F., & Pujolà, M. (2018). 3D printing technology: The new era for food customization and elaboration. *Trends in Food Science & Technology*, 75, 231–242. <https://doi.org/10.1016/J.TIFS.2018.03.018>

3D printing technology: The new era for food customization and elaboration

Abstract

Background: Digitalizing food using 3-Dimensional (3D) printing is an incipient sector that has a great potential of producing customized food with complex geometries, tailored texture and nutritional content. Yet, its application is still limited and the process utility is under the investigation of many researchers.

Scope and approach: The main objective of this review was to analyze and compare published articles pertaining 3D food printing to ensure how to reach compatibility between the huge varieties of food ingredients and their corresponding best printing parameters. Different from previously published reviews in the same journal by Lipton et al. (2015) and Liu et al. (2017), this review focuses in depth on optimizing extrusion based food printing which supports the widest array of food and maintains numerous shapes and textures. The benefits and limitations of 3D food printing were critically reviewed from a different perspective while providing ample mechanisms to overcome those barriers.

Key findings and conclusions: Four main obstacles hamper the printing process: ordinance and guidelines, food shelf life, ingredients restrictions and post processing. Unity and integrity between material properties and process parameters is the key for a best end product. For each group, specific criteria should be monitored: rheological, textural, physiochemical and sensorial properties of the material its self in accordance with the process parameters of nozzle diameter, nozzle height, printing speeds and temperature of printing. It is hoped that this paper will unlock further research on investigating a wider range of food printing ingredients and their influence on customer acceptability.

Keywords: 3D food printing, benefits, technology, optimization, ingredient

1. Introduction

3D printing, also referred to as additive manufacturing (AM) and rapid prototyping (RP), is an emerging digitalized technology that is subjected to daily debate, grabbing a wide interest from researchers, industry and public with its diverse fields of applications that are constantly growing such as medicine, gastronomy, engineering, manufacturing, art and education (Murphy & Atala, 2014; Rayna & Striukova, 2016). Yet, its major challenge and complex applications are emerging in the field of gastronomy (Kietzmann, Pitt, & Berthon, 2015); in other words, the trending field that is stimulating researchers in 3D printing currently is “3D food printing”, (Table 1). The basic of 3D printing is a controlled robotic-process whereby a product is built up layer by layer from a 3D computer design program CAD or by downloading 3D platforms from some online services (e.g., Thingiverse, Shapeways, Ponoko or Sculpteo) (Gibson, Rosen, & Stucker, 2009; Kietzmann et al., 2015; Peppel, 2015; Rayna & Striukova, 2016). Once the 3D model is created, the information of the design is sent to the printer, which in turn slices the 3D model into layers and assembles them in the specified cross section pattern (Galdeano, 2015). For food sector, it is believed that RP technology will define new borders for food processing by being able to deliver a product that suits special consumer’s criteria of taste, cost, convenience and

nutrition (Deloitte, 2015). Moreover, it has the potential to eliminate many of the barriers of resources and skills that currently prevent ordinary inventors from establishing their own ideas, thus to allow for “Democratizing of Innovation” that opens the door for a new class of independent designers and a new economy of custom products (Malone & Lipson, 2007). Therefore, although foods are complex systems with wide variations in physio-chemical properties, researchers have worked on widening the application of 3D printing to various types of food products.

According to Lipson (2015), the engineering concept of how 3D food printers work have been cleared, nevertheless what could be creatively made is yet to be explored (Tess, 2016). By optimizing several parameters of the printing process (chain of processing, ingredients), some successful results of novel 3D printed shapes have been published using different food substrates starting from printing with chocolate (Periard et al., 2007 Hao et al., 2010;), to cookie doughs and cereals (Lipton et al., 2010; Severini et al., 2016, Hamilton et al., 2017), sugar powder (Holland et al., 2018; Lille et al., 2018), processed cheese (Periard et al., 2007.Le Tohic et al., 2018), meat gels (Lipton et al., 2010; Wang et al., 2018) and recently some fruits and vegetables (Severini et al., 2018; Yang et al., 2018).

Furthermore, several works have reviewed the topic of 3D food printing from different points of views; however, little knowledge still exists on the relationship between critical variables of the printing process and material structure to obtain the desired printed product (Severini et al., 2018). Actually, two reviews published in the same journal have dealt with the topic of 3D food printing. The first by Lipton et al. (2015) who focused on the key motivators behind the maturation of 3D food printing (reproduction of traditional foods, increasing shape fidelity and food customization) and which they considered to consequently increase the utility of 3D printing whether at a consumer or at an industrial scale; the second by Liu et al. (2017) who introduced three challenges (printing precision, process productivity and production of multi flavor-color-structural product) to be overcome in order to ensure broad applicability of 3D food printing as well as highlighting the idea on how to achieve a precise food printing but using the different food printing technologies. Therefore, different from the previously published reviews, the aim of this review is to focus in depth on interpreting how to optimize extrusion based food printing (process parameters and relatively specific substrate control) which supports the widest arrays of food while maintaining numerous shapes and textures. Moreover, to spotlight new regions and multi-sectors that 3D food printing can beneficially affect and incorporate. Also, to introduce critically the limitations of this process from a different perspective while providing chief trends and insights in order to overcome those barriers.

Table 1: Comparison between food 3D printing and non-food 3D printing

	Food 3D printing	3D printing	References
Differences	<ul style="list-style-type: none"> • Substrate: Food material with high variability of physiochemical properties both before and after printing process Flow able and able to hold its structure post processing (chocolate, cookie dough, cheese, hummus, hydrocolloids) • Preprocessing Fine tuning of foods recipe Ingredient mixing with different hydrocolloids • Printing process: Mainly extrusion based process Greater retraction to reduce pressure at nozzle tip due to lower viscosity of food • Post processing: Some products might be applied to temperature variations (cooking, oven drying, freeze drying) • Sensory attributes: appeal, texture, aroma, taste is critical for evaluation • Two major challenges Safety and Labelling 	<ul style="list-style-type: none"> • Substrate: Thermoplastic materials with invariable properties, plastic, resin, polymers. • Preprocessing Usually no preprocessing step is required • Printing process: Mainly photo-polymerization and selective laser sintering using photo-sensitive (laser and UV light) In extrusion modelling lower retraction is required due to high viscosities of plastic materials • Post processing: Polishing, chemical finishing • Sensory attributes: Appeal and texture are critical for evaluation 	(Bak, 2003; Gibson, Rosen, & Stucker, 2009; Kietzmann, Pitt, & Berthon, 2015; Kim, Bae, & Park, 2017; Le Tohic et al., 2017; Liu, Zhang, Bhandari, & Yang, 2017; Porter & Phipps, 2015; Rayna & Striukova, 2016; C. Severini, Derossi, Ricci, Caporizzi, & Fiore, 2017; Sun, Zhou, Yan, Huang, & Lin, 2017; Tumbleston et al., 2008; Wang, Zhang, Bhandari, & Yang, 2017; Yang, Zhang, & Bhandari, 2015)
Applications	<ul style="list-style-type: none"> • Industrial sectors • Restaurants • Hotels • Military services • Aerospace missions • Customized snacks for children, athletes, people facing mastication problems 	<ul style="list-style-type: none"> • Bio-printing: building transplanted tissues, bones, skin grafts • Dentistry: Crowns, denture impressions, dental devices • Pharmaceutical: Digital drug delivery system • Electronics: Automotive and Aerospace industry, arm weapons, musical instruments, jewelry 	(Azari & Nikzad, 2009; Bak, 2003, Bakarich et al., 2013; de Roos, 2013; Derossi et al., 2017; Gross et al., 2014; Hribar et al., 2014; Lipton et al., 2015; Malone & Lipson, 2007; Severini et al., 2017; Carla Severini & Derossi, 2016)
Similarities	<ul style="list-style-type: none"> • Same process principle: digitalized 3D model creation-slicing in to specific layers-outcome 3D printed model • Providing customized personalized products • Use limited number of raw materials • Shorter production runs (simplifying supply chain) • High degree of freedom 		(Galdeano, 2015; Kietzmann, Pitt, & Berthon, 2015; Murphy & Atala, 2014; Petrovic et al., 2011; Rayna & Striukova, 2016; Yang, Zhang, & Bhandari, 2015)

2. Why Print Food, Uses and Benefits of 3D Food Printing

2.1. *Creating Personalized Food Products for a Wide Variety of Consumers*

Personalizing food means simply connecting self-knowledge to food choices (German & Watzke, 2004). 3D printing provides a broad array of completely personalized food that precisely fit the needs, taste and dietary pattern of people from different ages, sexes, occupations, and health lifestyles by adjusting the composition, density or structure to the preferences and needs of the user (Peppel, 2015; Rodgers, 2016; Sher & Tutó, 2015).

Approximately 25% of people above the age of 50 have mastication and swallowing problems, so they obtain their required nutrition from pureed food, most of which is unappealing and unappetizing. Providing soft, nutritious and innovative textured food for the elderly and that meets the legislative boundaries for the corresponding country is a major challenge in the food industry (Aguilera & Park, 2016). Therefore, the Netherlands Organization for Applied Scientific Research (TNO) launched a project called “Performance” that aims at printing customized pureed food with a flexible degree of design to help the elderly cope with their chewing and swallowing problems. TNO has also suggested printing customized meals for seniors, athletes and sportsmen that need recovery products after training or for expectant mothers by varying nutrient components levels such as proteins and fats, reducing or eliminating undesirable ingredients and introducing healthy ingredients such as vitamins, fibers and phytochemicals (anthocyanins, carotenoids, betanidins). Actually this meal modification would be based on extensive understanding of genotypes, phenotypes and meta-biotypes that specifies the nutritional requirements of a specific individual (de Roos, 2013). Another susceptible group of people that could benefit from personalizing food are children since they would be more willing to consume healthy nutritious snacks with innovative shapes, that could be used as educational tools as well (Hamilton et al., 2017). Recently some articles have been published with the aim of developing customized snack products. Derossi et al. (2018) have evaluated the use of 3D printing technology to develop personalized food formula, a fruit based snack for children. This snack was nutritionally designed to meet the energy requirements of 3-10 years old children. The formula was also rich in essential vitamins such as vitamin D, Ca and Fe which were adequately present to fulfil the children’s daily intake. However, these nutrients are generally absent in commercial fruit-based products. Lille et al. (2018) have designed a 3D printed customized healthy snack made of protein, starch and fiber rich materials that are considered nutritive functional ingredients. These personalized foods for health form the next logical step in personalizing the quality of life. In fact, only when foods are personalized for health simultaneously with enjoyment will the true success of personalizing food be achieved (German & Watzke, 2004; Sun et al., 2015; Severini & Derossi, 2016).

2.2. *Enhancing the Process of Production*

There is an increasing market demand for customized food products with personalized values of convenience, cost, packaging, and taste to be introduced as distinguishable food in the marketplace (German & Watzke, 2004; Periard et al., 2007; McIntosh et al., 2011; Tran, 2016). However, most are designed and manufactured by special artisans and need a longer time for design and fabrication, making the cost of a piece relatively high; 3D printing can bridge the gap between culinary arts and non-professional food artisans (Sun et al., 2015; D’Angelo et al., 2016). Besides, 3D printing shows some

economic characteristics for the company by being able to replace multiple steps or even the complete food production process, hence, reducing the cost of mass customization and human errors in food production and at the same time increasing the production efficiency (Bak, 2003; Sun et al., 2015). In addition, products are made only after orders are received and paid for; this increases the capital working management as well and prevents the accumulation of stocked products (Berman et al., 2012; Kietzmann et al., 2015; Rayna & Striukova, 2016). The well-known PepsiCo company, after suffering huge problems in the sales market of sugary drinks and fatty snacks, had decided to incorporate 3D printing in the manufacturing of its potato chips, as a method of saving money and creating healthier food (Simon, 2015).

2.3. Novel Food Structuring Using a Broad Range of Alternative Food Ingredients

3D printing technology can create unique new products that other methods simply cannot emulate. The idea of fashioning food into aesthetical shapes takes many forms in the world today (Periard et al., 2007). It is a design freedom of innovative shapes, textures and flavors for both home users and designers. 3D food printers also allow for combining food ingredients and flavors in a completely new way. Some companies such as Bocusini have developed their own market place for sharing recipes and ingredients for 3D food printing. For instance, a 3D printed octopus potato puree was finely printed on the Bocusini blog page (Molitch-Hou, 2015). In addition, the TNO organization has been looking for the creation of novel food structures but with new ingredients instead of traditional ones. Alternative base materials can involve the usage of proteins from algae, insects, fungi, or lupine seeds to create tasty structured food. These raw materials are good not only for health but also for the environment. Thus, 3D food printers provide access to raw materials whose appearance presents an obstacle to use (Peppel, 2015; Sher & Tutó, 2015). Buddhist cuisine applies soy-based or gluten-based materials for cooking meat analogue or mock meat dishes for vegetarians and Buddhists, which taste very similar to meat (Sun, Peng, Yan, et al., 2015).

2.4. Environmentally Friendly and Sustainable Technology

The advantages offered by additive manufacturing involve the reduction of the ecological footprint by using fewer raw materials and less energy (Kietzmann et al., 2015; Petrovic et al., 2011; Tran, 2016). 3D Food printing will decrease the amount of food waste generated since it is a highly efficient process that can merge multiple steps during processing into one step, food will not be manufactured unless it is ordered, and consequently, this is translated into less water and energy consumption. Galdeano (2015) a/ determined that the total amount of waste generated in Europe is approximately 77 million tons per year, in which 70% of total waste is from manufacturing and household origin, b/ hypothesized that 3D printers can be one of the solutions for this problem because 3D printers are actually implanted in manufacturing and householder's fields and c/ supposing a background where the total implemented technology of 3D printers will account for 25% of the total European food consumption, this means that 25% of the total amount of the food wasted during traditional processing methods would be excluded, which approximates 19 million tons of food not thrown away.

2.5. Promoting Higher Social Bonding through Food Messaging

It has been stated that 3D food printing stimulates social bonding and life in the media (Huang, Liu, Mokasdar, & Hou, 2013). Conveying information with food creates an atmosphere of generosity and

provides the occasion with more specialties such as sharing cakes, chocolates, cookies with frosted words carved on them or food for promotion with printed business logos. The intervention of 3D printers and its availability to home consumers would facilitate the communication of food messages that previously had been hindered due to the requirements of special skills. Unlike other communication media, such as paper or electronics, food sensory stimulation enhances the mood and emotions and strengthens the social bonds between parties involved in the communication. In a study and survey conducted by Wei et al. (2014) to evaluate the impact of food messaging on people from different ages (20-38), sexes and cultural backgrounds using 3D printers, it was found that most participants believe that messages received by food such as “*Be Happy Everyday*”, “*You are the Best*”, or “*You will be Successful*” not only deliver a traditional text that is displayed on screen or paper but also serves as a physical sensation of affection and care. One interviewer noted, “*I usually forgot the content I sent or received from SMS, but I can remember clearly the words on food, and also who sent it to me*”. Thus, one of the important roles of 3D printers would be to enhance the social communication bond between people by providing an easier and quicker way of delivering better looking food messages on a wide variety of foods such as fruits and vegetables, not only cookies and cakes.

3. 3D Food Printing Technologies:

The key to determine which process to use is the nature of the materials being printed. In fact, there are a vast number of different foods, even more than with metals and polymers, and each with a unique combination of consistency, malleability and adhesion. Thus, the different types of 3D printing technologies (Fig. 1) applied on food, their principle, accessible materials, pros and cons as well as the company that applied each technology are summarized in Table 2.

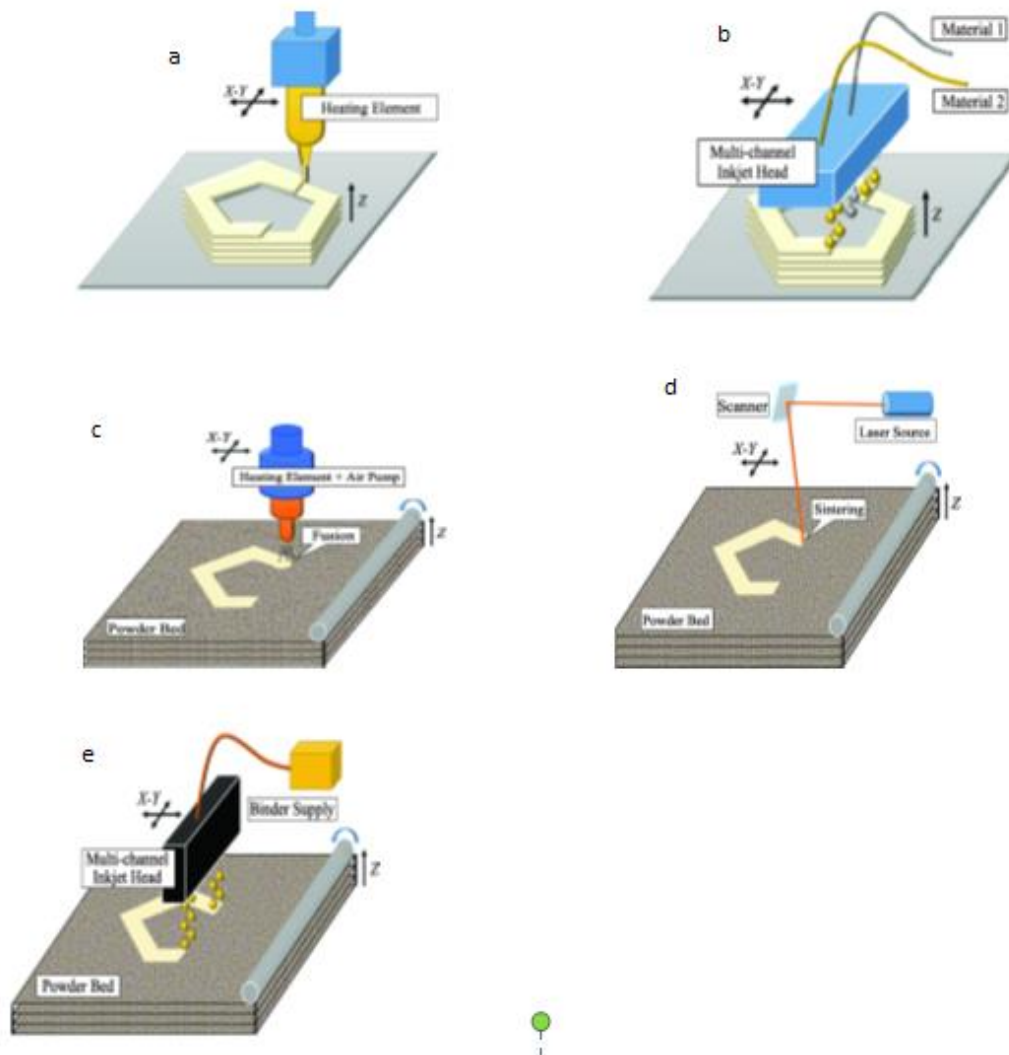


Figure. 1 A schematic representation of the different technologies applied in 3D food printing: direct printing through extrusion (a), ink jet printing (b), selective sintering technology through hot air (c) and laser (d) and binder jetting (e) (Sun, Peng, Yan, et al., 2015)

4. Available Printing Materials:

Raw materials and unprocessed ingredients usually have a longer shelf life than the final food products. Generally, the available materials can be classified into 3 categories based on their printability:

4.1. Printable Materials

Printable materials such as hydrogels, cake frosting, soft cheese, hummus and chocolate can be extruded smoothly from a syringe, they are stable enough to hold their shape after deposition and do not require further post-processing after printing. Food products made by natively printable materials can be fully customized for taste, nutritional value, and texture. However, most of these items are not considered as food materials for main dishes. Thus, they are more driven towards medical and space application. Other formulations such as protein pastes may require post-processing to improve taste and nutritional absorption, and this will make it more difficult for food product structures to retain their shape (Cohen et al., 2009; Izdebska & Zolek-Tryznowska, 2016; Jeffery Lipton et al., 2010; Sun, Peng, Yan, et al., 2015).

4.2. Non-Printable Traditional Food Material:

Food such as rice, meat, fruit and vegetables largely consumed by people daily are not printable by nature. To facilitate their extrusion, it is necessary to add additives (hydrocolloids) which have been approved and utilized in culinary fields. Some solid foods and semi-solid liquids have been modified to become printable. However, it is difficult to test and modify the entire list of traditional food materials (Cohen et al., 2009; Lipton et al., 2010; Sun, Peng, Yan, et al., 2015; Izdebska & Zolek-Tryznowska 2016).

4.3. Alternative Ingredients:

Food shortage, a global crisis issue, can be dealt with by introducing alternative ingredients in food products, such as insects. Food printing may play an important role in making the cultural background of insects more appealing to consumers. In the “Insects Au Gratin” project, Soares (2011) mixed insect powders with extrudable icing and soft cheese to shape food structures and make tasty pieces with 3D printing.

In addition, the alternative source of protein intake in insect powder was found to be slightly higher than the protein present in traditional meat products (Sun et al., 2015). Other sustainable and eco-friendly printing material sources may be the usage of residues from current agricultural and food processes to be transformed into biologically active metabolites, enzymes and food flavor compounds (Yang et al., 2001; Sun et al., 2015; Yang et al., 2015; Izdebska & Zolek-Tryznowska, 2016).

Table 2: Comparison of 3D food printing technologies

Printing technology	Principle	Fabricated materials	Advantages	Disadvantages	Company	References
Direct printing through extrusion	Extrusion and deposition from a nozzle	Chocolate, cheese, mashed potato, pizza, hummus, cookie dough, corn dough, hydrocolloids, peanut butter	Support wide array of foods, Can be coupled with more than one syringe allowing infinite combinations and degree of freedom for food	Appearance of seamline between layers Long fabrication time	NASA, 3D systems Foodini (Natural machines) Fab@Home	(Jeffrey Lipton et al., 2011; Malone & Lipson, 2007; Natural Machines, 2005; Porter & Phipps, 2015; Sher & Tutó, 2015; Southerland, Walters, & Huson, 2011; J. Sun, Peng, Yan, et al., 2015; Fan Yang et al., 2015)
Inkjet printing	Drop-on demand printing from a syringe nozzle	Confectionary fabrications, decorations on cookies, biscuits, cupcakes, drops on pizza bases	Easy method Innovative shapes of decoration	Form a 2D and half dimensional image Restricted more on decoration and surface fill on substrates	FoodJet	(Food Jet, 2016; Murphy and Atala, 2014; Sher and Tutó, 2015; Sun et al., 2015c)
Selective sintering technology	Powder binding and heat source (hot air) or (laser) that melts and fuses desired regions of the powder together	Sugar foods, Nesquick powder	Recycled powder More freedom to build complex food items Short time	Applicable to restricted materials with low melting point complicated	CandyFab Cornucopia	(CandyFab, 2015; Godoi, Prakash, & Bhandari, 2016; Kietzmann et al., 2015; Sher & Tutó, 2015; J. Sun, Zhou, et al., 2015; Zoran & Coelho, 2011)
Binder jetting	Apply binding agent to powder according to a predefined 3D shape	Sugar sculptures from sugar powders, caster, flour, starch	Precise Complex structures formation	Fragile end products, better to be used at a close point of consumption such as restaurants or home	3D systems	(iReviews, 2014; Porter & Phipps, 2015; J. Sun, Peng, Yan, et al., 2015; Wegrzyn, Golding, & Archer, 2012)

5. Challenges and Barriers to overcome in 3D Printing Process:

In particular, interested managers should consider constraints related to regulation, food safety, and the availability of ingredients.

5.1. Ordinance and Law Guidelines:

It is important to consider how regulatory agencies such as the US Food and Drug Administration (FDA) categorize these events and what impact their regulations will have on production. For example, FDA currently differentiates between locations that “produce” food and those that ultimately sell packaged food. If organizations choose to make this transition from a package seller to raw food dealer, they will need to consider new issues such as cleaning parameters, training of in-store personnel, and regular inspection. Since no regulations regarding the manufacturing of 3D printed food have been established yet, the FDA, collaborating with companies and certain governmental sectors, would be setting specific guidelines for particular foods, facility examinations, and staff training (FDA, n.d.; Porter 2015; Tran, 2016).

5.2. Food Safety/Shelf Life:

An important point to take into consideration for 3D printed food is that most of them have a limited shelf life. For example, purees or doughs prepared for 3D printing would often undergo a shift in their structural rheology after two hours of production and therefore the 3D printing of this material would be undesirable (Lipton et al., 2015). In addition, producing stable-printable materials is a major challenge for researchers and industry; most of the materials while being extruded are heated to create a malleable substance that can pass through the extrusion nozzle and that would otherwise be cooled down after being printed on the printer bed. This heating and cooling process might make food more susceptible to microbial growth of bacteria or fungus, therefore decreasing its effective shelf life (Lipson & Kurman, 2013; Fan Yang et al., 2015). A study conducted by Severini et al. (2018) detected the presence of a concentration in bacteria of 4.28 Log CFU/g after printing of fruits and vegetables, signifying that 3D food printers require proper sanitization of each part in contact with food prior to its application in restaurants and industries and again this correlates with the above mentioned challenge in the importance of developing explicit legislations by FDA for 3D food printing facilities and personnel. Yet, Companies could still adhere to the other FDA guidelines concerning the appropriate food temperatures and approved shelf lives. However, the advantage of edible printing, whether at-home or in-store is the ability to create food items only hours before sale or consumption, so shelf life may matter much less than for traditionally and centrally manufactured items (Porter et al., 2015).

5.3. Restrictions of Ingredients:

One of the food 3D printing barriers is the material set requirement (Lipton et al., 2010). Not every type of food can be printed; there is a limited quality of ingredients. For example, creating an organic product such as a carrot from scratch is too much science fiction (Lipson & Kurman, 2013). Trying to print meat, at the moment, involves mixing a powder protein with water to form a paste and then shape it into a form that mimics that of meat. Moreover, the printing of food often requires multiple ingredients of a wide range, including processed components such as cheese, sauce, or dough to more elemental ingredients such as sugars, proteins, and carbohydrates. It might be difficult to place all these ingredients in one container due to their different chemical compositions and different levels of storage conditions, such as

humidity and temperature. Thus, a person using 3D printing would better prepare all the ingredients at the time of use (Porter et al., 2015). Therefore, simplifying the process of manufacturing of a specific product into simple steps and combining them together to form a simulation model for manipulation is essential. Generally, 3D printers are optimized for thermoplastic materials; several physical and chemical properties affecting the printability of food such as viscosity, stickiness, etc. were never taken into account to improve the designed virtual model, the digital codes and the printed object (Severini et al., 2016). As a result, For each process of ingredients metering, mixing, printing, baking, the relationship between inputs and outputs data must be modelled and digitalized by measuring for each step the key process parameters such as density, electrical conductivity, printing viscosity, rheology, glass transition, permeability and firmness (Sun, Peng, Zhou, et al., 2015). The cooking properties of printed materials, its biochemical, microbiological and biological variation should also be considered (Yang et al., 2015).

5.4. Post-Processing:

Some 3D printed food materials requires a further post deposition step prior to consumption such as cooking (baking, boiling, frying) or freeze drying, which would involve the penetration of different levels of temperature inside the food matrix and result in altered textural properties that might be either agreeable or non-homogenous and unfavorable (Sun et al., 2018). During cooking, food is subjected to high levels of heat that stimulates many chemical reactions such as protein denaturation, water loss and evaporation, change in color, volume and nutritional value. A 3D printed pizza utilized by the Bee Hex 3D printer exhibited a new experience of mouthfeel, swallowing and chewing after being baked due to its ultra-thin crust texture. At the beginning it tasted exactly like a normal pizza and then after few minutes it turns more into sensing like crackers (Garfield, 2016). A comparison between two post processing techniques oven drying and freeze drying as a means of maintaining shape stability and increasing the stiffness of 3D printed blends of proteins and fiber-rich materials was conducted by Lille et al. (2018). It was found that freeze drying preserved better the 3D printed structure and provides samples with higher level of hardness and dry matter content than oven drying. Normally because the solid structure of a material dehydrated in frozen state can resist more the stresses induced by the process and therefore maintains better its structure (Ratti, 2001). Whereas oven drying caused some spread-ability of the printed samples due to the decrease in the viscosity of the material upon heating (Lille et al., 2018).

6. Optimizing a 3D Printing Process:

As stated above, the process of 3D printing might face some barriers that should be taken into consideration in order to overcome them. It is important to note again that each type of food would behave differently in the 3D printing process than others (ingredient-specific). Till now, there exists a knowledge gap in captiously linking material structure to process printing variables in order to obtain the desired 3D printed product (Severini et al., 2018). Therefore, in this part we try to cover up and analyze all the parameters that must be controlled during extrusion printing, based on merging all the information that have been published up to date in the field of 3D food printing.

The parameters to be controlled can be divided into two parts, first controlling the parameters concerning the printer machine and second controlling the parameters concerning the food itself, in a way such that each part will complement and perfectly suit the other as a (key-lock) fit, in order to result in the best 3D

printed product. Figure 2 represents a summary of these parameters and conditions.

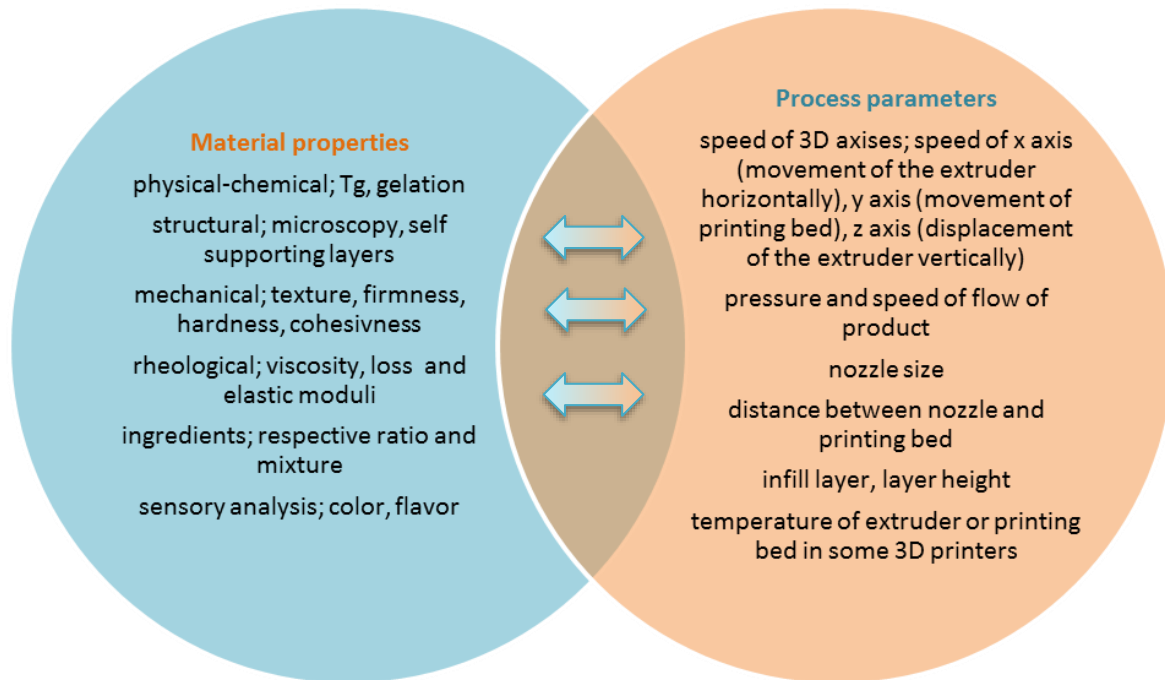



Figure. 2 Different properties and conditions that must be controlled while 3D printing;  resembles best 3D printing process and obtained product as a result of fit between both parameter.

6.1. Controlling Parameters of the 3D Printer:

First, controlling the speed of the 3D printers involves controlling the speed of its coordinates (print speed) X, Y, Z and E; the speed of the X-axis (movement of the extruder motor with the syringe horizontally), speed of the Y-axis (movement of printing bed), speed of the Z-axis (displacement of the extruder motor with the syringe upwards or vertically) and E controlling the speed of deposited material (extrusion of the paste out from the nozzle). According to Southerland et al. (2011) the most precise 3D printing for chocolate icing is obtained when working at a slower speed of extrusion over a longer period of time; even increasing the pressure helps in eliminating the small blockages of air bubbles in the syringe. In contrast, while printing a fruit based formulation customized for children, Derossi et al. (2018) found that samples improved their structural uniformity and integrity at high flow levels (130%) whereas samples printed at a low flow level (extrusion speed of 70 and 100%) displayed irregular shapes ($R^2 < 0.79$) with interrupted material lines and undesired oversized pores. Mainly because the amount deposited during printing is insufficient to cover the whole path along the nozzle. This behavior was also reported by Severini et al. (2016), Severini et al. (2018) and Yang et al., (2018) who by printing cereal based dough, fruit smoothies and lemon juice gels respectively found that irregular deposition of broken internal filaments and undesired structures were printed due to under deposition of food formula. Moreover, Derossi et al. (2018) examined the relationship between print speed and flow level on the

quality of printed materials and found that linear relationship is necessary between both speeds in order to ensure accurate final shapes with less pore size formations. As a complementary, a previous work carried by Zhuo (2015) established a positive linear relationship between print speed and extrusion speed using developed cookie dough recipe as an ingredient. It was found that a high extrusion speed (300 steps/mm) with a low print speed (5mm/s) lead to an inaccurate extrusion with too much dough being extruded per unit time, while a too slow extrusion speed (100 steps/mm) with a fast print speed (15mm/s), resulted in a low flow rate and almost no print was obtained. In a similar way, Severini et al. (2018) reported that the deposition rate of fruit smoothie formula and the speed of printer movements should be in equilibrium (positively proportional) with each other to obtain full interconnectivity between crossing filaments. Otherwise, over deposition of materials would occur and upper layers would crush first layers due to their weight, leading to poor resolution. Other parameter to take into account is retraction which also increases by raising the flow because it is a contrary movement of the stepper motor and is important to avoid the slipping of the material out of the nozzle during no-print movements. It is necessary to control this parameter during food printing because food formulas compared to other thermoplastic materials have a lower viscosity and requires a greater retraction to reduce the pressure at the tip nozzle (Table 1). Insufficient retraction could lead to defects in the internal structure such as crossing over of layers (Severini et al., 2018).

Actually (pressure—nozzle size--material printed) is a closely related loop, where choosing the best nozzle size for printing depends on the type of the material being printed and subsequently determines the pressure exerted upon the flow of the material from this nozzle size and that is dependent again on the rheology and structural properties of the material being extruded, and which consequently affects the resolution upon extrusion (Lipson & Kurman, 2013; Yang et al., 2015). Southerland et al. (2011) experimented with extruding cream cheese at different nozzle tip sizes; the ideal consistency of paste was obtained when using 0.84 mm tip (18 gage pressure); however trying with a smaller tip of 0.41 mm caused an increase in pressure (22 gage) and shearing force exerted that leads to sheared and separated cheese, similar approach was reported by Wang et al. (2018) while printing fish surimi gels, best resolution and surface quality of printed gels was obtained after using the corresponding optimal diameter of 2 mm nozzle, though printing surimi gels at a smaller nozzle diameter (0.8 mm) lead to inconsistent extruded filaments and poor models due to the higher shearing effect that is applied on a relatively less pore-nozzle size and which is required for pertaining the flow of the material. Whereas for chocolate, the ideal nozzle size was determined to be 1.25 mm (Hao et al., 2010).

The distance between the nozzle and printing bed (nozzle height) is another process parameter that critically determines the quality of the resulting printed product. There is an optimum distance for each specific material being printed. A critical nozzle height (h_c) can be estimated using the following equation (Wang & Shaw, 2005):

$$h_c = V_d / v_n D_n \quad (1)$$

V_d is the volume of the material extruded rate (cm^3/s), v_n the nozzle moving speed (mm/s), and D_n the nozzle diameter (mm). If the distance were lower than the critical height, the extruded lines would be thicker, while if the distance were higher, parts of the material would be detachably and inaccurately deposited. These results were confirmed by Wang et al. (2018) who printed fish surimi gel and found that

the nozzle height greatly influenced the geometry shape of the extrudates providing desired shapes with highest fidelity and good bonding between layers at a nozzle height of 5mm. However, Hao et al. (2010) found that this formula cannot be applied while printing chocolate using the CHocALM 3D printer, since theoretically, the hc was equal to 0.102 mm much less than 2.9 mm which was the optimal height found experimentally. Again this emphasizes the idea that optimizing the technique would be specific to the ingredient and the setup that is performed.

Additional process parameters of 3D printing were controlled by Severini et al. (2016), who studied the relationship between infill density and layer height on affecting the final quality of printed wheat dough. The infill level refers to the solid fraction in the inner part of the designed structure and can be inferred as printing quality. It was found that the appearance of the samples was rougher as the layer height increased. Moreover, an increase in the diameter of samples was detected with an increase of both infill level and layer height. In fact, as mentioned before, all printing variables are related in one way or another. Therefore, increasing layer height and infill speed is accompanied by a greater time needed for the deposition of the layer and thus a subsequent automatic increase in the print speed to obtain equilibrium between the amount of material extruded and printing speed.

6.2. *Controlling Parameters of the Food Itself:*

6.2.1. *Physio-Structural and Rheological Properties:*

Hao et al. (2010) studied the relationship between the process parameters of additive layer manufacturing and resulting chocolate using a (ChocALM) 3D printer. They compared the physical structure of seeded chocolate (chocolate tempered by seeding in the lab) with commercially tempered chocolate as received using Differential Scanning Calorimetry (DSC). The DSC thermograms of both types of chocolate showed melting peaks over the same temperature range (26-36 C°), and the same crystal phase (V crystals) was formed, concluding that seed tempering is a desirable process to be applied on chocolate.

The knowledge of rheological properties of food products is important for predicting the analysis of process design and flow conditions in 3D printing such as pump sizing, syringe size and length, total time of printing, extrusion layer and conformation stabilization. One of the important rheological parameters to determine in food before 3D printing is the viscosity. Building 3D dimensional objects in good resolution requires that the materials have high enough viscosity for its layers to be self-supporting and stackable (Godoi et al., 2016; Periard et al., 2007), using some food additives to retain rheological properties of printable products, such as transglutaminase in meat and agar in vegetables (Lipton et al., 2010). Likewise, Dankar et al. (2018) evaluated the effect of four food additives (agar, alginate, glycerol and lecithin) on the rheological properties of commercial potato puree, all samples showed a pseudo plastic non-Newtonian behavior which is beneficial to be extruded through a nozzle. Also, only agar and alginate showed a moderate effect and stabilizes more potato puree (increasing its yield stress) while having an exclusive effect of acting either as an increasing or decreasing agent on viscosity according to their respective used level of concentration (0,5-1%). In a similar approach, Liu et al. (2018) examined the rheological properties of mashed potatoes combined with potato starch in order to evaluate its behavior during 3D printing. Best printability was obtained combining 2% potato starch to mashed potatoes,

exhibiting shear thinning behavior and yield stress equal to 312.16 Pa. Mashed potatoes alone possessed low yield stress and deformed printed products afterwards whereas increasing potato starch to 4% increased yield stress (370.33 Pa) but deterred extrudability due to its high viscosity. Likewise, Yang et al., (2018) found that the addition of high starch content (17.5, 20 g.100g⁻¹) to lemon juice gels led to high viscosity and small $\tan\delta$ (0.144) which revealed a more solid like behavior and resulted in difficulties in extrusion with broken lines, while the addition of 15g.100g⁻¹ starch was optimal and resulted in a higher $\tan\delta$ (0.155), consequently causing a smoother flow of the lemon gel and allowing to obtain a final product that better matched with the target geometry. Other findings demonstrated also the importance of rheology in determining the flow of a particular food product during processing. For instance, Wang et al. (2018) revealed that the rheological behavior of fish surimi gel with 1.5g.100g⁻¹ NaCl is suitable for printing, since the addition of NaCl plays the role of decreasing in general the viscosity of surimi gel, thus facilitating its extrusion through the nozzle while possessing the ability to form a stable gel pattern post deposition. Improvements in gel strength and network structure is mainly due to the swelling in myofibrillar protein and therefore an increased protein-protein interaction as triggered by NaCl addition (Tahergorabi & Jaczynski, 2012). Hao et al. (2010) used parallel plate rheometer to test the viscosity of chocolate before being printed with the ChocALM printer. It was found that chocolate behaved with a relatively constant viscosity between 32 and 40 °C with a range of 3.5-7 Pa.s. Besides, an important variable parameter that might be considered during printing is temperature which affects directly the rheological profile of printed products. Hamilton et al. (2017) stated that high temperatures (65 C°) decreased the yield stress and consistency of vegemite and marmite, hence decreasing the pressure exerted during extrusion and smoothing printing. However, the structural integrity of printed vegemite and marmite was better retained at room temperature (25 C°) due to exhibiting higher levels of yield stress. On the other hand it should be noted that a lack of correlation between rheological measurements and pressures used during 3D printing could be tackled. This can be explained by the fact that food materials are subjected to different magnitudes of shear and deformation during extrusion through the nozzle tip than in the rheometer (Lille et al., 2017).

6.2.2. Mechanical Properties:

In 3D printing, it is necessary to study the material structure with its ratio components and mechanical properties to reach the desired product design (Jing et al., 2014). Studying the mechanical characteristics of a food product is done by measuring its firmness, consistency, cohesiveness and hardness. The hardness of edible gels was measured for the purpose of 3D printing enjoyable soft food for the elderly; compression test was performed on different types of edible gels prepared with different percentages of agar and gelatin. The results showed that the compression strength (hardness) became higher as the additive amount of agar and gelatin increased, and the highest hardness value dropped sharply when half of the agar was replaced by gelatin. The overall range of hardness possessed by the samples was between 8-45 KPa, which is a good fit to be considered as soft food for the elderly since the maximum lingual pressure of aged person is estimated to be between 20-40 KPa (Serizawa et al., 2014). Severini et al. (2016) studied the hardness of wheat dough printed at several height levels and infill speeds (Section 6.1). It was concluded that the higher was the infill density, the higher was the hardness value since more solid

material would be accounted for the product. Also, the effect of 3D printing on textural properties of processed cheese was studied by Le Tohic et al. (2018) who found that the printing process decreased the hardness value of printed cheeses compared to unprinted ones. However, printing at different speeds (high and low speeds) did not alter the textural properties of processed cheese. In addition to being tested on printed edibles, the method of determining the textural properties has been applied on different types of food such as comparing the structure of low fat mayonnaise with full fat mayonnaise, determining the textural properties of dark chocolate, and determining the mechanical strength of selected fiber blends with gelling properties (Liu, Xu, & Guo, 2007; Afoakwa, Paterson, Fowler, & Vieira, 2008, 2009; Angioloni & Collar, 2009).

6.2.3. *Optimizing the Food's Ingredients:*

Optimizing the printing material itself is the bottleneck of 3D printing. As listed above, some foods are natively printable such as cheese and chocolate while others such as fruits and vegetables are non-printable traditional food materials that may require some extra reformulation. Printed food must have the two characteristics of being follow-able and self-supportable of the structure post printing. Flow ability might be achieved by plasticization while the structure post processing is maintained by process of gelation through modifying the temperature and/or adding additives (Godoi et al., 2016). Furthermore, adjusting a recipe of a food item would affect significantly the printability of the food and the shape stability post printing (Lipton et al., 2015). Many cases are listed below; Cohen et al. (2009) worked on making some solid foods such as meat extrudable by adding hydrocolloids; they allowed a machine to use a small amount of base materials to generate large printable materials. Lipton et al. (2010) tested the effect of traditional cooking techniques on printed structures after modifying the ingredients' components first by modifying the recipe of ingredients and second by using food additives to maintain the complex structure of printable products. Initially, cookies were studied. In traditional cookie recipes, the butter tends to liquefy when baked, causing the shape to be lost. Lipton et al. (2010) tested the addition of some food additives on facilitating the printing of specific food materials. Transglutaminase was tested for its ability to maintain the complex geometry of meat upon printing and after deep frying; this additive was added right before printing, and it aids in retaining the material's rheological properties, but a new protein matrix was formed over time (Lipton et al., 2010). This can be explained by the fact that the proteins found in meat puree were enzymatically cross linked by transglutaminase, which catalyzes the formation of the covalent bond between lysine and glutamine residues in a calcium dependent reaction (Davis et al., 2010). Printed meat objects were then fried and retained their shape with minimal loss of detail due to deep-frying. Another food additive, agar, known for its shear thinning properties was examined for printing vegetables. Adding agar powder to celery fluids allowed for its reconstruction. Tests for printability were done using Fab@Home 3D printers (Lipton et al., 2010). Moreover, Lipton et al. (2010) found a new ratio of ingredients for cookie recipe, suggesting that printed cookies must be freeze chilled following extrusion to maintain their structure post-baking (Table 3). In his thesis research project, (Zhuo, 2015) investigated the parameters of printing food materials using his developed 3D Desktop Food Printer for home use potential. The ingredients of cookie dough were first investigated, and the first cookie recipe printed was based on the one developed by Lipton et al. (2010). However, a great amount of

force was required for extrusion, leading to extruded strings that kept breaking into parts. After many trials and substitutions, a new cookie dough recipe that suits the new platform printer was developed (Table 3).

In another attempt to optimize 3D printing materials, it was apparent that the combination of 50% semi-skimmed milk powder (SSMP) with 0.8% cellulose nanofiber (CNF) and 60% SSMP alone resulted in best printed shape due to the merging of different factors starting from the fat present in SSMP that acted as a lubricant for easing the flow as well as the CNF that is known for its great potential to act as a reinforcing ingredient in composite materials (Abitbol et al., 2016). Using the Rapman 3D Printer, Southerland et al. (2011) tested the extrusion of real mashed potato versus “Mr. Mash” instant mashed potato. It was found that Mr. Mash extruded consistently with a smooth even paste while real mashed potato puffed once being extruded due to the high level of pressure exerted by the auger valve that was inserted to the Rapman 3D printer.

Table 3: Finalized Cookie Dough Recipe both by Lipton et al. (2010) to be printed using Fab@Home extruder printer and by Zhuo (2015) to be printed using his developed Desktop extrusion 3D Printer.

Ingredient of cookie dough by Lipton et al. (2010)	Ingredient of cookie dough by Zhuo (2015)
220 g unsalted butter	30 g unsalted butter
110 g powdered sugar	20 g powdered sugar
3 egg yolk	10 egg white
330 g flour	55 g all-purpose flour

6.2.4. Sensory Properties:

Using the Fab@Home printer, (Cohen et al., 2009) tried to assemble the structure and flavor of non-printable food through the combination of different hydrocolloids xanthan gum and gelatin, at different concentrations with different flavoring additives of raspberry, strawberry, banana and chocolate. Upon extrusion, gel ripping of the product resulted in a mouthfeel texture that was tested with the help of specialist trainers. Pure xanthan and gelatin fit only within the weak to firm range and shifted more to granularity when both hydrocolloids were combined (Table 4). Generally, the higher is the concentration of xanthan and gelatin, the firmer and more granular the gels become. Both mouthfeel and flavor were simulated for a broad range of common foods (Table 4) The production of such controlled food is directed more to medical and space application, and this method may solve the problem of material set-bloat of optimizing the solid freeform fabrication for a very broad range of products (Lipton et al., 2010). Sensory attributes of 3D printed blends of fruits and vegetables were assessed by Severini et al. (2017). No difference in color, taste and odor was detected between 3D printed and non-printed smoothies. However, the appearance of 3D printed smoothies was more valued. This supports the idea that 3D printing technology is not only able to preserve the food formula while printing but also to improve its final visual aspect. Therefore, grabbing consumers and particularly children towards healthier food choices. Furthermore, the ability of 3D printing technology to provide a unique taste for 3D food pieces due to its layered build up structure was conveyed by Alec (2015) who tried printing chewing gum. In

addition to sensing the customized shape, color and flavor, people would explore a new form of chewing experience by feeling the staircase texture of the 3D printed chewing gum in their mouth. Additionally, Le Tohic et al. (2018) studied how 3D printing can affect the color of final printed cheeses extruded at low and high speeds respectively and compared them to melted and untreated cheeses. Printed cheeses were slightly darker than untreated cheeses with small decrease in the luminosity parameter. Differences in color were also detected between cheeses extruded at different speeds such that cheeses extruded at high speeds showed a bluer (lower b values) and darker color (Less luminosity) mainly due to the effect of high shear rate during printing that resulted in smaller fat globules and consequently caused this darkness in color. Therefore, one can relate that 3D printing parameters affect the final color of printed products, but whether this change is favorable or not is still debatable and should be studied from different consumer preferences and again this preference could be variable according to the type of printed food product.

7. Summary:

3D food printing is an innovative technology with loads of benefits for both consumers and companies, by being able to provide personalized food in a novel multi-flavored, colored and textured structure while promoting higher social bonding through food messaging and also enhancing process production and sustainability for companies while serving as a more environmental friendly technology. Nevertheless, 3D printing has some critical challenges (lack of specific rules and regulations, food safety problems, ingredient limitations and post processing) that must be taken into consideration in order to certify a wide future application of this process. These challenges might be overcome by setting international specific guidelines (FDA) for facilities, personnel, food safety and shelf life and most importantly by developing a simulation model of behavior for a particular batch of product during 3D printing (optimization). In fact, optimizing 3D printing is the major competitive barrier for food manufacturers and researchers due to the presence of an infinite array of ingredient combinations and the complexity of determining their respective compatible process parameters.

From previous works and examinations, some of the best processes and ingredient parameters during 3D printing for a specific type of food can be concluded as follows:

- For cookie dough, the best 3D printing was achieved while maintaining proportionality between extrusion and print speed. Different ingredient optimization was assessed for cookie dough.
- Extruding at high enough flow level reduces the microstructural porosities and maintains better the shape for cereal based dough, fruit smoothies and fruit based snacks.
- For cheese, better consistency was obtained using a 0.84-mm tip nozzle. Printing parameters reduces the luminosity of printed cheese with this effect being enhanced at higher speeds.
- For chocolate, ideal nozzle size and distance between nozzle and printing bed were determined to be 1.25 and 2.9 mm, respectively. Seed tempering for chocolate is desirable while printing with an ideal temperature of extrusion between 32° and 40° C and a viscosity range of 3.5-7 Pa.s.
- The hardness value of wheat dough increases with increasing the infill density.
- Transglutaminase can maintain the complex geometry of meat upon printing and after deep-frying. For fish surimi gel, the optimal nozzle diameter and nozzle height were found to be 2mm and 5mm

respectively.

- Printing at high temperature, 65 °C smoothens the printing of vegemite and marmite, but shapes were better retained at room temperature 25 °C.
- Instant mashed potatoes behaved better during 3D printing than real mashed potatoes, which puffed during extrusion under high pressure. Mashed potatoes with the addition of 2% potato starch possessed a suitable viscosity and a strong enough yield stress (370.33 Pa) to provide a good end printed product with smooth extrusion.
- The addition of (15g.100g⁻¹) starch to lemon juice gel recorded a high $\tan\delta$ (0.155) that resulted in smooth flow while extrusion and a high retention of product geometry post printing.
- Different hydrocolloids (such as xanthan gum and gelatin) at varying percentages can be used as substrates for 3D printing, and their combination with different flavor additives can simulate and substitute for a broad range of common foods.
- Printability provides a staircase textural mouthfeel to printed products
- 60% of semi-skimmed milk powder (SSMP) or a combination of 50% SSMP with 0.8% of cellulose nanofiber (CNF) represents an optimal substrate for 3D printing.

Table 4: Mouthfeel matrix of hydrocolloid mixture showing the formulations related to the closest common foods listed below; the hydrocolloid concentrations in bold (Cohen et al., 2009)

	4% gelatin Close to chocolate/mushroom				
Most firm		16% xanthan Cooked spaghetti			
				1% gelatin 8% xanthan Close to tomato	
	2% gelatin Jello	2% gelatin 8% xanthan Close to cake icing/Meringue	0.5% gelatin 8% xanthan Close to cake icing/Meringue		
		4% xanthan Mashed potato			
	1% gelatin Self-supporting loose gel				
Weakest	2% xanthan Non-self-supporting loose gel			0.5% gelatin 4% xanthan Apple sauce	1% gelatin 4% xanthan Risotto
	0.5% gelatin Milk				
	Smoothest				Most Granular

8. Conclusion:

3D printing has been applied to make personalized chocolate, cookies and snacks mainly, and the works done are still primitive. To unlock the 3D food printing potential, we need to think about the specific technical challenges standing in the way. More investigation should be conducted on printing materials, their behavior in printing technologies, (optimizing the printing technology) and their influences on the food market and customer acceptability. Whether used in market or at home, a solid coordination between 3D printer designers and users of this technology in food production is essential to facilitate their application. More importantly, 3D printing should shift from a focus on printing snacks to printing more nutritional foods; the idea of enhancing the nutritive quality of food while printing should be strongly emphasized. In addition, it is important to identify to which sector of people this 3D printing is targeted:

children, athletes, pregnant women, adults, modern gastronomy lovers, soldiers or astronauts. Identifying our target illuminates our path to further proceed with 3D printing; what food materials should be printed, what printing technology should be used, and the appropriate shape and work on optimizing all these factors together to have the best printing that is applicable and desired by the target customer.

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- **Chapter 3; Objectives**

▪ Objectives

The main purpose of this thesis was to determine and optimize the ideal conditions for best extrusion 3D printing and best printed end product, by characterizing the physical, chemical, microstructural and rheological properties of the material mixture to be printed, in this case potato puree combined with different food additives, in complementary with optimizing the printing process parameters its self. In order to fulfill the main objective, the following particular objectives were developed;

1. Assessing the changes induced by food additives on the microstructure and rheological properties of potato puree (mashed potatoes).
2. Understanding the changes tempted by food additives on potato puree in terms of the internal molecular level.
3. Characterizing the mechanical energy and specific mechanical energy of each blend, and relating all the previous characteristics while performing 3D printing trials while optimizing some process parameters of the 3D printer in accordance of the printed substrate as well.
4. Analyzing the effect of cooking treatment (microwave and boiling) and water presence on the molecular structure of starch in an attempt to develop such a material (this time potato tubers) for 3D printing.
5. Interpreting the effect of different additives inserted as well as cooking treatment (microwave and boiling) on the mechanical, rheological and microstructure aspects of potato tubers, while identifying the substrate blend with the ideal characteristics for best 3D printing.

- **Chapter 4; Experimental Setup**

- **Over view of the experimental setup**

Tasks	Materials used	Parameters tackled
Task 1; Assessing the microstructure and rheological changes induced by food additives on potato puree	Mashed potatoes, milk, agar, alginate, lecithin, glycerol	Compound light microscopy, Viscosity, yield stress, thixotropy, viscoelastic properties (storage and loss modulus), Cox-Merz rule
Task 2; Characterization of food additive-potato starch complexes by FTIR and X-ray diffraction	Mashed potatoes, milk, agar, alginate, lecithin, glycerol	Fourier transform infrared spectroscopy (FTIR), X-ray Diffraction (XRD)
Task 3; Impact of mechanical and microstructural properties of potato puree-food additives complexes on extrusion-based 3D printing	Mashed potatoes, milk, agar, alginate, lecithin, glycerol	Assembling extrusion via specific mechanical energy (SME), mechanical characteristics, scanning electron microscopy (SEM), 3D printing, color detection
Task 4; Impact of water removal and temperature treatment on microstructural changes in potato tubers	Kennebec potato tubers, raw, boiled and microwaved, freeze drying at time intervals	Fourier transform infrared spectroscopy (FTIR), X-ray Diffraction (XRD), scanning electron microscopy (SEM),
Task 5; Influence of rheological properties, mechanical characteristics and cooking treatments on 3D printing potato puree samples	Kennebec potato tubers, boiled and microwaved, olive oil, butter, carrots, alginate, agar	Compound light microscopy, yield stress, viscosity, thixotropy, moisture content, mechanical characteristics, 3D printing

▪ Chapter 5

Assessing the microstructural and rheological changes induced by food additives on potato puree

▪ *This chapter has been published as:*

Dankar, I., Haddarah, A., El Omar, F., Sepulcre, F., & Pujolà, M. (2018). Assessing the microstructural and rheological changes induced by food additives on potato puree. *Food Chemistry*, 240, 304–313.
<https://doi.org/10.1016/j.foodchem.2017.07.121>

Assessing the microstructural and rheological changes induced by food additives on potato puree**Abstract**

The effects of agar, alginate, lecithin and glycerol on the rheological properties of commercial potato puree were investigated and interpreted in terms of starch microstructural changes, and the applicability of the Cox-Merz rule was evaluated. Each additive was applied separately at two concentrations (0.5 and 1%). Microscopic observations revealed more swollen starch aggregations in lecithin and glycerol compared with those of potato puree and agar, consequently affecting the rheological properties of potato puree. All samples exhibited shear thinning non-Newtonian behaviour. Rheological measurements were strongly concentration dependent. At 0.5% concentration, additives exerted decreases in all the rheological properties of potato puree in the order of glycerol>alginate>lecithin>agar, while at 1% concentration, the order changed to glycerol>lecithin>alginate, whereas 1% agar behaved differently, increasing all rheological values. This study also showed that agar and alginate in addition to potato puree could be valuable and advantageous for further technological processes, such as 3D printing.

Keywords: Dynamic rheological test, Starch microstructure, Steady rotational test, Potato starch.

1. Introduction

There is a movement towards potato vegetable purees as high-quality products and part of the rapidly growing ready-to-eat (convenience) food market. Recently, potato purees have been used as a potential substrate for the innovative technique of 3D food printing due to the malleable textural properties of starch, its capability of water retention and its capacity as an excellent colloidal stabilizer and bulking agent (Eliasson A.C. 2004). Potato starch is a natural-versatile biopolymer composed of linear amylose chains and highly branched amylopectin. It can be easily obtained and modified using different chemical, enzymatic and physical methods to improve its functional characteristics, making potato starch one of the preferred polymers used in many technological manipulations in the food industry, such as in thickening, coating, and gelling and as an encapsulating agent (Singh et al. 2007).

In addition to the technological complexity of producing, processing and handling potato starches and potato purees, accepting these perishable food materials requires a wide knowledge of their physical properties, emphasizing the importance of studying their rheological properties. Monitoring the rheological behaviour of a product can aid in the development of a new successful product with the specific desired textural characteristics and quality attributes, enhancing the acceptability of the food. Additionally, this knowledge is important in food processing and handling for predicting the analysis of process design and flow conditions, such as in 3D printing (pump sizing, syringe size and length, total time of printing, extrusion, layer and conformation stabilization, etc.). Above all, investigating the rheological properties of a food, specifically potato puree, can serve as vital basic research into the different ingredient interactions (Tabilo-Munizaga and Barbosa-Cánovas 2005; Maceiras et al. 2007).

Structurally, potato puree prepared from commercial potato flakes consists of single starch cells and cell aggregates embedded inside a matrix of starch gel released from damaged cells during the cooking, mashing and drying processes of preparation (Alvarez and Canet 1999). Thus, the rheological behaviour

of commercial potato is governed by the starch structure, amylose content, granule size distribution, granule shape, granule volume fraction and interactions among different starch granules (Kaur et al. 2004), in which the maximum viscosity at a given concentration depends on the capacity of granules to swell freely prior to their physical breakdown (Adebowale and Lawal 2003). This swelling is attended by consequent leaching of granules constituents and the formation of a three-dimensional network responsible for rheological modifications upon heating and shearing starch (Li and Yeh 2001).

Potato starch and its derivatives, such as potato puree, are generally used in food industrial applications after being mixed with different hydrocolloids and food additives since native starches generally do not possess ideal properties for the preparation of food products. This mixing improves the functionality, stability, and texture of the product and facilitates its performance during processing and at the same time adjusts its rheological properties to compatible values (Chaisawang and Suphantharika 2005). However, it is very difficult to identify optimal combinations and rheological characterizations in a complex food system such as potato puree with different additives. BeMiller expressed the difficulty of finding a unique mechanism to explain the effects that several hydrocolloids have on starch structure. Because of the complexity and variety of those systems, their properties depend on both the starch-hydrocolloid ratio and the particular starch-hydrocolloid combination (BeMiller 2011). In the same sense, it was found that the addition of sodium alginate and carrageenan to starch could preserve the granular structure of amylose-rich, swollen rigid granules, consequently attributing to an increase in the rate of viscosity (Hongprabhas et al. 2007). The addition of other types of hydrocolloids revealed different methods of interaction, such as xanthan and guar gum, which inhibit the swelling of granules by preventing water penetration; they promote granular association by bridging and stabilizing the granular shape, forming a stronger three-dimensional network due to an amylose and amylose-gum system and allowing the starch paste to exhibit a more solid-like behaviour (Chaisawang and Suphantharika 2005).

Therefore, four food additives, agar-agar gum, alginate, lecithin and glycerol, with different known modes of behaviour, were used in this study at two different concentrations. Gum (Agar-Agar) was used based on its known capacity to interact with other polysaccharides, leading to a synergistic increase in viscosity, as in whipped cream and starch-based mixtures (Zhao et al. 2009). Alginate is a polysaccharide made up of 2 polymers, β -D-mannuronic acid (M) and α -L-guluronic acid (G), which provide thickening, stabilizing, film-forming and gel-producing properties to the food agent (Koushki and Azizi 2015). Lecithin has been used to modify the properties of waxy maize starch because of its emulsifying property, colour and taste; it has been used also as a lubricant in food industrial applications, such as extrusion, resulting in less nozzle wear and tear. Lecithin is also used as an emulsifying agent in many confectionary and chocolate products (Lončarević et al. 2013), while glycerol is used more as a plasticizing agent with edible starch films to reduce their tensile strength, thus reducing their viscosity (Bonilla et al. 2015). Although glycerol is not widely used for food processing, we included it in the study because of its chemical and physical characteristics in comparison with the other additives used. Therefore, the present work aims to contribute to the knowledge of the effects that these additives can exert on commercial potato starch microstructure and rheology and to provide proper explanations for such effects and mechanisms to improve the usage of potato puree in advanced food technologies. To this end, two types of rheological tests were conducted: dynamic oscillatory and steady rotational tests. Additionally, the Cox

Merz rule, which is used to characterize material properties by examining the relationship between dynamic viscosity and steady shear viscosity, was applied and evaluated.

2. Materials and Methods

2.1. Sample Preparation

Dehydrated potato puree (Maggi, origin) and whole milk were purchased from the local supermarket. Agar-agar, soybean lecithin, sodium alginate and glycerol (food grade) were procured from Sigma–Aldrich Co. Potato puree samples were prepared according to the following ratio (90 mL milk and 10 mL water heated previously to 40 °C, to which 23 g of potato powder was added). The mixture was then homogenized for 3 minutes using an electrical hand blender (Braun, Germany). The same procedure was followed for preparing the puree samples with the four different additives at two different concentrations (0.5 and 1%). Additives at their corresponding percentages were added and dissolved in the warmed solution (milk and water) prior to the incorporation of the potato powder. However, for agar, the solution was boiled to 100 °C, after which the dehydrated potato powder was added. Subsequently, all samples were placed in an incubator, and the temperature was maintained at 20 °C prior to the microscopic observations and rheological measurements.

2.2. Microscopic Observations

To compare the structure and the alignment of the starch particles between the different preparations, a thin film from each of the potato puree samples was spread on a glass slide and stained with diluted Lugo's Solution; the stained films were then examined under a compound light microscope (better images were taken at 10x magnification).

2.3. Rheological Measurements

The rheological measurements were performed in a rheometer (Rheostress RS1, version 127, Barcelona, Spain) controlled with commercial computer software (HAAKE RheoWin 3 Job and Data Manager Software). Samples were analysed for their flow properties using 35-mm plate-plate geometry (PP60 sensor) with a 2.5-mm gap between the plates. The upper plate was lowered, and the excess sample was trimmed off. After loading, samples were rested for 3 minutes prior to testing. Two types of rheological tests were conducted: a dynamic oscillatory test and a steady rotational test. The temperature of the rheological tests was kept constant at 20.0±0.1 °C. The results were reported as the average of three replicates (a new sample was loaded for each repetition).

2.3.1. Dynamic Rheological Measurement, Frequency Sweep Test:

The strain sweep test was performed to identify the linear viscoelastic region. Thereafter, a shear rate of 0.0025 s⁻¹ was selected and deformation within the elastic property was detected. Moreover, oscillatory tests were performed from 0.1 to 10 Hz to determine the strength and stability of the material and to clarify the behaviour of the sample, whether viscous or elastically dominated. Storage modulus G' (indicator of the elastic behaviour), loss modulus G'' (indicator of the viscosity behaviour) and complex viscosity n* (related to the global viscoelastic response) were recorded.

Results were reported as the average of three replicates (a new sample was loaded for each repetition).

2.3.2. Steady Rotational Rheological Measurements, Thixotropy and Yield stress:

A hysteresis loop test was performed to provide an indication of whether the sample was thixotropic and to determine the degree of thixotropy. The shear rate was increased logarithmically from 0.1 to 10 s⁻¹ during the first 30 secs, was then maintained at 10 s⁻¹ for 30 secs, and finally was decreased logarithmically again to 0.1 s⁻¹ over 30 secs. Consequently, the viscosity (η) and the shear stress (τ) were recorded, along with the yield stress for each sample. Accordingly, a rapid drop in viscosity as a response to increased shear stress and shear rate was registered. Two methods were used to quantify the yield stress. The first one involved attempting to fit the experimental data to the best mathematical equation or model (Hershel Bulkey, Casson Model, Power Law, Bingham). Bingham was determined to be the best model to fit the flow characteristics of the samples, with a high coefficient of determination ($R > 0.957$). The Bingham equation is ($\tau = \tau_0 + \eta_p \gamma$), where τ (Pa) is the shear stress, τ_0 (Pa) is the yield stress, η_p (Pa s) is the viscosity and γ (s⁻¹) is the shear rate. Nevertheless, this model was not suitable for 1% agar (w/v). Therefore, an alternative method was used to estimate the yield stress, considering the point at which viscosity as a function of the shear stress ($\eta = f(\tau)$) changes abruptly (Tabilo-Munizaga & Barbosa-Cánovas, 2005).

3. Results and Discussion

3.1. Microscopic Observations

Optical microscopic images of commercial starch puree (with and without additives) are shown in Figure 1. Observations for all samples showed swollen single cells and cell aggregates in which starch was encapsulated inside the cell wall; at the same time, these aggregates are embedded in a starch gel that is released from damaged cells due to preparation processes such as cooking, mashing and drying stages (Alvarez M.D. et al. 2004) or due to additives added to potato starch that may enhance or decrease starch rupture and swelling. Furthermore, swelling in the granule starch and cell separation were observed with this cell separation (cells push against each other due to the steric hindering effect of the added groups), accompanied by a rounding off of the cells as a result of the swelling of gelatinized starch (Damodaran and Parkin, 2017). Furthermore, minor cell rupture with large-sized swelling cells were detected with lecithin and glycerol. Conversely, 1% agar showed obvious changes in size and shape (more rupture and reduced swollen cell size), which could be explained by the fact that the bonding forces within the granules of starch were affected by these additives, consequently affecting the swelling power (Adebowale et al. 2002).

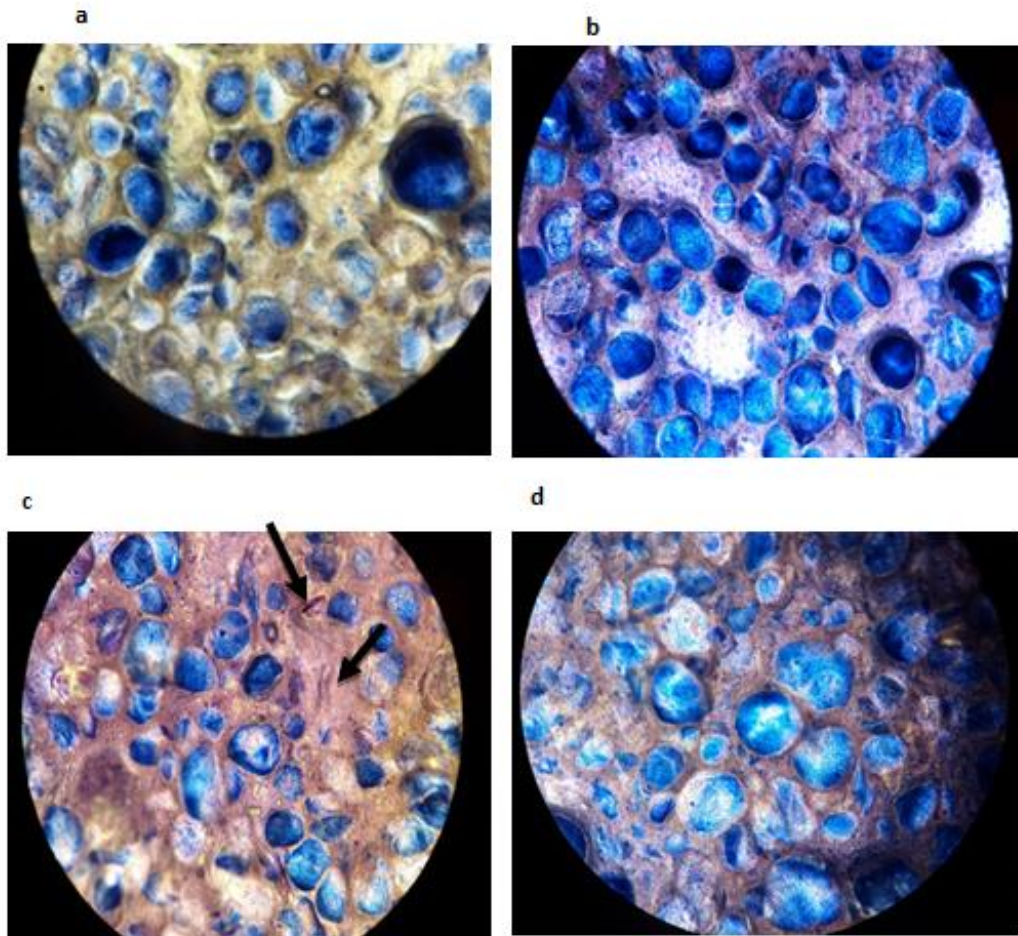


Figure 1. Microscopic observations (10x) of (a) commercial potato puree, (b) with lecithin 0.5%, (c) with agar 1%, and (d) with glycerol 1%, stained with Lugol's iodine solution. *arrows refer to starch leached out due to cell rupture.

3.2. Steady Rheological Characteristics

3.2.1. Viscosity

The rheological starch properties with the different additives were studied using the behaviours of viscosity curves. Flow curves (Fig. 2) of puree samples exhibited an exponential decay of the shear viscosity, indicating a non-Newtonian, strong shear-thinning behaviour, in agreement with several authors (Maceiras et al. 2007; Yousefi and Razavi 2015). Figure 2 shows that glycerol and lecithin decreased the viscosity of the potato puree from 80% to 90% and from 60% to 85%, respectively, as their concentrations increased (from 0.5 to 1%, respectively); hence, their effects on decreasing the viscosity of potato puree were enhanced at a higher concentration. Alginate also had a decreasing effect on the viscosity of potato puree, though this effect was more moderate compared with glycerol and lecithin and was inversely proportional to the alginate concentration; alginate produced a higher decrease in the viscosity of the puree at a lower rather than at a higher concentration (Fig. 2). Furthermore, agar exerted different effects on the shear viscosity of the commercial potato puree depending on the amount of agar added: at a low concentration (0.5%), an approximate 32% decrease in the viscosity of the commercial potato puree was observed, whereas at a higher concentration (1%), the agar increased the concentration

of the potato puree by approximately 20%, completely eliminating the elastic behaviour of the commercial potato puree and allowing it to behave more as a rigid solid-like material. This effect is clearly elaborated as an abrupt stop, as observed in the viscosity curve versus the shear rate of puree with 1% agar (Fig. 2b).

The rheological behaviour of starch is governed by granule size distribution, granule shape and granule-granule interaction, among other factors (Sing et al. 2003; Kaur et al. 2004). In this sense, viscosity reflects the capacity of the granules to swell freely prior to their physical breakdown. As mentioned previously, agar has a distinct effect on the viscosity of the commercial potato puree, depending on the concentration. It has been postulated (Achayuthakan and Supphantharika 2008) that some hydrocolloids decrease the viscosity of starch by retarding the water accessibility to the starch granule, inhibiting swelling. Another effect also has been reported (Liu et al. 2006) in which interactions between hydrocolloids and starch granules can create a network that increase starch's viscosity. In agreement with these findings, 0.5% agar can inhibit swelling, limiting water accessibility inside the starch granules and consequently reducing the viscosity, whereas at a high concentration (1%), the increase in viscosity can be explained by an agar gel formation and/or a network formation through the interactions among agar chains and starch granules, thus bridging between granules and promoting their association, confirming previous microscopic observations regarding 1% agar (Fig. 1).

Regarding the other additives, alginate (an anionic hydrocolloid), glycerol and lecithin, the response was always a decrease in the viscosity of the commercial potato puree at both concentrations studied (0.5 and 1%). Glycerol and lecithin act in similar ways, in both cases reducing the viscosity in proportion to their added concentration (Fig. 2). This action could be explained by the fact that the molecular weights of glycerol and lecithin are much smaller compared to those of agar and alginate, which would facilitate their entry inside the starch granule, consequently altering the microstructure by disrupting the intermolecular hydrogen bonds and/or crystalline and amorphous regions. It has been reported that surfactants and emulsifiers such as glycerol and lecithin have the capacity to penetrate starch granules and form weaker complexes (Hasenhuettl and Hartel 2008). Likewise, decreasing associations within the starch granules would increase their capacity to swell (Adebowale et al. 2002), in agreement with the microscopic observations on the effects of lecithin and glycerol (Fig. 1). At the same time, applying shear rate or force to starch with large swelled granules would cause their instant rupture and cause a dramatic decrease in viscosity (Achayuthakan and Supphantharika 2008) (Fig. 2). Alginate also decreases the viscosity of the commercial potato puree (Fig. 2), in agreement with other authors, which has been explained by the repulsion forces between the phosphate groups in potato starch granules and the negative charge on the alginate molecule when this hydrocolloid interacts with the starch granule surface (Shi and BeMiller 2002). The inversely proportional relationship between alginate concentration and viscosity can be explained by the domination of either of one effects of alginate: at low concentration (0.5%), the effect of repulsion among the starch granules due to alginate's negative charge dominates, leading to a decrease in viscosity, whereas at high concentration (1%), the capacity of alginate to interact among several starch granules predominates due to its high molecular weight, leading to a consequent increase in viscosity.

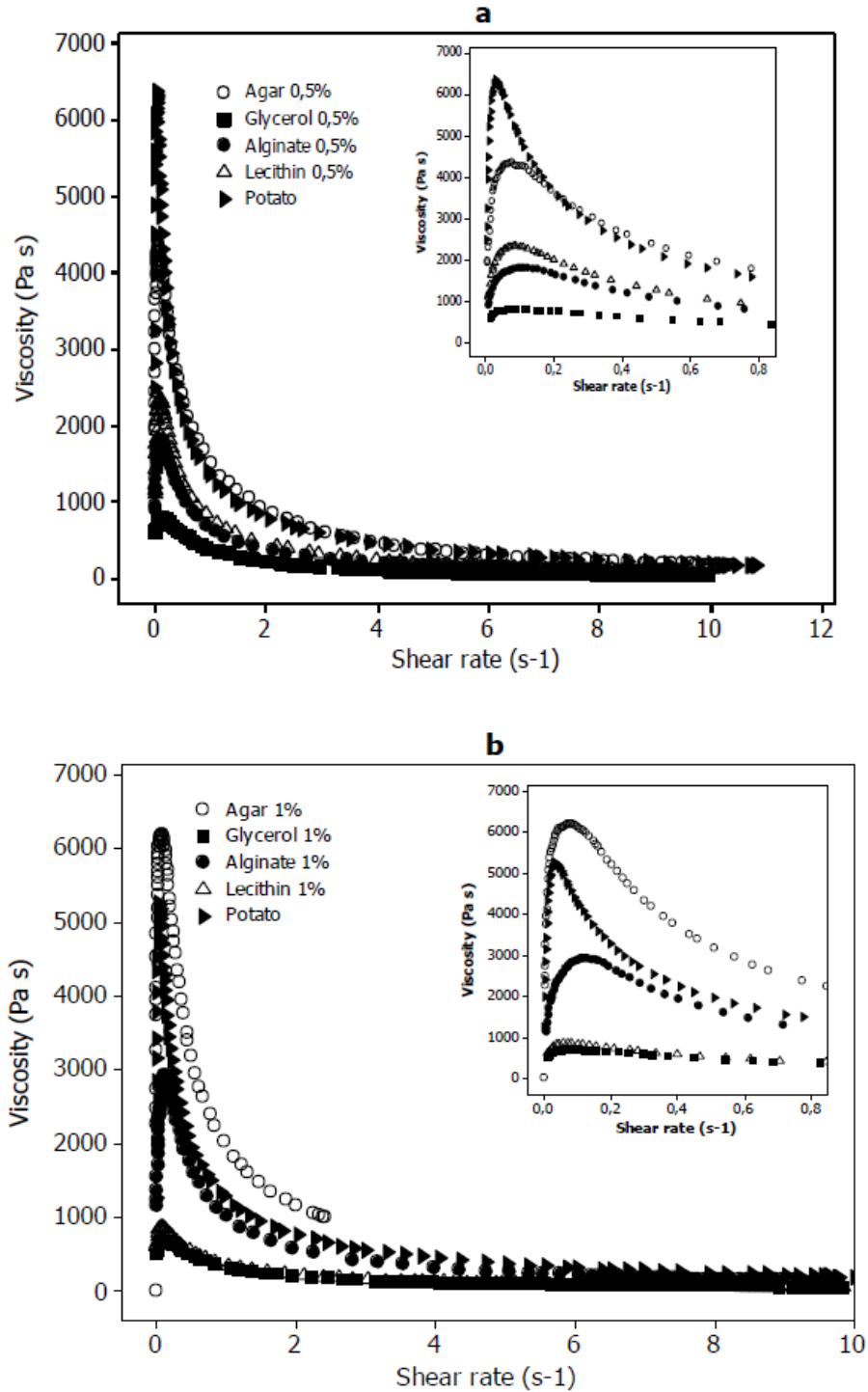


Figure 2. Typical flow curve of potato puree alone and with different additives at 0.5% concentration (a) and at 1% concentration (b). Inset: flow curves at a shear rate below 1s⁻¹.

3.2.2. Yield stress

Several methods have been applied for the determination of the yield stress of food systems (Tabilo-Munizaga and Barbosa-Cánovas 2005, Sun and Gunasekaran 2009). In Figure 3a, a stress ramp was used to estimate the yield stress (see 2.3.2 section), which is one of the most frequently used techniques. This

critical stress level is an important parameter, below which the material is fully elastic, and above which the structure breaks and flows (Sun and Gunasekaran 2009). At first, flow curves showed a slight increase in viscosity and then reached a plateau as shear stress increased to ~ 100 , ~ 300 , ~ 250 , ~ 30 , and ~ 30 (in Pa) for potato, agar, alginate lecithin and glycerol, respectively, at a concentration of 1% (Fig. 3a). This region corresponds to the shear stress in which the sample was fully elastic and was still able to absorb the stress energy without changing its internal microstructure (Sun and Gunasekaran 2009). When the critical stress level (in Pa) was reached (~ 1000 for agar, ~ 500 for alginate, ~ 400 for potato, ~ 200 for lecithin and ~ 200 for glycerol), the viscosity rapidly decreased for all samples. This abrupt decrease indicated a change in the starch microstructure because starch molecules were unable to absorb more energy without being deformed (Tabilo-Munizaga and Barbosa-Cánovas 2005). Therefore, a steep decrease in viscosity occurred as a result of the breakdown in the microstructure of starch molecules. The yield stress results corresponding to both concentrations are shown in Table 1.

All additives at 1% concentration exhibited different yield stress for potato puree compared with puree free of additives (~ 400 Pa). Indeed, agar presented the highest yield stress and had the effect of increasing the puree yield stress up to ~ 1000 Pa. Likewise, alginate increased this yield stress up to ~ 500 Pa, despite its capacity to decrease the viscosity of the puree in an inversely proportional manner. This lengthening in stress yield could be explained by the fact that the starch internal microstructure was affected by both agar and alginate, which contributed to the elasticity of the network of the potato starch puree, consequently generating a starch internal microstructure that was more resistant to deformation in the shear stress region, where the sample is fully elastic. BeMiller (2011) and Visakh (2015) reported that starch mixed with hydrocolloids usually had a better texture and appearance in starchy food since starch and hydrocolloids have certain degrees of similarity (both are polysaccharide molecules). Conversely, lecithin and glycerol had decreasing effects that reduced potato puree yield stress (in the region of full elasticity) to ~ 200 Pa in both cases, indicating less resistance of the starch internal microstructure to deformation in the shear stress region preceding the yield stress.

As the concentration changed from 0.5% to 1% (Table 1), the yield stress increased for agar and alginate, while it decreased for glycerol and lecithin. Thereby, glycerol and lecithin had decreasing effects on the stability of potato puree, whereas agar and alginate had increasing effects.

Table 1 shows the values of the yield stress obtained using the two different approaches cited above. Good agreement with viscosity results can be observed for all of the samples studied.

3.2.3. Thixotropy

In the hysteresis loop test (Fig. 3b), all potato samples with and without additives were subjected to increasing shear rate (forward measurements 0 to 12 s^{-1}), maintained shear rate and then decreasing shear rate (backward measurements 12 to 0 s^{-1}). Flow curves obtained with a controlled shear stress for puree and puree-containing additives at 1% concentration are presented in Figure 3b; the values of thixotropic areas for puree with additives at 0.5% concentration are represented in Table 1. The results showed hysteresis loops, indicating that all samples of puree alone and with 0.5 and 1% additives exhibited thixotropic behaviours, except for 1% agar (see Table 1). Similar results have been reported by Hoover and Vasanthan (1994), who found that among oat, wheat, lentil and potato starches, a thixotropic loop was evident only in oat and potato starches. Others reported thixotropic behaviour of potato starches only

under low shear rates below 10 Pa and at high shear rates above 150 Pa, whereas at intermediate shear rates between 10 and 150 Pa, potato starch possessed rheopectic behaviour (Zhang et al. 2011), findings that are in good agreement with our results since the thixotropic test performed in our study was conducted at low shear rates, from 0.1 to 10 s⁻¹.

Puree without additives exhibited the highest degree of thixotropy, with the largest area (the greater the hysteresis area, the stronger the thixotropic properties (Ma et al. 2014)) compared with those of the agar, alginate lecithin and glycerol samples. Moreover, it is assumed that the hysteresis loop area is a key indication of the energy required to destroy the internal structure of the material responsible for the flow time dependence (Tarrega 2004); thus, puree alone required the highest energy to breakdown the internal structure, indicating a high resistance to time-dependent flow and high levels of internal viscosity and stability. Among the other additives at 0.5%, agar represented the highest degree of thixotropic behaviour, followed (in decreasing order) by lecithin, alginate and glycerol. Whereas at 1% additive concentration, agar showed a high increasing effect until the elimination of the thixotropic loop; alginate also triggered an increase in the thixotropic loop, possessing a higher hysteresis area at this concentration than those of lecithin and glycerol but still lower than that of potato puree alone (Table 1). Additionally, for 1% lecithin and glycerol, smaller loops with nearly identical weak thixotropic behaviours were observed, which is an indication of poor tolerance of the sample under shear, as expressed by structure changes and collapses, reduced product resistance and a more disrupted internal network (Costa et al. 2016). Upon decreasing the shear rate, all puree samples showed the capacity to reform the damaged internal network and to recover their viscosities; only agar at 1% did not recover its viscosity after the shear rate decreased. This finding could be related to the increase in agar concentration and the formation of a harder gel that was unable to recover its viscosity (due to the loss of elastic and viscous characteristics). Thus, at 1% and in terms of thixotropic behaviour, with a highly stabilized internal network and a high product resistance to collapse and disruption, potato purees with the different additives can be classified in the following decreasing order: puree with agar, potato alone, alginate, lecithin and glycerol. Again, these thixotropy results are in good agreement with those obtained for yield stress and viscosity in this work.

Table 1: Experimental characterization of the yield stress τ_0 (Pa) using both Bingham model and the intersection point of $\gamma=f(\tau)$ as well as representing the values of the Thixotropy Hysteresis Loop area (in Pa·s⁻¹), and the Cox Merz parameters: shift factor (α), and R² coefficient for the different potato puree samples

		Potato puree	Agar		Alginate		Lecithin		Glycerol	
			0.50%	1%	0.50%	1%	0.50%	1%	0.50%	1%
yield stress τ_0 (Pa)	Bingham model	1508 R=0.992	1309 R=0.998	-----	773 R=0.983	1150 R=0.958	867 R=0.991	429 R=0.992	418 R=0.966	393 R=0.997
	* Abrupt change in $\eta=f(\tau)$	400	600	1000	400	500	450	200	250	200
Thixotropy (Pa·s ⁻¹)	Hysteresis loop area	3.9·10 ⁴	2.64·10 ⁴	-----	4660	1.27·10 ⁴	1.26·10 ⁴	3469	2605	1449
Cox Merz Rule	(α) Shift factor	0.37	0.45	0.61	0.35	0.43	0.34	-----	0.30	0.38
	Determination coefficient R ²	0.9943	0.9909	0.9998	0.9978	0.9913	0.9914	-----	0.9967	0.9984

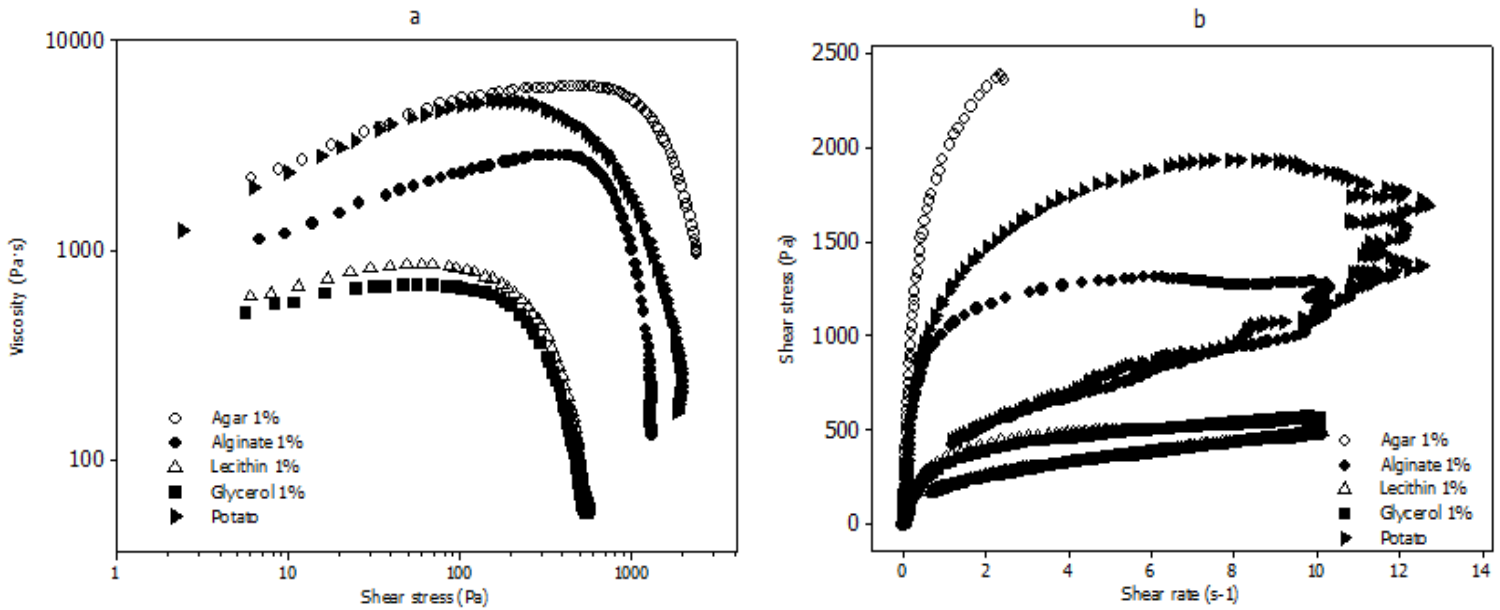


Figure 3. Measurement of the commercial potato puree and puree samples with additives (1% w/v, 20°C), for (a) Yield stress based on the stress ramp method. (b) Thixotropic hysteresis loop- Stress ramps at 20°C.

3.3. Viscoelastic behaviour

Viscoelastic properties are determined by the level and nature of the leached material and the molecular interactions upon starch granule disintegration in a three-dimensional network structure (Alcázar-Alay and Meireles 2015). The mechanical spectra of all studied puree samples are illustrated in Figure 4. Figure 4 a, b, c and d showed that the storage or elastic modulus G' (which measures the recovered or accumulated energy in each deformation cycle and determines the elastic behaviour of the sample) of commercial potato puree remained higher than the loss or viscous modulus G'' (the loss of energy or dissipated energy in each deformation cycle, which describes the viscosity behaviour of the material), indicating an elastic (gel) property with an internal network structure of the potato puree sample being analysed (Tabilo-Munizaga and Barbosa-Cánovas, 2005). Similar observations were reported by several authors, such as Svegmak and Hermansson, (1993) and recently Chaisawang and Suphantharika, (2005) and Ahmed and Ramaswamy, (2006), who found that for potato starch and purees and cationic tapioca starch, G' was always higher than G'' , indicating the presence of a network arrangement and a gel-like structure. Among all the additives used, and at 0.5%, only agar had the capacity to increase the elastic and viscous modulus of potato puree up to peaks of 8500 and 5000 Pa, respectively, whereas the other additives decreased both moduli of potato puree in the following increasing order: lecithin, alginate, and glycerol, indicating a stretchy gel-like formation (Fig. 4 a, c). At a 1% concentration, the effects of agar on increasing the elastic and viscous moduli of potato puree were further enhanced, reaching peaks of 10,000 and 6500 Pa, respectively, indicating a firmer gel formation. In contrast, the other additives kept decreasing both moduli of potato puree, shifting their order of

decreasing effect. When compared with potato puree, it was observed that alginate 1% decreased the G' modulus slightly to 3600 Pa while maintaining the same value as that of G'' : 3200 Pa at ~100 Hz. The decreasing effect of glycerol 1% was more pronounced, decreasing the optima of the elastic and viscous moduli of potato puree to 1800 and 1200 Pa, respectively (Fig. 4 b, d). Concerning the sample of lecithin at 1% concentration, it was not possible to calculate both G moduli due to the strong effect of lecithin as an emulsifier in decreasing viscosity and reducing stickiness since it inhibits molecular interactions (Johansson and Bergenstahl 1992a, 1992b; Servais et al. 2003). In that case, lecithin acted by decreasing the viscosity approximately 90%, with the result that the viscoelastic behaviour practically disappeared (Fig. 2b).

Additionally, at a concentration of 0.5% additives, puree samples exhibited values of G' and G'' ranging between 1000-9000 Pa and 500-5000 Pa, respectively (Fig. 4a, c). Similarly, for the 1% concentration, the values of G' and G'' ranged between 900-10000 Pa and 600 to 6500 Pa, respectively (Fig. 4b, d). Therefore, in absolute value, all the samples exhibited greater changes in G' modulus compared with G'' ($|\Delta G'| > |\Delta G''|$), indicating that both elastic and viscous moduli were modified, but with all additives having a predominant effect on the elastic (solid) behaviour of the puree, thus possessing a higher capacity to recover energy from deformation. In other words, additives enhanced the capacity for reformation rather than deformation of the initial molecular structure after the cessation of stress.

A different effect on the G' dynamic modulus of the commercial potato puree was revealed by agar depending on its concentration. For the less concentrated agar sample (0.5%), at low frequencies, the G' was found under the curve corresponding to the potato puree, whereas at high frequencies, the G' rose slightly above it (Fig. 4a). This finding can be explained by the fact that at low concentration, the agar is not plentiful enough to form a gel network, but there is enough to connect different starch granules via hydrogen bonds with agar OH groups, making it harder to recover quickly upon deformation (less elastic) behaviour. Additionally, at low frequencies, these interactions build up in the presence of agar 0.5% have enough time to break and make up again, maintaining a less-elastic property when compared with puree alone, in which the molecules are free (not connected or entangled with other additives via hydrogen bonds), and thus this facilitates its faster recovery from the deformation (more elastic). At high frequencies, and due to the short period of oscillation, the network (agar-starch interactions) is broken and cannot recover after it is disentangled, resulting in an increase in the elasticity of the puree with 0.5% agar, which is explicated by the fact that its G' curve rises slightly above that of commercial potato puree. At the 1% concentration, the G' modulus of agar is higher than that corresponding to the pure alone over all the range of frequencies studied and can be clarified by the formation of a strong interconnected network due to the effect of having both interactions, where the major part of the granules is strongly connected to each other by the high molecular weight and length of the agar molecule (agar-starch) interactions and the formation of (agar-agar) gel-like interactions. These interactions would result in a more elastic, structured and gel-like microstructure than in the case of the commercial puree.

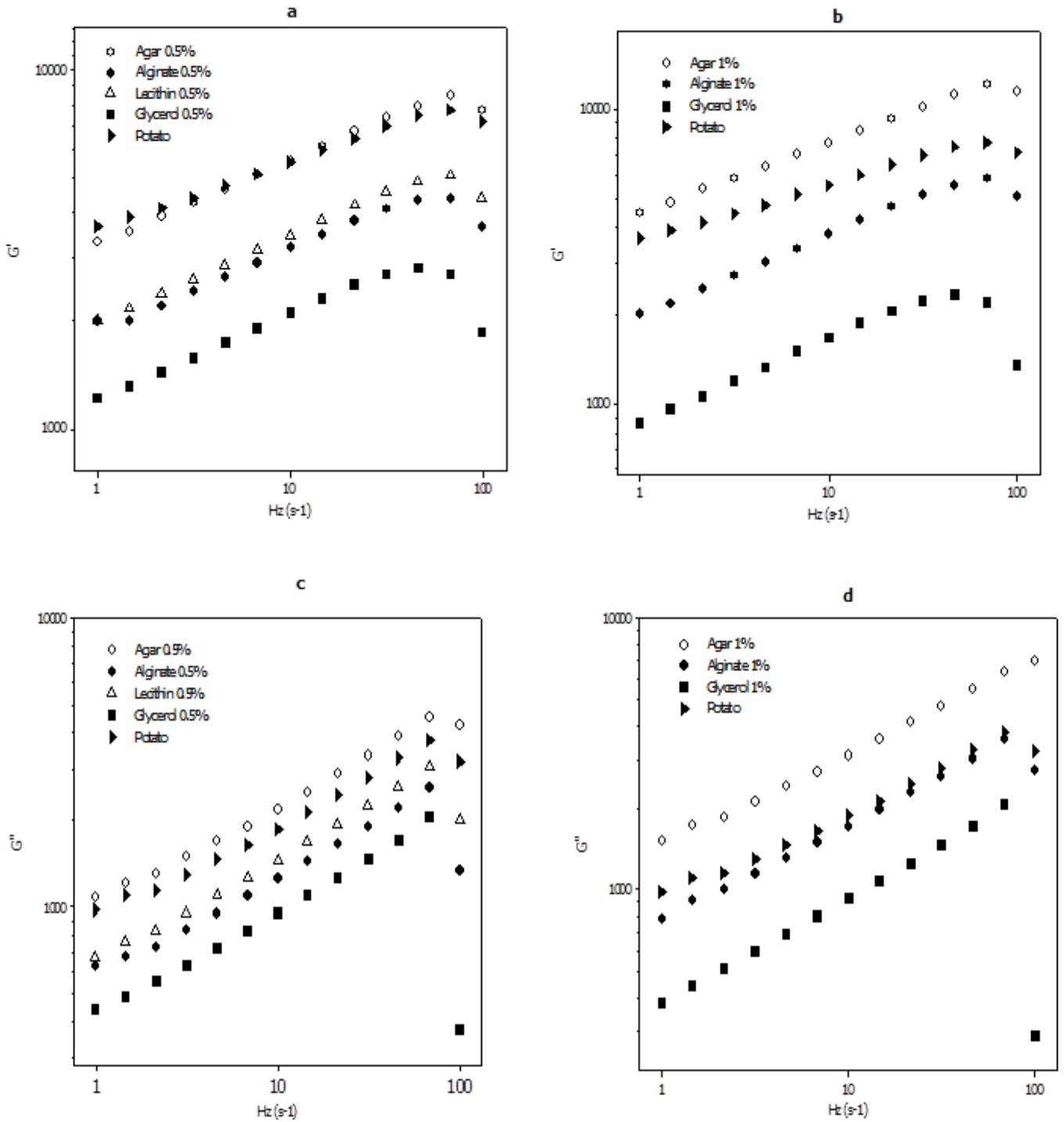


Figure 4. Dynamic mechanical spectra of potato pure alone and with different additives for storage modulus (G') at 0.5% concentration (a) and at 1% concentration (b) and Loss modulus (G'') at 0.5% concentration (c) and at 1% concentration (d).

3.4. Applicability of the Cox-Merz rule.

The empirical Cox-Merz rule (Cox and Merz 1958) states that values of the complex viscosity (η^*) and the steady shear viscosity (η) must have equal magnitudes at equal values of frequency and shear rate (Eq. 1).

$$\eta(\dot{\gamma}) = \eta^*(\omega)|_{\dot{\gamma}=\omega} \quad \text{Eq. 1}$$

The relationship between dynamic complex viscosity (η^*) and the shear viscosity data (η) in the frequency range 0.1-to 10 sec^{-1} was studied for all of the potato puree samples. Parallel dependencies of $\eta^*(\omega)$ and $\eta(\dot{\gamma})$ were obtained for all of the samples, and some of them are illustrated in Fig. 5. As detected in most food systems, the complex viscosity was greater than the apparent viscosity, indicating that these purees did not obey the Cox-Merz rule.

A generalized Cox-Merz equation introducing a multiplicative horizontal shift factor (α) (see Eq. (2)) fitted well for the different potato purees; the two sets of data were superimposed on each other, following a single line, with R^2 factors always higher than 0.99.

$$\eta(\dot{\gamma}) = \eta^*(\alpha \cdot \omega)|_{\dot{\gamma}=\omega} \quad \text{Eq. 2}$$

Table 1 represents the multiplicative constant (α) and R^2 factors found for all of the different puree samples studied. Variances among α value can be spotted between the different potato puree samples, signifying differences within their structural organizations. For instance, the shift factor α was observed to increase with an increase in all of the additive concentrations in potato puree, (from 0.45 to 0.61 for agar, from 0.35 to 0.43 for alginate and from 0.30 to 0.38 for glycerol; it was not possible to record the oscillatory values for lecithin 1% (see section 3.3)). This increase in the α shift factor implied the enhanced effect exerted by the additives on modifying the internal structure of the potato puree at their respective higher concentration, regardless of whether this modification would lead to a more stable and elastic material, as in the case of agar and alginate, or to an un-stable and viscous material, as in the case of glycerol.

In fact, potato puree alone or combined with different additives make up a complex system with many entanglements, intermolecular aggregations and dispersions, which in turn make the purees more susceptible to considerable structural breakdown and decay upon the application of an extensive strain, which can explain the non-fitting of the potato puree samples to the Cox-Merz rule (Ahmed and Ramaswamy 2006).

The modified Cox-Merz rule obtained in this work is potentially useful for the determination of the rheological properties of commercial potato puree combined with different additives by predicting either of the materials' dynamic or steady-state data due to the linear relationship that was found between η and η^* among all of the puree samples, permitting for direct predictions of texture perceived in the mouth, in contrast to the results obtained by (Alvarez M. D et al. 2004), who found a non-linear relationship between steady and dynamic measurements for commercial potato puree but a linear one for purees made

from natural potatoes. However, dynamic experiments are not always preferably applicable (due to the low strain at which the test is done), especially when considering material characterization under various food processing techniques (such as pumping, mixing, and extrusion) that require large and strong deformation rates. In these cases, steady-state shear measurement must be proposed.

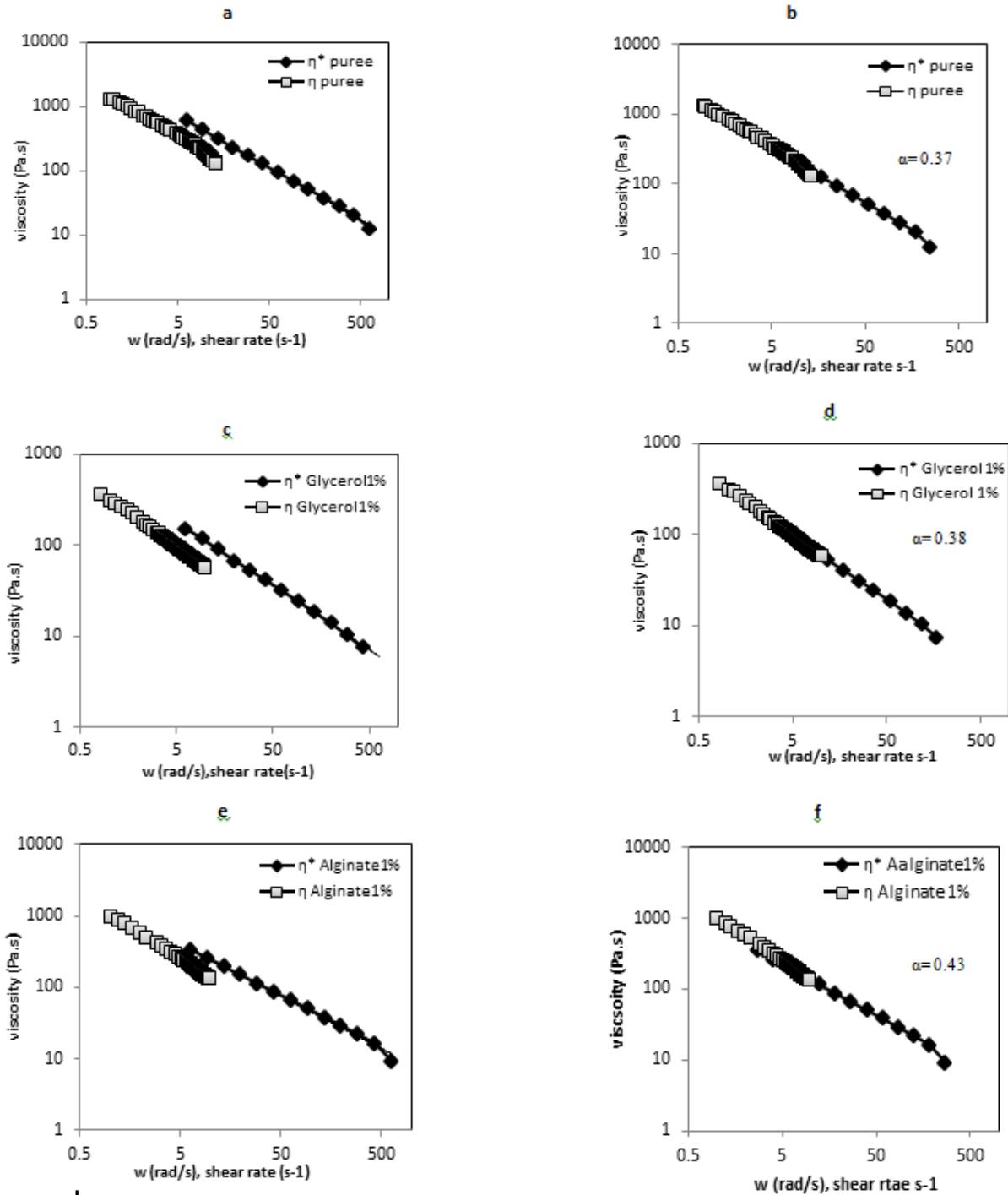


Figure 5. Plots of $\log(\dot{\gamma})$ against $\log(\eta)$ and $\log(\omega)$ against $\log(\eta^*)$ for (a) commercial potato puree, (c) with glycerol, (e) with alginate. Modified Cox-Merx rule for (b) commercial potato puree, (d) with glycerol and (f) with alginate. α is the shift factor for ω .

4. Conclusions

The impacts of agar, lecithin, glycerol and alginate were studied to define the rheological and structural properties of commercial potato starch puree. Microscopic observations revealed large aggregations of starch granules in potato puree. These granules appeared more swollen in purees containing glycerol and lecithin, while more ruptured and reduced-size swollen granules were detected in puree with agar. These observations were correlated to and confirmed with the rheological findings.

Additionally, all samples possessed non-Newtonian, shear-thinning behaviour. Furthermore, the effects of all additives were concentration-dependent. At low concentration, agar and alginate decreased the viscosity of the puree, while at higher levels, they increased it. In contrast, glycerol and lecithin decreased the viscosity of the puree at both concentrations, with this decrease being more enhanced at the 1% concentration. Apparently, the sharp decreases in viscosity, yield stress and thixotropic behaviour observed when glycerol and lecithin (at 0.5% and 1%) were added were correlated with the abrupt starch granule disintegration under shearing, while the effects of agar and alginate were governed by their high molecular weights, retarding their entry inside the starch granules and triggering a (hydrocolloid-starch) network formation.

Agar increased both G moduli, whereas all the other additives studied decreased them. Additionally, the steady shear and complex viscosities of all puree samples did not follow the Cox-Merz rule. However, a linear relationship between these data was obtained that fits well upon modifying the rule and introducing a frequency shift factor.

Generally, agar and alginate demonstrated their capacity to moderately affect and stabilize more potato puree, while having an exclusive effect of acting either as an increasing or decreasing agent on viscosity according to the concentration. Conversely, glycerol and lecithin showed strong and destabilizing effects on potato puree even at very small concentrations. These findings suggest that alginate and agar are good and helpful options to be used in food technology processes such as 3D food printing.

Acknowledgements

The authors wish to thank Dr Jordi Saldo from Universitat Autònoma de Barcelona for his assistance and for the use of the Rheostress RS1, version 127). The authors are grateful for the financial support of the Azm Saadeh Foundation.

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▪ Chapter 6

Characterization of food additive-potato starch complexes by FTIR and X-ray diffraction

- *This chapter has been published as*

Dankar, I., Haddarah, A., Omar, F. E. L., Pujolà, M., & Sepulcre, F. (2018). Characterization of food additive-potato starch complexes by FTIR and X-ray diffraction. *Food Chemistry*, 260, 7–12. <https://doi.org/10.1016/j.foodchem.2018.03.138>

Characterization of food additive-potato starch complexes by FTIR and X-ray diffraction

Abstract

Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) techniques were used to study the effect of four food additives, agar, alginate, lecithin and glycerol, at three different concentrations, 0.5, 1 and 1.5%, on the molecular structure of potato puree prepared from commercial potato powder. Vibrational spectra revealed that the amylose-amylopectin skeleton present in the raw potato starch was missing in the potato powder but could be fully recovered upon water addition when the potato puree was prepared. FTIR peaks corresponding to water were clearly present in the potato powder, indicating the important structural role of water molecules in the recovery of the initial molecular conformation.

None of the studied puree samples presented a crystalline structure or strong internal order. A comparison of the FTIR and XRD results revealed that the additives exerted some effects, mainly on the long-range order of the starch structure via interacting with and changing -OH and hydrogen bond interactions.

Keywords: X-ray diffraction, FTIR, structural properties, Starch, Food additives

1. Introduction

Recently, modified starches have gained interest in the gastronomic field due to their enhanced functional properties compared to unmodified starches (Perera, Hoover, & Martin, 1997; Sun, Si, Xiang & Chu, 2013). Processing starch with different types of food additives promotes a wider range of variation in its chemical, mechanical and sensorial characteristics and thus stimulates a broader array of functional applications. In fact, these modification practices applied during food processing lead to the formation or absence of certain molecular structures as a result of the interactions among the molecular components of the ingredients, subsequently modulating important physiochemical, mechanical and organoleptic properties of food (BeMiller, 2011; Chaisawang & Suphantharika, 2005; Fu et al., 2015; Singh, Kaur, & McCarthy, 2007; Stephen, 1995). Therefore, while developing new food products, it is important to consider all possible interactions among the molecular ingredients and to examine these interactions at the structural level to develop a better understanding and to ensure integrated linking between the structural properties and food texture. This will permit food scientists and technologists to gain the keys for the overall control, modulation and improvement of food properties that will meet the perceptions and desires of consumers.

Generally, the raw starch found in potato tubers is organized into structurally void granules consisting of two types of α -glucans: amylopectin (a heavily branched α -glucan polymer of high average molecular weight with an α (1 \rightarrow 4)-linked backbone and α (1 \rightarrow 6)-linked branches) and amylose (a linear and relatively long α -glucan polymer linked by α (1 \rightarrow 4)-linkages). Raw starch granules show a crystalline/amorphous structure that can be recognized at both the short- (nm) and long-range (several μ m) scales. In particular, short-range ordering corresponds to double and single helical amylose or

amylopectin, embedded in amorphous or crystalline lamellar regions, as well as amylose-amylopectin helices complexes (Tester, Karkalas, & Qi, 2004). The arrangement and ordering of double helices into concentric alternating stacks of microcrystalline and amorphous lamellar structures is associated with long-range ordering.

Moreover, these raw starch microstructures and conformations change with industrial treatment, which generally includes heating and/or changes in the amount of absorbed water, varying its crystalline/amorphous regions ratio and its susceptibility to enzymatic hydrolysis, texture, and/or sensorial or rheological properties, among others.

Several techniques have been used in numerous starches and modified starch studies by various authors to characterize the molecular interactions that are responsible for short- and long-range organization (Liu et al., 2011). Using Fourier-transform infrared spectroscopy (FTIR), the most characteristic vibrational bands of several starches have been assigned, providing information on amylose and amylopectin chain folding (Ramazan Kizil et al., 2002) and the crystalline/amorphous ratio (Ispas-Szabo, Ravenelle, Hassan, Preda, & Mateescu, 1999). Retro-gradation of potato starch has also been studied by FTIR (Flores-Molares et al., 2012; Van Soest et al., 1994) and led to the conclusion that the spectral region 800-1100 cm^{-1} contains bands that are sensitive to the starch polymer conformation (α (1 \rightarrow 4)-linked backbone, - CH_2 backbone, etc.) and that can be used to follow crystallite melting and the multi-stage processes of retro-gradation (Flores-Molares et al., 2012; Zhang et al., 2013). Several works affirm that the ratio between the absorbance intensity of bands located at 1047 and 1022 cm^{-1} can be used to quantify the index of crystallinity because these bands can be associated with ordered and amorphous structures, respectively (Flores-Molares et al., 2012).

X-ray diffraction (XRD) is another important chemical analysis that has been used to characterize starch structures and detect any changes in the starch pattern crystallinity due to different processing techniques. For example, Ribotta et al. (2004) found that amylopectin retro-gradation and B-type crystalline structure were augmented during ageing using DCS and XRD, and Liu et al. (2002) studied thermal phase transitions in potato starch-water systems.

In a previous work (Dankar et al., 2018), we investigated the effect of four food additives (agar, glycerol, alginate and lecithin) at different concentrations on the rheological properties of potato puree prepared from commercial potato flakes. The results were strongly concentration dependent; for example, at higher concentrations, agar and alginate elevated the viscosity and yield stress of potato puree, whereas glycerol and lecithin diminished them and produced more unstable products. Accordingly, the present work aims to contribute to knowledge about the effects that these additives exert on the structural molecular level of potato starch and its induced conformational changes. This aim was achieved by collecting FTIR spectra (short-term order) and XRD patterns (long-term order) of potato puree and potato puree samples containing additives and determining correlations between them.

1. Materials and Methods

1.1. Sample preparation

Dehydrated potato puree (Maggi, origin) and whole milk were purchased from the local supermarket. Agar-agar, soy bean lecithin, sodium alginate and glycerol (food grade) were procured

from Sigma–Aldrich Co. Potato puree samples were prepared according to the following recipe: 90 mL of milk and 10 mL of water were pre-heated to 40°C, and then, 23 g of potato powder was added. The mixture was then homogenized for 3 minutes using an electric hand blender (Braun, Germany). The same procedure was followed to prepare puree samples with four different additives at three different concentrations, 0.5, 1 and 1.5%. Additives with their corresponding percentage were added and dissolved in the warmed solution (milk and water) prior to the incorporation of potato powder. However, for agar, solutions were boiled to 100°C, and dehydrated potato was then added. Subsequently, all samples were set in an incubator to maintain a temperature of 20 °C preceding the chemical analysis. To compare the structures of the commercial potato powder and native potato, a small fraction of raw potato was taken from the middle of a tuber, ground and subjected to FTIR chemical analysis.

2.2 Chemical analysis

2.2.1 FTIR:

FTIR spectra were collected for all additives, potato powder, potato puree and their mixtures (alone and with various concentrations of additives) and raw potato alone using an STS FTIR spectrometer. Spectra were recorded from 349 to 4000 cm^{-1} using an MCT detector cooled with liquid nitrogen. The samples were blended with KBr and pressed into tablets before measurement. Spectra were collected at a resolution of 4 cm^{-1} and at an average of 35 scans per sample.

2.2.2 X-ray Diffraction:

XRD patterns of potato puree and the mixtures (potato puree alone and with various concentrations of additives) were prepared using an X-ray diffractometer (Bruker D8 Discover AXS GmbH, Germany) equipped with Cu radiation at a wavelength of 1.5406 Å. Measurements were obtained at room temperature with a scanning rate of 0.02°/s and a diffraction angle range of 5 to 80° (2-Theta° range), where theta is the angle of incidence of the X-ray beam on the sample. The diffraction patterns were analysed using EVA software.

3. Results and Discussion

3.1 Fourier-transform Infrared Spectroscopy

Comparison among commercial potato powder, potato puree and potato starch

For clarity, we divided the IR spectra into two regions from 4000 to 1500 cm^{-1} and from 1500 to 400 cm^{-1} .

Spectral region from 4000 to 1500 cm^{-1}

Figure 1 shows the IR of the commercial starch powder, potato puree prepared from commercial starch powder, and raw potato. All 3 samples showed the same characteristic peaks at 3500 cm^{-1} , 2900 cm^{-1} , 2100 cm^{-1} and 1650 cm^{-1} . Peaks at 1650 cm^{-1} were assigned to water molecules absorbed in the amorphous region (Ramazan Kizil, Joseph Irudayaraj, & Seetharaman, 2002) and the stretching vibration of the C=O band (amide I). The peak at 2100 cm^{-1} originates from the free water content (Olsson & Salmén, 2004), and peaks at 2900 and 3500 cm^{-1} are due to CH₂ deformation and OH bonds, respectively (Kačuráková & Mathlouthi, 1996).

The dehydrated sample (commercial potato powder) presented the same peak characteristics assigned to the hydrated samples (commercial potato powder and potato starch) but with lower intensity, except for the peak at 2100 cm^{-1} (corresponding to the free water content) (Fig. 1). This finding indicates that even when dehydrated, starch retains some water molecules strongly bound to some starch chemical groups via OH bonds, probably because these water molecules have some structural role. Peaks centered at approximately 2100 cm^{-1} have not been assigned yet for starch, but Olsson & Salmén (2004) found that its IR intensity increased in a sample of Kraft paper when absorbed water increased and were thus assigned to vibrations from the scissoring and rocking of water. In our case, the intensity of this peak increased when water was added to prepare potato puree from potato powder (dehydrated starch) (Fig. 1), and therefore, we assigned it to free water molecules that are not directly bound to starch.

Spectral region from 1500 to 400 cm^{-1}

The most important structural differences among these three samples can be observed in the region from 1500 to 400 cm^{-1} (Fig. 1). Changes in the bands located in this region, considered the fingerprint region, provided information about changes in the polymeric structure and conformation of starch. Characteristic peaks for potato starch were previously described by several authors: 1412 cm^{-1} assigned to $-\text{CH}_2$ bending and $-\text{COO}$ stretch (Cael, Gardner, Koenig, & Blackwell, 1975; Ramazan Kizil et al., 2002); 1048 cm^{-1} and 1022 cm^{-1} assigned to the crystalline and amorphous regions of starch, respectively (Kačuráková & Mathlouthi, 1996); and 1164 cm^{-1} assigned to vibrations of the glucosidic C-O-C bond and the whole glucose ring that can present different modes of vibrations and bending conformations. The bond at 930 cm^{-1} was assigned to the skeletal mode vibrations of α 1 \rightarrow 4 skeletal glycoside bonds (JAO & KO, 2002), 780 cm^{-1} was assigned to C-C stretch (Sekkal, Dincq, Legrandb, & Huvenne, 1995), and 577 cm^{-1} was assigned to skeletal modes of the pyranose ring (Cael et al., 1975). Comparing the 3 samples, raw potato and potato puree expressed similar peaks but with small differences in intensity; the peaks expressed by potato puree were of slightly higher intensity than those by raw potato. The commercial potato powder expressed relatively low-intensity vibrations, indicating the absence of a definitive internal structure for the potato powder, which was nevertheless regenerated upon the addition of water and preparation of the potato puree. In fact, the mitigation in the internal structure of potato powder could be attributed to the disruption of both hydrophilic and hydrophobic interactions since both integrally contribute in maintaining the starch-helical structural integrity and order (BeMiller, 2011).

Moreover, upon comparing the FTIR spectra of raw and dehydrated starches, the processing effect or temperature effect can be distinguished by the shifting of similar peaks towards a slightly higher or lower wavenumber; for example, the glycosidic bond located in the spectrum of native starch at 1150 cm^{-1} shifted to 1170 cm^{-1} after heating, and the skeletal modes of the pyranose ring originally at 717 cm^{-1} wavenumber moved to 615 cm^{-1} in dehydrated flakes. This effect was also stated by Siemion et al. (2004), who studied the effect of temperature on native starches. However, after adding water to potato flakes, the spectra of potato puree and raw potato starch were very similar (only small difference in intensity levels as stated above). Even the small peaks and vibrations that appeared in the potato powder spectrum between 900 and 500 cm^{-1} disappeared, demonstrating the importance of water in maintaining the whole structure of starch, as its effect surpasses the effect that temperature had already exerted on

dehydrated flakes. Evidently, this suggests that potato starch that was previously dehydrated can almost completely recover its original internal structure with the addition of water. Perhaps water molecules that are strongly bound to starch and remain even in the dehydrated sample have an important structural role and help to partially recover the internal starch structure when it is rehydrated.

Furthermore, the relative intensity between peaks at 1022 and 1048 cm^{-1} has been used to characterize the content of the crystalline starch, because these two peaks have been respectively assigned to amorphous and crystalline starch (Sevenou, Hill, Farhat, & Mitchell, 2002). In the case of the raw potato and potato puree samples, peaks at 1022 cm^{-1} were relatively higher in intensity than those at 1048 cm^{-1} . Thus, a more amorphous starch conformation rather than a crystalline conformation exists in the structure of potatoes. In good agreement with this result, a high-intensity band located at 1640 cm^{-1} (assigned to water molecules absorbed in the amorphous region) was also present in the potato puree and raw potato spectra.

Additionally, important differences were also observed in the vibrational region from 930 to 500 cm^{-1} , which has been assigned to the “secondary starch structure” that primarily originated from the vibrations of the skeletal mode of α (1 \rightarrow 4) glycosidic linkage, the skeletal modes of the C-C stretch and the skeletal modes of the pyranose ring (Fan et al., 2012). Raw potato showed intense and narrow peaks at these normal mode vibrations, but potato puree showed an intense but smoothed band at 900 to 400 cm^{-1} , suggesting an increase in the number of α -glucan polymers conformations and therefore a decrease in the short-order range of starch (i.e., a decrease in the helical content/skeletal mode vibration of the α linkage/backbone of the CH₂-CH₂ bending vibrations and/or the pyranose ring, which consequently leads to a decrease in the long-range ordering).

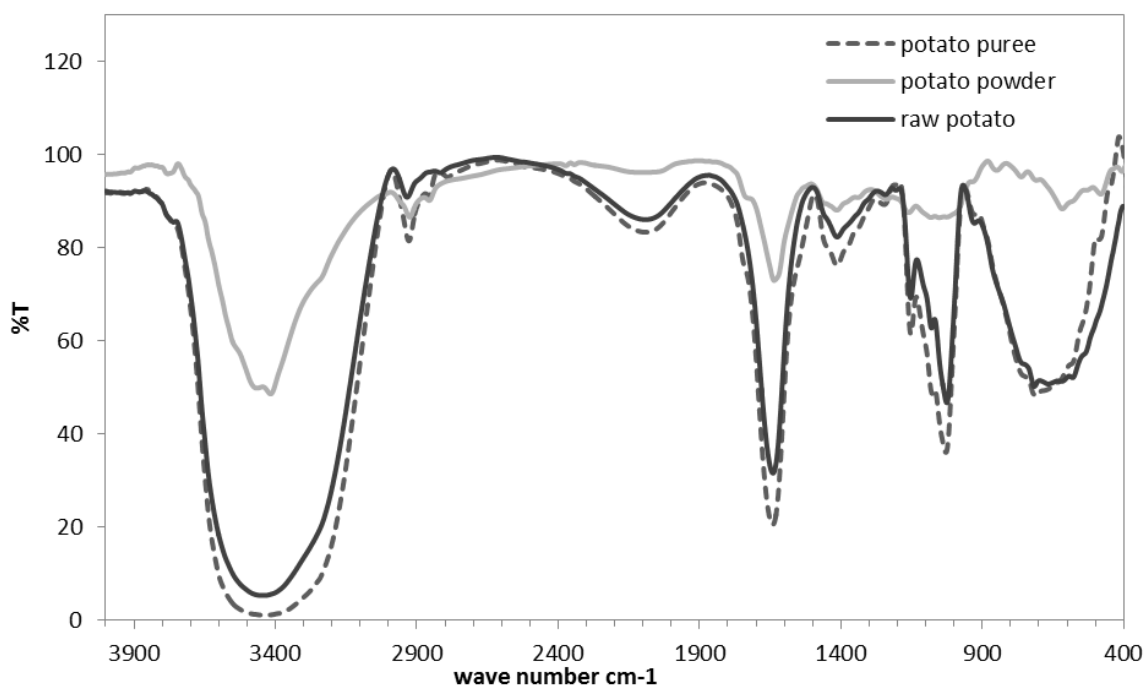


Figure 1. Vibrational spectra of raw potato, commercial potato powder and potato puree prepared by using commercial potato powder.

Adding additives

FTIR spectra for the commercial potato puree and potato puree containing different additives at different concentrations were all similar in shape but not intensity (Fig. 2), indicating that additives have some effect, mainly on long-range ordering and crystallinity.

Lecithin is the only additive that at both concentrations of 0.5 and 1% increased the IR intensity of the peaks centered at 1020 cm^{-1} , 1412 cm^{-1} and 2900 cm^{-1} (Fig. 2a, b). Peaks at 1412 and 2900 cm^{-1} were assigned to the $-\text{CH}_2$ bending/ $-\text{COOH}$ stretch and $-\text{CH}_2$ stretching, respectively (Fan et al., 2012). Compared to the other additives, lecithin possesses more $-\text{CH}_2$ groups that may be responsible for this increase. Therefore, in this case, what is observed most is the contribution of these lecithin methyl groups, rather than a starch-additive interaction.

Moreover, except for lecithin, all other additives studied here decreased the IR intensity of the potato puree sample over the entire spectral range (4000 to 400 cm^{-1}). The three characteristic peaks related to water content (3500 , 2100 and 1642 cm^{-1}) all decreased in intensity when additives were added to the potato puree. The change in the intensity at 3500 cm^{-1} can be related to rearrangement of the hydrogen bonds between the starch $-\text{OH}$ groups and some groups from additive molecules, which is more significant than the change with water content. A similar interpretation can be made for peaks centered at 2100 cm^{-1} and 1642 cm^{-1} in terms of the interaction of additives with water molecules initially bound to starch chemical groups. In fact, additive addition prompted a movement/sequestration of several water molecules from starch, inducing a decrease in the water content in the amorphous part of the starch (1642 cm^{-1}) and a general decrease in the amount of the free water.

Furthermore, changes in the intensity of the IR bands assigned to the structural motifs of starch (characteristics peaks at 2900 , 1412 , 1022 , 930 and 570 cm^{-1}) can be interpreted as a loss of the long-range order of the polymeric starch secondary structure, for example, changes in amylose and/or amylopectin helix content or the α (1 \rightarrow 4)- and α (1 \rightarrow 6)-linked backbone, which could be the result of starch-additive granule interactions either directly by entering and rupturing the starch granule or indirectly by holding and retarding water penetration inside the starch granules, in both cases inducing conformational changes in the starch molecules (Dankar et al., 2018).

At an additive concentration of 0.5%, a change in the IR intensity of the region from 1000 to 400 cm^{-1} was observed with respect to that of potato puree (Fig. 2a). Glycerol and lecithin were the additives that most decreased the IR intensity of potato puree at this corresponding range, most likely due to their smaller molecular size compared to agar and alginate. This in turn facilitates their complete penetration into the starch granule and allows their direct interaction with the starch OH groups, consequently altering the α (1 \rightarrow 4)-linked backbone of the potato starch components. However, the relatively long and large molecular sizes of agar and alginate retarded their penetration into the starch granule. Thus, the type of interaction between these two additives and the starch molecule would be more constrained to the OH groups located on the granule surface, which permit the partial maintenance of the integrity of the starch granules and determines the conformation of amylose and amylopectin. This effect was reflected in the

FTIR spectra in small differences between the intensities of puree with agar and alginate and those of puree alone in the 1000-400 region, which is a reflection of any conformational changes in the starch structure, as stated above.

When the additive concentration increased from 0.5 to 1%, the IR intensity of the potato purees containing glycerol, alginate and agar clearly decreased (Fig. 2b), indicating a total loss of secondary structure (helical content) and the α -glucan backbone polymeric conformation as a consequence of the interaction between additives and starch. A further increase in the additive concentration from 1% to 1.5% increased the IR intensity for all samples, except for potato puree containing alginate (Fig. 2c). This increase in IR intensity can be explained by the formation of additive aggregates and/or networks among the additive molecules due to their high concentration (1.5%), rather than interactions between additives and starch.

Hence, the demonstrated FTIR results corroborate the imperative role that water molecules exert on starch structure, in agreement with several authors (Blazek & Gilbert, 2011; Dankar, Haddarah, El Omar, Sepulcre, & Pujolà, 2018; Liu et al., 2002). The ability of dehydrated starch to almost totally recover its short- and long-range structures (regain its original structure) upon the addition of water was also established.

In this sense, the inter-dependence and reliance between peaks corresponding to water content and those that originated with the polymeric conformation of starch and the skeleton (secondary structure) were demonstrated.

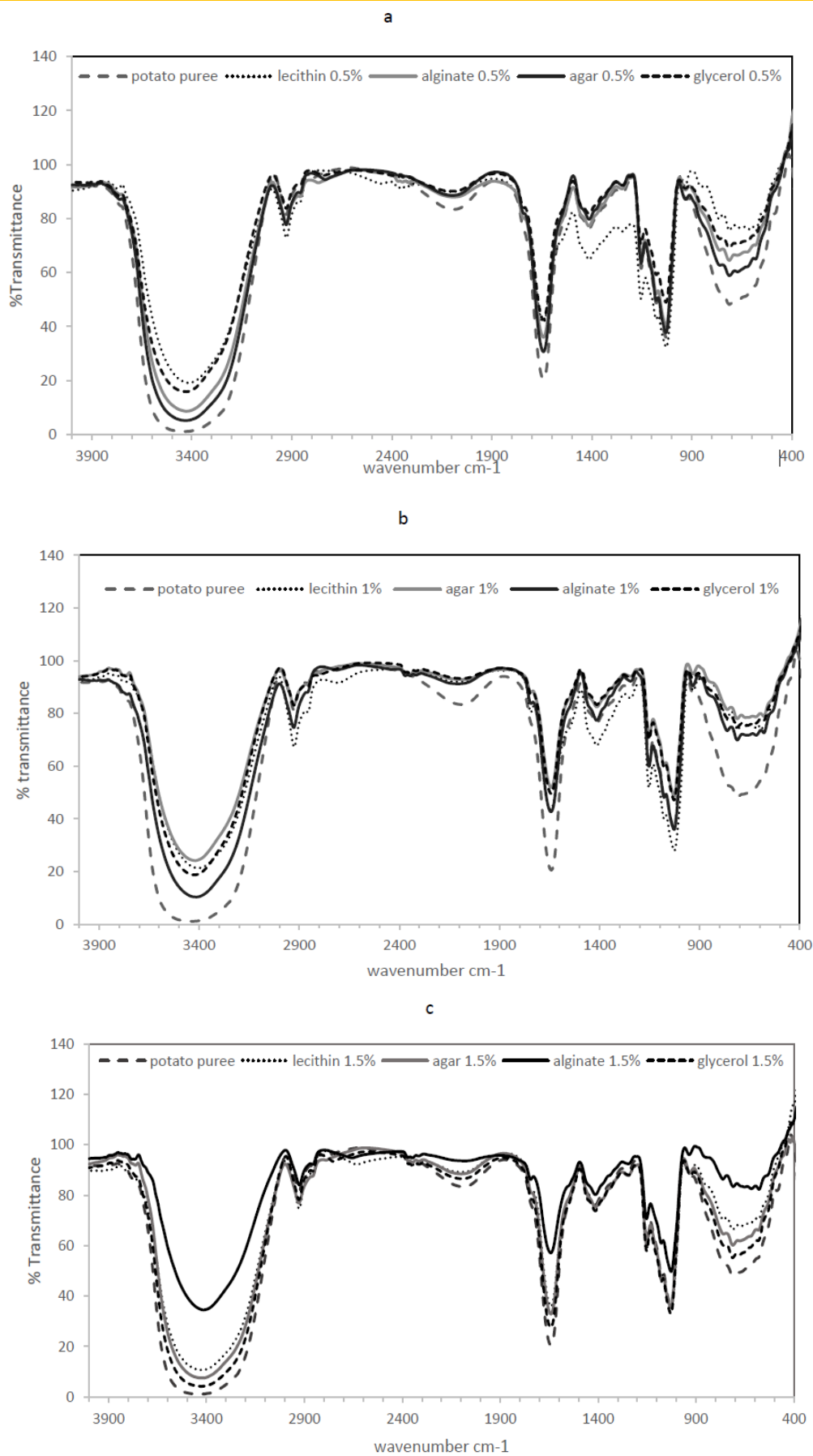


Figure. 2. Vibrational spectra of potato puree and potato puree containing additives at different concentration: 0.5% (a): 1% (b) and 1.5% (c).

3.2 X-ray Diffraction

Figure 3 shows XRD patterns for potato powder (Fig. 3a), potato puree and potato puree containing additives. XRD of commercial potato powder showed a broad peak centered at about 16° (Fig. 3a), corresponding to an amorphous starch due to the decrease in the crystallinity of the raw potato starch after being subjected to several treatments (Yadav, Guha, Tharanathan, & Ramteke, 2006). This result validates the absence of an intense and sharp FTIR signal in the 400 to 900 cm^{-1} region, corresponding to the internal structure and helical conformation of starch of the potato powder sample (Fig.1). Potato puree presented a unique broad peak centered at approximately 26° . Likewise, a similar diffraction pattern was recorded by Ribotta et al. (2004) for bread, Yadav et al. (2006) for dried potato starch, Ispas-Szabo et al. (1999) for cross-linked-high amylose starch, and Liu et al. (2002) for potato starch-water systems. In all these cited references, the XRD pattern of starch was related to a V-type starch structure that appeared as a unique broad band centered at approximately 20° , indicating that the crystal lattice had become irregular or amorphous due to the different physical and/or chemical treatments applied in each case. Accordingly, the peak found at 26° could be interpreted as a small change in the V-type structure (primarily a change in d-spacing). In fact, potato puree prepared from commercial potato flakes, is derived from potato starch that was previously dehydrated (heated approximately to 60°C) and rehydrated. It is well known that all these treatments alter starch conformation, decreasing the amount of crystalline starch (responsible for the narrow XRD peaks in the potato starch) and therefore increasing the amount of the amorphous lamellar region. This prompts its appearance as a broad and weak intense band.

Figure 3a shows the X-ray diffraction patterns of potato puree with additives at 0.5% concentration. In all cases, the same broad and weak peaks were observed. These diffraction patterns can be explained by the presence of an amorphous starch with some internal order at a short-range level, such as different helical content.

Although diffraction patterns from the different purees containing additives revealed the absence of a strong internal ordered structure, some interesting changes on the long-order range can be seen. At a 0.5% concentration, all additives decreased the maximum 2θ angle (i.e., increased d-spacing), followed by a decrease in intensity in the following order: potato>alginate>agar>glycerol>lecithin.

Furthermore, an increase in the additive concentration (from 0.5% to 1.0%) produced a decrease in the intensity for agar, alginate and glycerol. In fact, the intensity of the XRD spectrum of potato puree containing glycerol showed a tendency towards zero. However, lecithin revealed an opposite tendency of an increase in the intensity of the XRD spectrum compared to potato puree (Fig. 3b).

The submissive and obliterating effect induced upon the addition of glycerol on the XRD intensity of potato puree was more evident when the glycerol concentration increased (Fig. 3b, c). This corroborates that glycerol has a more direct interaction with starch than the other additives, probably entering the starch granule and destroying it, as proposed previously (Dankar et al. 2018) and in agreement with the FTIR results.

In addition, the agar additive produced a monotonous decrease in the intensity of the diffraction pattern as its concentration increased. In the case of alginate and lecithin, a first decrease in intensity was followed by an increase when the additive concentration increased to 1.5% (Fig. 3b, c). These results can be explained by the fact that the water content available in the molecule controls the rate of crystallization and the sharpness of the XRD pattern (Van Soest & Vliegthart, 1997). As previously reported (Dankar et al., 2018) for the effect of additives on the microstructure of potato starch, lecithin facilitates the penetration of water inside the starch molecules, rendering a greater availability for maintaining the structure and inducing a more ordered assembly, as revealed by the higher peak with lecithin addition at higher concentrations. Conversely, the addition of agar sequesters water molecules and induces a transversal crosslinking between polysaccharide chains, which in turn alters swelling and hinders a favourable conformation. Therefore, the structure remained almost unordered, which was revealed in the decrease in the intensity of the XRD peaks for puree with agar.

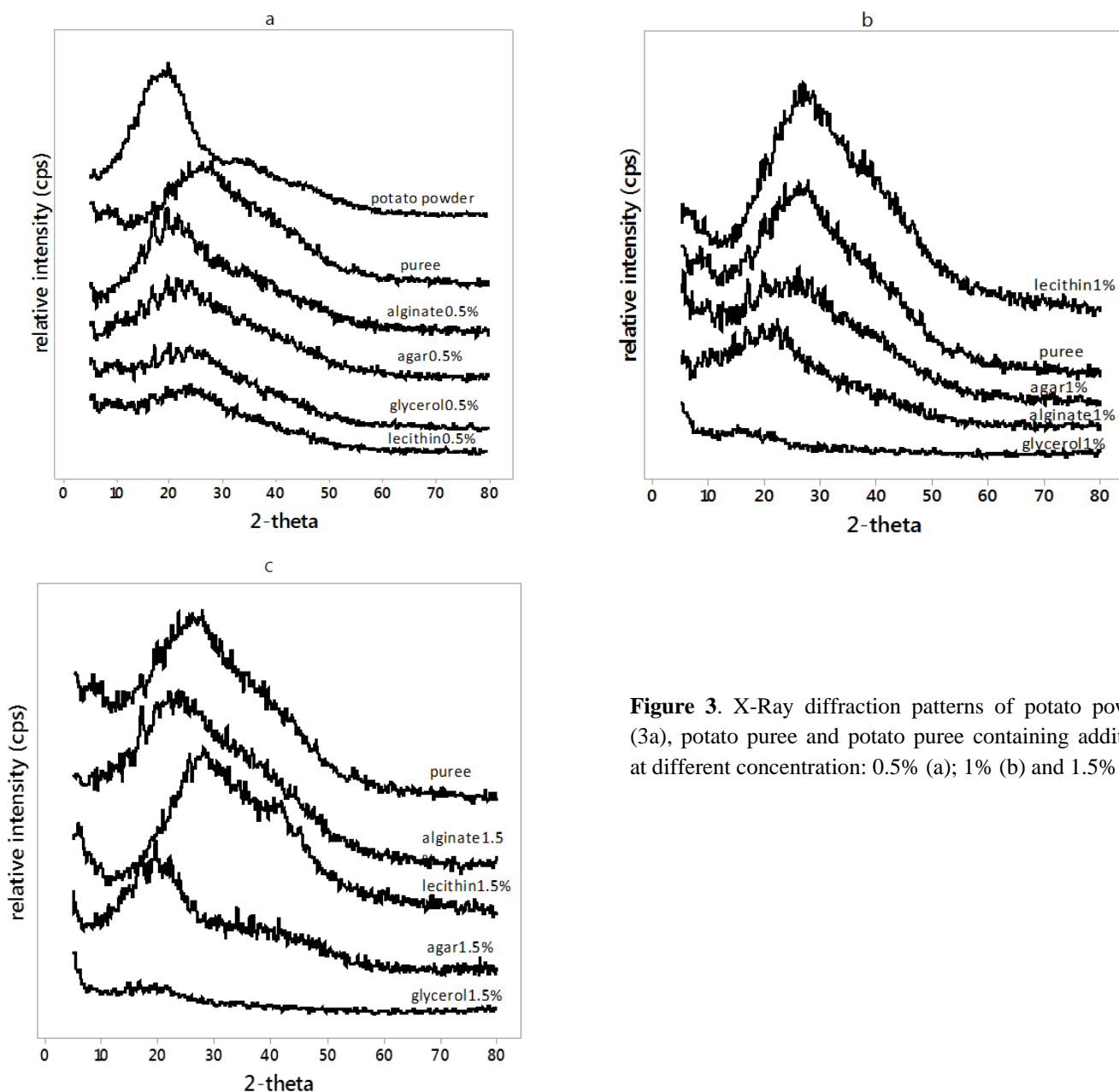


Figure 3. X-Ray diffraction patterns of potato powder (3a), potato puree and potato puree containing additives at different concentration: 0.5% (a); 1% (b) and 1.5% (c).

4. Conclusion

The effect of food additives on the molecular structure of potato puree prepared from commercial potato powder was investigated. Using FTIR, it was found that the skeleton formed by amylase and/or amylopectin is somehow hidden in the dehydrated commercial potato flakes but can be recovered to a great degree by adding water to the original raw potato starch structure. Although the skeleton of amylase and/or amylopectin is missing in the dehydrated commercial starch, this sample retained an important amount of water, as can be deduced by the intensity of the FTIR peaks, which actually had some role in recovering the structure. Therefore, water molecules have a central role in the maintenance of the starch structural conformation.

Although potato puree primarily consists of amorphous starch (lost crystallinity), its XRD pattern is compatible with the presence of a V-type starch structure.

Additives interact with starch at the molecular level, disrupting the OH bonds and altering the starch conformation. Small molecules such as glycerol and lecithin can enter the starch granules and induce a more intense effect on the structure as their respective concentrations increase by either suppressing the starch structure (e.g., as exerted by glycerol) or stimulating a more ordered structure upon the addition of lecithin. In contrast, long polymeric molecules such as agar and alginate interact partially via the surface of the starch granules or with just one part of the starch and thus partially modify the conformation of potato starch structure.

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▪ Chapter 7

Impact of mechanical and microstructural properties of potato puree-food additives complexes on extrusion-based 3D printing

- *This chapter has been published as:*

Dankar, I., Pujolà, M., El Omar, F., Sepulcre, F., & Haddarah, A. (2018). Impact of Mechanical and Microstructural Properties of Potato Puree-Food Additive Complexes on Extrusion-Based 3D Printing. *Food and Bioprocess Technology*, 1–11. <https://doi.org/10.1007/s11947-018-2159-5>

Impact of mechanical and microstructural properties of potato puree-food additives complexes on extrusion-based 3D printing

Abstract

This paper studies the applicability of extrusion-based 3D printing for constructing novel shapes from potato puree and the effects of four additives (agar, alginate, lecithin and glycerol) added separately at three concentrations (0.5, 1, 1.5%) on the internal strength, mechanical properties, microstructure and color of potato puree. The printability of the potato puree and the mixtures was assayed by examining the consistency of the extrusions and the stability and accuracy of the printed patterns. The results indicate that better printing was achieved at a nozzle height of 0.5 cm and a nozzle diameter of 4 mm, with concentrations of alginate and agar between 0.5-1.5% and 0.5-1%, respectively, providing the best printability and end-product stability, which was attributed to their respective high mechanical characteristics and specific mechanical energy (SME) values. Scanning electron microscopy (SEM) revealed that more convolutions were induced in the potato puree upon the addition of agar or alginate, which increased the puree stability. Three-dimensional printing did not significantly affect the surface color parameters of the final product. This study showed that the 3D printing process is a critical factor for initializing the production of customized healthy products.

Key words: Texture, Scanning Electron Microscopy (SEM), Color, Specific Mechanical Energy (SME), 3D printing

1. Introduction

There is a growing demand for the development of customized food for specialized dietary needs, such as products for athletes for recovery after training or products for expectant mothers that vary nutrient component levels by reducing amounts of undesirable ingredients and enhancing the presence of healthy ones (e.g., protein, vitamins, fiber). Moreover, elderly people who are facing physiological changes that occur with aging such as dysphagia and decreased sensory perception require special nutritive meals. Nevertheless, pureed food is delivered to them in an unappealing and unappetizing way. Children are another group of people who require special dietary intake. Children are more willing to consume healthy and nutritious snacks if they are presented in an innovative and fun way (Dankar et al., 2018a, b). However, the development of such customized foods must be conducted in a very precise and inventive way, which is where the role of 3D printing appears.

Three-dimensional food printing is an innovative technique that is of great potential interest and is continuously under debate for both consumers and food scientists due to its broad array of uses (Severini, Derossi, Ricci, Caporizzi, & Fiore, 2017). The application of 3D food printing could be summarized as the ability to provide customized food to certain groups of people (de Roos, 2013) and to automatically generate a specific code to adjust composition, density or structure to the preferences and needs of the user. Moreover, 3D printing has demonstrated some interesting applications for industry by enhancing efficiency through the consolidation of multiple steps or even entire food production processes (Bak,

2003; Sun et al., 2015). For instance, the PepsiCo company decided to incorporate 3D printing in the manufacturing of its potato chips to save money and create healthier food after suffering serious problems in the sales of sugary drinks and fatty snacks (Simon, 2015).

Extrusion printing through a syringe nozzle is the most popular technique employed because of its ability to process the widest array of foods, such as printing with mashed potatoes (Southerland, Walters, & Huson, 2011), chocolates (Hao et al., 2010), cookie dough (Lipton et al., 2010), soft cheeses (Le Tohic et al., 2017), hydrogels and fibers (Lille, Nurmela, Nordlund, Metsä-Kortelainen, & Sozer, 2017; Wang, Zhang, Bhandari, & Yang, 2017) and blends of fruits and vegetables (Severini et al., 2017), and if coupled with more than one syringe, this technique can provide an infinite number of combinations of and a high degree of freedom for foods.

On the other hand, important factors should be taken into consideration when extrusion printing. Maintaining compatibility between specific printing parameters and the corresponding printed substance is crucial to ensure high feasibility for 3D printing. The essential process parameters that can be modulated are the printing speed, the distance between the nozzle and the printing bed and the nozzle size; these are critical criteria that influence the final resolution of the constructed shape (Hao et al., 2010; Zhuo, 2015; Derossi, Caporizzi, Azzollini, & Severini, 2017). Additionally, monitoring the properties and composition of the food material itself (ingredient rheology, electrical conductivity, density, textural quality, and physiochemical and microstructural properties) is imperative and aids in predicting the behavior of a particular food during 3D printing and in assembling a complex shape with many layers that is stable enough to maintain its profile for a long time post-deposition (Dankar et al., 2018a, b; Godoi, Prakash, & Bhandari, 2016; Periard, Schaal, Schaal, Malone, & Lipson, 2007; Yang, Zhang, Bhandari, & Liu, 2018).

Potato purees, now considered part of the nutritious ready-to-eat food market, could be combined with hydrocolloids that interact with potato starches in an attempt to improve the overall product quality and facilitate processing (Shi & BeMiller, 2002). Therefore, scrutinizing the effects that certain food additives have on the starch structure and textural characteristics is important, because these effects affect the functionality of the whole food product.

The objectives of this study were to study the effects of food additives (agar, lecithin, glycerol, and alginate) and their concentrations on the mechanical and microstructural properties of potato puree, to evaluate the feasibility of the substances for 3D printing, to characterize the printing process parameters, such as the distance between the nozzle and the printing bed and the nozzle size and to investigate the effects of the printing process on the superficial color of the final products.

2. Materials and Methods

2.1. Sample Preparation

Commercial potato powder and whole milk were purchased from the local supermarket. Agar-agar, soy bean lecithin, sodium alginate and glycerol (food-grade) were procured from Sigma–Aldrich Co. The potato puree samples were prepared according to the following procedure: 450 mL of milk and 50 mL of water were first heated to 40°C, and then, 115 g of commercial potato powder was added. The mixture was then homogenized using an electrical hand blender (Braun, Germany). The same procedure was followed for preparing the puree samples with the different additives at concentrations of 0.5, 1.0 and

1.5% (Shi & BeMiller, 2002). Additives were added at quantities corresponding to the desired concentrations to the warmed solution (milk and water) prior to the incorporation of the potato powder. However, for the agar samples, the solutions were boiled to 100°C, and the dehydrated potato was then added. All prepared puree samples were placed in an incubator and held at a temperature of 20°C preceding any measurements.

2.2. Extrusion Parameters and Determination of Specific Mechanical Energy

To optimize the 3D printing process, the effects of additives (agar, alginate, glycerol and lecithin), applied speed (1, 2 and 4 mm·s⁻¹) and extruder hole diameter (3 and 5 mm) on the extrusion process were studied using a TA.XT Plus Texture Analyzer (Stable MicroSystems, Godalwig, UK) device with a 50-kg cell load.

The specific mechanical energy (SME) was measured as an indicator of the energy efficiency and ease of flow of materials in the extrusion process (Guerrero, Beatty, Kerry, & De La Caba, 2012). Potato puree samples with and without additives were carefully scooped into acrylic cylinders to a height of 35 mm. The extrusion process was carried out by locking the distance traveled by the compression disc along the cylinder to 20 mm. For each extruder hole diameter (3 and 5 mm), speeds of 1, 2, and 4 mm·s⁻¹ were applied. The weight collected in kg and the force (kg·ms⁻²) applied during extrusion was measured. The SME was then calculated using the following formula:

$$\text{SME (kJ/kg)} = [\text{Force (kg}\cdot\text{ms}^{-2}) \times \text{Distance (m)}] / \text{Weight collected (kg)} \quad (\text{Eq. 1})$$

2.3. Mechanical characteristics

The mechanical characteristics of the additives alone at different concentrations (0.5, 1 and 1.5 g of additive in 100 ml of distilled water) and after being added to the potato puree were tested, including the firmness, consistency and cohesiveness, using the aforementioned TA.XT Plus Textural Analyzer coupled with a back extrusion cell and a 35 mm disc. Samples of potato puree up to 40 mm high were placed in a standard-size cylinder. During the test, the disc penetrated a distance of 30 mm at a speed of 2 mm/s, after which the probe returned to the original position. The peak in the positive area is taken as the measurement of firmness (kg). The area under the curve up to this point is defined as the consistency (kg·s). The maximum negative force is taken as an indication of the cohesiveness (kg) (Angioloni & Collar, 2009). Each sample was tested at least 5 times.

2.4. SEM, Scanning Electron Microscopy

Scanning electron microscopy (SERON SCI2100) was used to determine the surface structure of all puree samples, which were first subjected to vacuum in a vacuum chamber to be dehydrated and to avoid swelling under the microscope. Samples were then mounted on circular aluminum stubs with double-sized adhesive tape, followed by coating with 20 nm gold prior to observation. The SEM experiments were carried out at 15 KV x 4.0 K.

2.5. Color Measurements of Potato Puree Samples

To evaluate the color properties of the puree samples, a MINOLTA tristimulus colorimeter CR-400 (MINOLTA camera, Osaka, Japan) calibrated with a white ceramic standard was used. Parameters of luminosity (L^*) a^* , b^* were recorded, and Chroma ($C=(a^{*2}+b^{*2})^{1/2}$ (saturation) and hue angle ($H=\arctan(b^*/a^*)$ (matrix color)) were calculated. Color measurement values presented are the means of 6 replicates detected before and after 3D printing.

2.6. 3D Food Printing conditions

A RepRap BCN3D+ printer (designed by CIM Foundation) coupled with a syringe tool (100 ml volume and 4 mm diameter) was used for 3D printing of the potato puree. The process is based on extrusion, which works on the principle of joining materials layer-by-layer to make the final 3D object. The code of this 3D object is transferred through an SD card from a CAD program (CURA 15.02.01). Speeds in the CURA program were set as follows; travel speed= 100mm.s⁻¹, Infill speed= 40mm.s⁻¹, printing speed= 40mm.s⁻¹, flow %= 100 and retraction speed= 40mm.s⁻¹.

2.7. Statistical Analysis

Statistical analyses of the data were conducted on Minitab 18 (Minitab Ink. Coventry, UK). Data concerning SME, textural characteristics and color assessment were tested for significant differences ($p<0.05$) using analysis of variance, one-way ANOVA and Tukey's HSD comparison test.

3. Results and Discussion

3.1. Effect of the Extrusion Parameters in Specific Mechanical Energy values of potato puree

Varying the extruder hole diameter at a constant extrusion speed showed that decreasing the diameter of the extruder hole caused an increase in the SME of the samples due to higher acquired friction during extrusion, which necessitates an increase in the applied force (Table 1). Thus, a larger hole diameter (5 mm) facilitated extrusion with proper ordering of the layers. Moreover, significant differences were seen in the SME exerted at various extrusion speeds at a fixed extruder hole diameter; the SME and the extrusion speed were found to be inversely proportional, where the highest value for the SME was recorded at the lowest speed and gradually decreased significantly as the speed increased (Table 1). These results are in agreement with (Chen et al., 2000) and Guerrero et al., (2012), who reported that increasing the speed facilitated the flow of soybeans, hence decreasing the SME and the force required for extrusion.

Table 1: Values of Force, weight collected and SME of potato puree extruded at different speeds and hole diameter

Extrusion conditions		Parameters		
Diameter hole	Speed (mm.s ⁻¹)	Force (kg.ms ⁻²)	Weight collected (g)	SME (KJ.kg ⁻¹)
5mm	1	113.4 ±0.6 ^a	36.6 ±0.3 ^a	62.0±0.2 ^a
	2	86.1 ±1.6 ^b	35.5 ±0.4 ^a	48.5±1.5 ^b
	4	68.1 ±1.3 ^c	34.0 ±1.5 ^a	40.1±1.0 ^c
3mm	1	198.2 ±7.8 ^A	35.0 ±2.1 ^A	120.8±3.1 ^A
	2	141.9 ±2.2 ^B	31.0 ±0.7 ^B	91.7 ±3.5 ^B
	4	107.5 ±2.7 ^C	31.8 ±0.7 ^B	67.7±0.1 ^C

Values are mean of three replicates ± standard deviation. Different letters of Mean values in the same column differ significantly (P<0.05) (small and capitals letters for 5 and 3 mm diameter hole respectively)

3.2. Effect of additives on specific mechanical energy value of potato mixtures

Table 2 shows a comparison between the potato puree and potato puree with 1% of different additives (alginate, agar, glycerol or lecithin) at 3mm hole diameter and 2 mm.s⁻¹ speed. The value of SME of the potato puree decreased significantly when 1% glycerol or lecithin were added (Table 2). This decrease could be attributed to the ability of glycerol and lecithin to retain moisture via destabilizing the internal microstructure of starch granules, therefore softening the material in accordance with Dankar et al., (2018a, b) and Guerrero et al., (2012). Conversely, the addition of 1% alginate or agar in potato puree, increase significantly the SME with respect to the potato puree alone (Table 2). This could be explained by the fact that hydrocolloids (agar or alginate) have a tendency of forming a continuous network of entanglements with starch molecules upon the addition to potatoes, leading to a higher tensile strength and hardness, which required a higher force to push the material out of the extruder (Fang, Zhang, & Wei, 2015). Yet, agar had proven its ability to form a more complex gelling network with starch molecules, concluded before by being able to provide the highest values of yield stress and thixotropy (Dankar et al 2018a, b). Therefore, the SME results allowed classification of the samples based on their internal mechanical strength as follows:

glycerol ≤ lecithin ≤ potato puree < alginate < agar.

Furthermore, these results displayed greater stability of the shape of the extruded layers when alginate and agar were added to potato puree since layers obtained were more consistent and able to hold up an ordered arrangement for a long time post-extrusion; while although the extrusion of puree and puree with glycerol and lecithin was smoother, extruded layers of these samples collapsed and rejoined together a few minutes after extrusion.

Table 2: Values of extrusion parameters and Specific Mechanical Energy (SME) obtained at 3mm hole diameter and 2mm.s⁻¹ speed printer of potato puree with 1% of different additives

Samples	Force applied (kg.ms ⁻²)	Weight collected (g)	SME (kJ.kg ⁻¹)
potato puree	141.9±2.2 ^c	31.0±0.7 ^b	91.7±3.5 ^c
potato puree+1% alginate	261.6±3.8 ^b	32.2±1.3 ^{a,b}	162.4±10.1 ^b
potato puree+1% agar	332.1±10.6 ^a	30.6±1.0 ^{a,b}	217.0±0.3 ^a
potato puree+1% glycerol	82.3±1.0 ^d	31.7±0.5 ^{a,b}	51.9±2.1 ^d
potato puree+1% lecithin	86.5±2.8 ^c	33.3±0.8 ^a	52.0±0.6 ^d

Values are mean of three replicates ± standard deviation. Different letters of Mean values in the same column (corresponding to the same parameter) differ significantly (P<0.05)

3.3. Mechanical Characteristics of Potato Puree Combined with Additives

The characterization of the mechanical properties of food is important and aids in assessing the behavior of the food during processing and consumption. The mechanical characteristics of the food additives alone and at the three different concentrations were first measured to understand the effects of the additives on the potato puree. The results showed that the mechanical strength of the agar additive was significantly different ($p<0.05$) from the other additives used in this work. On the other hand, the mechanical characteristics of the glycerol, lecithin and alginate additives showed no significant differences when the concentrations were changed from 0,5, to 1 and to 1,5%, whereas significant differences were detected in the mechanical properties of the agar measured at the different concentrations (Table 3).

The firmness, consistency and cohesiveness of the potato puree alone and the potato purees with the additives are summarized in Figure 2. The results of statistical analyses showed no significant differences ($p<0,05$) between the firmness, cohesiveness and consistency of the potato puree and the purees with lecithin or glycerol at concentrations of 0.5, 1.0 and 1.5%. The addition of glycerol or lecithin to potato puree promotes more swollen starch granules (Dankar et al., 2018a, b) with a wider spread in the particle size distribution, giving rise to low values for firmness, cohesiveness and consistency (Afoakwa, Paterson, Fowler, & Vieira, 2008) since these additives have emulsifying effects and the ability to lessen the structural integrities of foods such as waxy maize starch, cocoa spread cream, cassava starch and dark chocolate (Afoakwa, Paterson, Fowler, & Vieira, 2009; Souza et al., 2012 Koushki & Azizi, 2015; Yang et al., 2016). On the other hand, the addition of alginate or agar significantly increased the mechanical values of the potato puree, with this elevation being enhanced when the concentrations of the additives were higher. However, the only significant difference in the consistency and cohesiveness between the agar and alginate samples was obtained at the concentration of 1%, which was marked by a higher consistency (Fig. 2). This behavior is attributable to the conveyed network structure that occurs between polysaccharide chains and the large-sized long additive molecules (agar or alginate) within the matrix and

to the enhancement of the particle-particle surface contact (Huang, Kennedy, Li, Xu, & Xie, 2007; Dankar, et al. 2018a, b). Similar mechanical strength results are obtained when carboxy-methyl cellulose, xanthan or carrageenan are added to sweet potato puree, whipped cream and carrots, respectively (Truong & Walter, 1994; Zhao, Zhao, Yang, & Cui, 2009; Sharma et al., 2017). The alginate alone showed mechanical property values similar to that of the glycerol and lecithin, but when the alginate was incorporated in the potato puree, the resulting mixture had high mechanical property values comparable with that of the agar.

This difference could be related to the interaction of the alginate with the calcium ions abundantly present in the milk and the potatoes used in the preparation of the samples, which consequently enhanced the textural strength and viscoelastic properties of the puree as also reported by Truong et al. (1995) and Fasina et al. (2003). On the other hand, the agar solely formed a gel that, upon interaction with other molecules, formed a more complex entangled network, which enhances its thickening ability (BeMiller, 2011; Milani & Maleki, 2012).

Thus in terms of mechanical strength, the greatest strengthening effect exerted by the agar and the alginate on the potato puree allows for products with the sufficient mechanical integrity to support a built-up layered geometry without deformation, in contrast to those with glycerol and lecithin.

Table 3 Values of Mechanical Characteristics: firmness, consistency and cohesiveness of additives at 0.5, 1 and 1.5 % concentration

Additive	Concentration (%)	Firmness (g)	Consistency (g.s)	Cohesiveness (g)
Glycerol	0.5	15.4±0.9 ^a	275.0±29.2 ^a	-3.6±3.0 ^a
	1	15.0±1.4 ^a	293.8±36.4 ^a	-2.4±0.4 ^a
	1.5	13.5±1.5 ^a	249.5±43.1 ^a	-2.5±0.9 ^a
Lecithin	0.5	13.9±0.9 ^a	255.0±25.5 ^a	-3.1±0.5 ^a
	1	14.7±1.4 ^a	269.8±13.5 ^a	-2.4±0.4 ^a
	1.5	14.2±0.9 ^a	275.2±29.2 ^a	-2.3±0.6 ^a
Agar	0.5	336.0±54.9 ^b	2347.0±699.5 ^b	-74.0±36.5 ^b
	1	1202.3±158.8 ^c	11858.7±417.5 ^c	-245.3±31.7 ^c
	1.5	5864.7±193.6 ^d	55070.0±1714.5 ^d	-687.7±86.5 ^d
Alginate	0.5	13.5±1.3 ^a	204.2±50.0 ^a	-3.4±0.5 ^a
	1	16.0±0.8 ^a	313.7±34.5 ^a	-4.3±0.5 ^a
	1.5	15.3±0.6 ^a	291.2±13.2 ^a	-2.7±0.4 ^a

Values are mean of three replicates ± standard deviation.

Different letters of Mean values in the same column (corresponding to the same parameter) differ significantly (P<0.05)

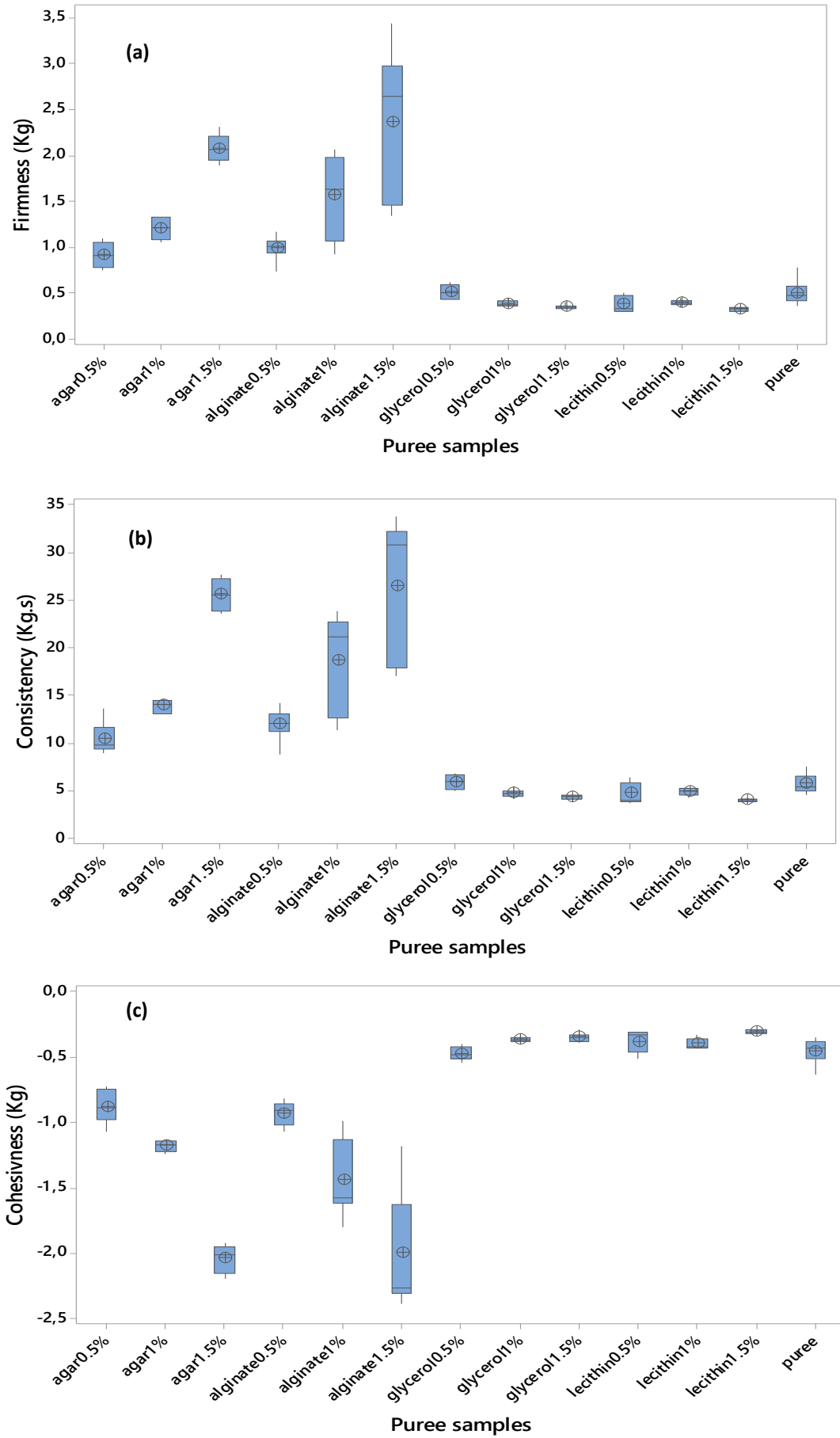


Figure 1. Box plot analysis of the mechanical characteristics firmness (a), consistency (b) and cohesiveness (c) of potato puree and potato puree with agar, alginate, glycerol and lecithin at 0.5, 1 and 1.5 % concentration.

3.4. SEM- Scanning Electron Microscopy

SEM micrographs highlighted clear microstructural differences between the different puree samples. At 0.5%, lecithin was comparable to potato puree alone but with produced a more cotton-like texture, whereas more noticeable changes in the potato puree were detected upon the addition of glycerol, agar and alginate. Alginate induced more folding, while agar and glycerol yielded a fibrillary network-like structure (Fig. 2b1, d1). However, this network-like structure was more compact with glycerol, which could be explained by its ability to enter the interior of polysaccharide chains and disrupt inter- and intramolecular hydrogen bonds, making the polymer more elastic (Mali, Sakanaka, Yamashita, & Grossmann, 2005). An expanded network with tiny wrinkles on the surface was produced with agar. As the concentration of agar increased, these tiny wrinkles evolved into a continuous phase of more folding and convolutions (Fig. 2d1, d3), which was a result of intense interactions between starch and agar (Phan, Debeaufort, Luu, & Voilley, 2005), agar gel formation and agar-agar interactions at higher concentrations (Dankar et al., 2018a, b). Therefore, a firmer and more complex network of interactions was seen in the structure of puree and 1.5% agar, as revealed in the figures.

Similarly, the folding formed upon the addition of 0.5% alginate could be attributed to the formation of alginate-cation-polysaccharide complexes (Truong et al., 1995). Upon increasing the concentration of alginate to 1%, a more consistent and firm structure was formed. This reflects the characteristic mechanical behavior of alginate, where at 1%, a significant difference was detected between the agar and alginate with a higher consistency value recorded for alginate, compared to a more cohesive structure with 1% agar expressed through higher folding formation. Again, with 1.5% alginate, internal folding and convolutions were observed within the structure. The addition of additives at higher concentrations promotes greater availability of reactive sites and, hence, increases their mode of functionality (Chen, Dickinson, Langton, & Hermansson, 2000). In fact, these convolutions mainly explain the increase in the internal strength and mechanical characteristics of potato puree upon the addition of agar and alginate. In contrast, upon increasing the concentration of lecithin in the potato puree, a smoothed surface with the formation of tiny pores was produced (Fig. 2c1, c2). This behavior was ascribed to the two internal modes of action of lecithin. First, on the starch structure, lecithin can penetrate inside the starch molecule and induce modifications within the internal amylose-amylopectin and amylopectin-amylopectin binding (Dankar et al., 2018a, b).

Consequently, the penetration of more water molecules into the starch granules is facilitated, leading to a more swelled starch structure that promotes the smoothness observed in the SEM figures (Fig. 2c1). Second, the emulsification property of lecithin promoted assembly of fine droplets that are an indication of a uniformly dispersed structure inside the food matrix (Afoakwa et al., 2009; Koushki & Azizi, 2015). Likewise, increasing the concentration of glycerol induced a similarly smoothed surface comparable to that of potato puree. This explains the absence of significant differences between the mechanical characteristic of potato puree alone and that with glycerol and lecithin added. The microstructures of the potato puree samples combined with the textural data provides vital input for the 3D printing process, since formation of strong networks, such as the ones displayed with agar and alginate addition, could be used to yield an integrated shape-retention property with a stabilizing effect.

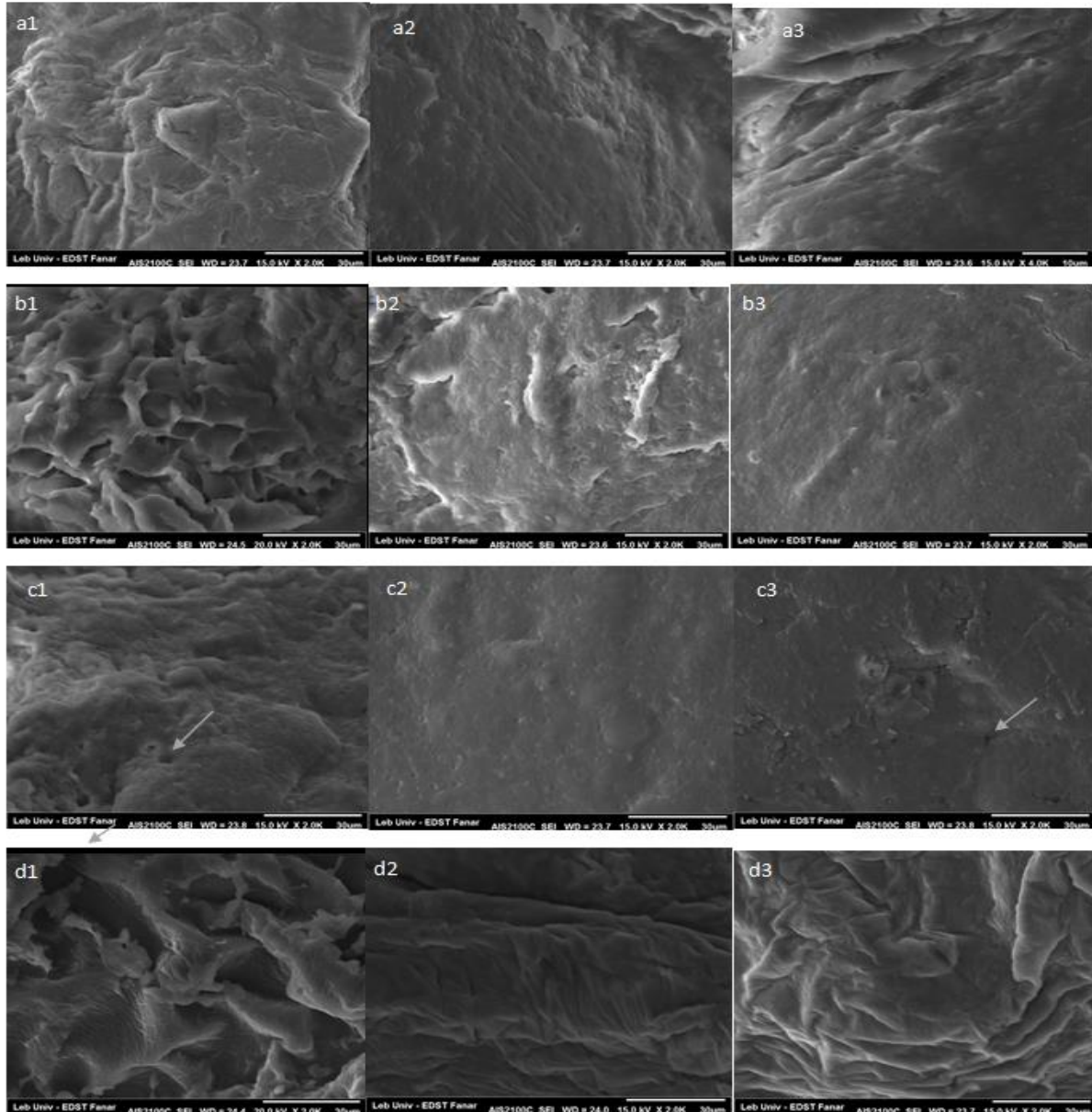


Figure 2. Scanning electron microscopy analysis of potato puree samples with 0.5% (column 1), 1% (column 2), and 1.5% (column 3) of additive concentration: a1, a2, a3 potato puree with alginate; b1, b2, b3 b potato puree with glycerol; c1, c2, c3 potato puree with lecithin; d1, d2, d3 potato puree with agar. *arrows correspond to pores formation within lecithin

3.5. 3D printing Conditions for potato puree and potato puree with additives

Many trials were performed on the BCN3D+ printer system to obtain the best printed product. When the distance from the nozzle to the printed bed was ≥ 1 cm, the flow of material was irregular due to delayed deposition, and the layers extruded were breakable and incompatibly attached to the previous layers for all the puree samples. After many trials, the critical nozzle height for high-quality printed potato purees was determined to be 0.5 cm. Similar results were obtained by Wang et al. (2017) and Hao et al. (2010) when printing surimi and chocolate gels, respectively; they found that the nozzle height critically affects the final geometry of the product.

The second optimization was the nozzle diameter, which directly affects the surface roughness and precision of printed objects (Yang et al., 2018). Because the 3D printer and the textural analyzer have different nozzle diameters, using the same diameter for both tests was impossible. This difference was minimized by using similar sized diameters, in both cases in the same range: 3 and 5 mm in the case of textural analyzer and 2 and 4 mm for the 3D printer.

Using a 2 mm nozzle, printing with the potato puree and the potato purees with additives produced poor-quality products in which the layers did not overlay with one another properly, and the shape was not well-maintained, leading to a poor product mainly because the thin filament size that was extruded was not large enough to support the desired final structure for the potato puree. Whereas when a 4 mm nozzle was used, all the puree samples showed better printing quality. This result validates what was hypothesized while determining the extrusion parameters and SME values, where extrusion with the larger diameter size of 5 mm provided better layer organization than extrusion with a 3 mm diameter nozzle (refer to the SME results). A 4 mm nozzle is sized within the range of these two values and hence, the 2 mm nozzle was excluded. The critical nozzle diameter is specific to the particular type of food extruded, as has been stated by several authors (Hao et al., 2010; Yang, Zhang, Bhandari, & Liu, 2018).

Another consideration for the printing process is the type of substrate to be printed. Of the mixtures prepared, the potato purees with the agar or alginate at the different concentrations tested were able to be printed in stable structures with many built-up layers that held their shape for a long time without collapsing (Fig. 3a and 3b, puree with 0,5% alginate and potato puree alone, respectively). This result could be directly attributed to the high internal strengths, demonstrated by the highest values measured for the textural properties (firmness, consistency, cohesiveness) and the high SME values exhibited by the purees with agar or alginate; the incorporation of gums into mashed potatoes has reportedly generally increased their resistance to deformation (Liu, Zhang, & Bhandari, 2018). Furthermore, the stabilization of the final shapes printed with the purees with the alginate or agar increased with increasing additive concentration in the potato puree, except for the 1.5% agar, which displayed high SME and mechanical values compared with the other additives and in which the sample was more solid-like, retarding the process of printing.

The potato puree and the purees with glycerol or lecithin showed different behavior, in which printing a multiple-layered 3D structure started well with a smooth flow of potato paste (Fig. 3d). Nevertheless, when the structure reached its final stage, the many layers that were printed collapsed into each other (Fig. 3e), resulting in a poorly defined and deformed product, due to the low firmness, consistency and internal stability possessed by these samples, which confirms the previous results concerning the shape stability of the extruded layers from the texturometer. Conversely, these materials behaved well during the printing of flat structures with few layers. Thus, the stability of the final product depends not only on the substrate properties but also on the targeted geometry shape to be printed. The effect of the printed substrate on the quality of the final product has been reported by several authors. Yang et al. (2018) and Liu et al. (2018) observed that the addition of potato starch in certain concentration ranges in lemon juice and mashed potatoes, respectively, increased the viscosity of the printed substrate and therefore, ensured

the delivery of more stable end-products. These results confirm that alginate and agar serve as better additives in food technological applications like 3D printing.

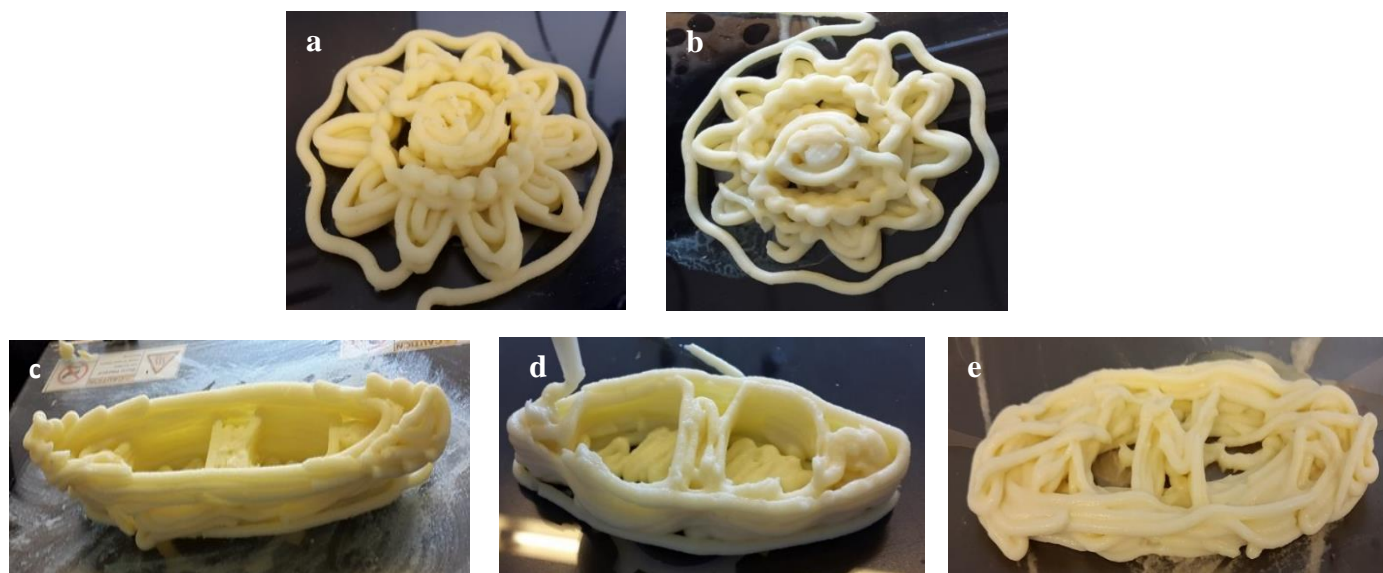


Figure 3. The influence of the substrate and shape design on 3D printed products of potato puree alone or with additives when is extruded at 4mm nozzle. Fig 3(a, b) Influence of substrate printed: (a) potato puree with 0.5% alginate, (b) potato puree alone, Fig 3 (c, d, e) Influence of shape design (c) potato puree with 1% alginate, (d) potato puree alone at primary stages of printing and (e) potato puree alone at final stages of printing.

3.6. Characteristics of the Final 3D Printed Products

The color surface parameters for the puree samples, including the luminosity, chroma and hue angle, are dependent on the particulate distribution, absorptivity and scattering coefficients (Hutchings, 2011).

Each food additive used had a different effect on the surface color of the potato puree due to their distinct effects on the starch structure and the distribution of the particles and their respective arrangements. Only the alginate and agar produced significant differences ($p < 0.05$) in the luminosity parameters of the potato purees, with decreases in their values (Fig. 4), which could be attributed to alterations of the starch globule sizes and morphologies. Additionally, solely the agar exhibited an effect on the hue angle of the puree by elevating the level. The glycerol and lecithin produced significant differences in the chroma of the potato purees by decreasing the saturation property, which could be ascribed to changes in the starch granule morphologies and sizes and the starch internal networks (Dankar et al., 2018a, b). However, Afoakwa et al., (2008) reported that the addition of lecithin did not affect the luminosity, chroma or hue angle of dark chocolates.

Generally, increasing the concentration of the additives in the potato puree did not cause any significant differences in the luminosity or hue angle. However, increasing the concentration of lecithin to 1.5% produced a significant difference in the chroma of the potato puree by further decreasing the degree of saturation (Fig. 4). This result could be attributed to the lecithin (at 1.5%) producing increased modifications of the internal starch granule interactions, yielding a dull surface appearance (less saturated).

On the other hand, Le Tohic et al. (2017) found that the printing process affected the surface color of printed cheeses, inducing a small decrease in the luminosity in contrast to our work, where the 3D printing process had no significant effect on any of the color parameters studied for all the puree samples. Thus, the 3D printing process was proven to not influence the surface color of printed potato purees, which satisfies some consumers and companies.

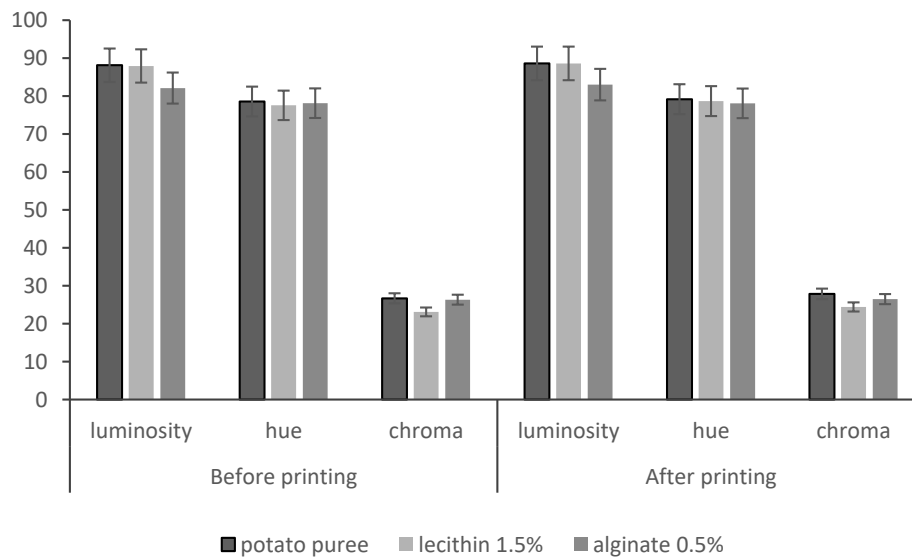


Figure 4. Values of Luminosity, Chroma and Hue angle in color surface of potato puree alone, potato puree with 1.5% lecithin and potato puree with 0.5% alginate before and after 3D printing. Values are mean \pm standard deviation (n=6)

Additionally, several attempts have been made to design soft and tasty products to satisfy the desires of the elderly and those facing swallowing and mastication problems, enhancing their appetites with safe, novel and nutritious foods (Aguilera & Park, 2016). Table 4 presents the firmness values for all the puree samples in kPa, which were converted according to the following formula:

$$\text{kPa} = \text{kg/cm}^2 \times 98.0665 \quad (\text{Eq. 2})$$

The accessible range of consumption for elderly or people facing mastication problems is within the firmness value range of 20 to 40 kPa (Serizawa et al., 2014), and all the tested puree samples fit well within this acceptable range. Although the maximum firmness for agar was measured at the concentration of 1.5% (25.8 kPa), no significant difference was detected between the firmness values of the purees with

agar or alginate at 1.5% (Table 4). Similar work was conducted by Serizawa et al. (2014) to study the feasibility of printed hydrocolloids, agar and gelatin at different concentrations for the elderly. The higher the concentration of agar in water, the higher its hardness, such that 20% agar possessed the highest hardness of the tested samples (45 kPa). The addition of gelatin demolishes the strength of the agar, which was demonstrated by a decrease in the hardness of the samples. This result confirms the results showing that the agar was the additive that increased the firmness and mechanical properties of the potato puree. The purees with 1.5% glycerol or lecithin showed the lowest firmness pressures, approximately equal to 3.82 kPa; however, neither functioned as proper additives for maintaining the stability and structure of the 3D products post-printing.

Potato purees could also serve as a healthy customized food for the second most susceptible sector of people, children. Studies have reported that children are willing to try a wider variety of foods if they are plated in an aesthetic and funny way (Zampollo, Kniffin, Wansink, & Shimizu, 2012).

Table 4: Firmness values (Kpa) of potato puree samples with glycerol, lecithin, agar and alginate at 0.5, 1 and 1.5% concentrations

Sample	Concentration (%)	Firmness (kPa)
Potato puree +Alginate	0.5	10.0 ^c
	1	13.2 ^{b,c}
	1.5	22.7 ^a
Potato puree +Agar	0.5	10.9 ^c
	1	17.1 ^b
	1.5	25.8 ^a
Potato puree +Lecithin	0.5	4.3 ^d
	1	4.4 ^d
	1.5	3.6 ^d
Potato puree +Glycerol	0.5	5.0 ^d
	1	4.2 ^d
	1.5	3.8 ^d
Potato puree	-----	5,5 ^d

Values are mean of three replicates, Different letters with Mean values in the same column (corresponding to the same parameter) differ significantly ($P < 0.05$).

4. Conclusion

Alginate (from 0.5% to 1.5%) and agar (0.5 and 1%) were the additives that provided more stability for printed products with corresponding increases in specific mechanical energy (SME).

The mechanical characteristics of firmness, consistency and cohesiveness showed significant differences ($p < 0.05$) after the addition of agar or alginate to potato purees, and the effect was greater at higher concentrations. Nevertheless, when not mixed with potato puree, only agar had a significant difference in mechanical characteristics among the additives.

The SEM figures demonstrate the different microstructural characteristics within the potato puree samples, wherein lecithin produced a cotton-like structure, alginate produced more folding, glycerol induced a more continuous network-like structure due to its ability to disrupt the inter- and intra-network interactions between the polysaccharide chains, and agar induced more folding and convolutions, which complements the textural value results.

The best extrusion conditions for the 3D-printed potato purees were achieved with a nozzle size of 4 mm and a critical nozzle height of 0.5 cm using a printing substrate of potato puree mixed with alginate (0.5 to 1.5%) or agar (0.5 and 1%) to provide the finest resolution of stable end-products with many built-up layers.

The optimal mechanical characteristic values for obtaining good quality 3D printed potato purees with additives fall within the following ranges: a firmness between 0.94 and 2.10 kg, a consistency between 11.6 and 26.5 kg·s and a cohesiveness between 0.9 and 2.1 kg. The color of the final product is not affected by the 3D printing process and all the printed samples showed good firmness values that fit well within the range of the maximum lingual pressure (20-40 kPa), thus enabling potato puree or other foods to be used in innovative designs to produce a good substitute for the unappealing meals available for people facing mastication problems.

Acknowledgements

Authors wish to thank the CIM foundation for providing the BCN 3D+ printer and Dr. Roland Habchech for the use of the SEM.

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▪ Chapter 8

Impact of water removal and temperature treatment on microstructural changes in potato tubers

▪ *This chapter has been submitted as:*

Dankar, I., Haddarah, A., Omar, F. E. L., Sepulcre, F., & Pujolà, M. (2018). Impact of water removal and temperature treatment on microstructural changes in potato tubers, *Journal of Food Chemistry*. (In revision)

Impact of water removal and temperature treatment on microstructural changes in potato tubers

Abstract

Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Scanning-electron microscopy (SEM) were used to study the effects of heat treatments and water removal by lyophilization after different time intervals (6, 12, 24, 48, 72 hours) on the molecular structure of potato tubers. SEM images show structural differences between raw (RP), microwaved (MP) and boiled potato (BP). MP and BP were able to re-associate into a granule-like structure after 6 hours of freeze drying, whereas RP had dried granules within a porous matrix after 24 hours of lyophilization. These results agree with the FTIR results for MP and BP, which had dried spectra after 6 hours of lyophilization, and coincided with RP results after 24 hours of lyophilization. Comparison of the FTIR and XRD results indicated that lyophilization induced more ordering in all samples and that the absence of water overcomes heat effects to generate an integral starch molecule.

Keywords: Microwaved potato (MP), Boiled Potato (BP), Raw Potato (RP), lyophilization

1. Introduction

Potatoes are considered to be the second major root crop in the world after cassava (Chen et al., 2017). Freshly harvested potato tubers contain approximately 200 g·kg⁻¹ dry matter, with starch being the predominant substance. Generally, raw starch found in potato tubers is structurally organized into a void containing granules consisting of two types of α -glucans: amylopectin (a heavily branched α -glucan polymer of high average molecular weight with an α (1→4)-linked backbone and α (1→6)-linked branches of α -glucosidic bonds) and amylose (a linear and relatively long α -glucan polymer linked by α (1→4)-linkages). Raw starch granules have a crystalline/amorphous structure that can be recognized at both short- (nm) and long-range (several μ m) scales (Dankar *et al.*, 2018).

Potato tubers are commonly cooked before consumption using various methods, such as boiling, frying, baking or microwaving, which produces potatoes with different mechanical and sensorial characteristics according to the type of cooking method used. For instance, it was reported that microwaving potatoes induced more a firmer texture than boiling and baking and that the individual sugar content increased during baking and microwaving compared to that during boiling (Yang, Achaerandio, & Pujolà, 2016). The major changes induced during cooking can be summarized as follows: softening of the potato tissue due to heating, which causes a loss of integrity of the cell membranes; weakening of binding between intact cells, leading to their separation and resulting in a loss of turgor. Moreover, cooking promotes starch swelling by modifying the percentage of available water and inducing gelatinization (Fedec, Ooraikul, & Hadziyev, 1977; Ormerod, Ralfs, Jobling, & Gidley, 2002; Singh, Kaur, Ezekiel, & Guraya, 2005).

Additionally, differences in water availability play a role in the composite of swollen granules that fill the intercellular space between amylose and the amylopectin network, which consequently affects the texture of potatoes by increasing starch stiffness. The increased stiffness of the starch gel is accompanied by the formation of crystals (Cameron & Wang, 2005; Soest, Hullemann, Wit, & Vliegenthart, 1996). In fact, temperature applied along with the water content present govern the internal microstructure of starch and directly affect its textural organoleptic properties (Kaláb, Allan-Wojtas, & Miller, 1995; Singh et al., 2005). Therefore, good knowledge of starch at the microstructural level would be key to understanding the physio-mechanical and organoleptic modifications induced in potatoes upon cooking. The microstructural level of starch could be investigated in the short-range order using FTIR (Fourier transform infrared spectroscopy) to detect amylose/amylopectin chain folding, the crystalline/amorphous ratio or even the retro-gradation of potato starch (Flores-Molares, Jimenez-Estrada, & Mora-Escobedo, 2012; N. Zhang et al., 2013). Additionally, the microstructural level of starch could be investigated in the long-range order using XRD (X-ray diffraction) to characterize the structure of starch and detect any changes in the crystalline pattern (starch ageing, softening or gelatinization) caused by different processing techniques (van Soest, Hullemann, de Wit, & Vliegenthart, 1996). A more comprehensive and evidential integration of both data in the short and long-range orders (FTIR and XRD, respectively) can be obtained via visual inspection and characterization of the starch microstructure using SEM (scanning electron microscope), which enables rigorous visualization of starch molecules and their ordering, along with providing a more affirmative way of spotting and understanding differences between different structures of different origins or different processing properties.

The purpose of this study is to reveal whether structural changes in starch molecules (arrangement and association) of potato tubers are associated with heat treatment (boiling, microwave) or freeze-drying treatment/water availability. Therefore, FTIR spectra, XRD patterns and SEM images were collected for raw potato (RP), microwaved potato (MP) and boiled potato (BP) before ($t=0$) and after lyophilization at intervals of 6, 12, 24, 48 and 72 hours.

2. Materials and Methods

2.1. Sample preparation

Fresh potato tubers (*Solanum Tuberosum* L cv Kennebec) acquired from a local supermarket were selected, washed thoroughly and subjected to two different treatments: microwave heating and boiling. During microwaved heating, a potato tuber was cooked at full power (700 W for 12 minutes). For boiling, a potato tuber was placed in a beaker filled with distilled water and left to boil for 25 minutes. Samples were then removed and, along with raw potato tubers (control), were peeled and cut into cubes (2 cm side) in preparation for further analysis.

2.2. Freeze Drying (Lyophilization)

Samples were frozen overnight at $-80\text{ }^{\circ}\text{C}$ and then dried using a CHRIST freeze drier (Alpha 1-4 LD plus, 15386, Germany) for 6, 12, 24, 48 and 72 hours. After each time point, samples were taken, grinded and examined by FTIR (Fourier Transform Infrared Spectroscopy), XRD (X-Ray Diffraction) and SEM (Scanning Electron Microscopy).

2.3. *Fourier Transform Infrared Spectroscopy (FTIR)*

FTIR spectra were collected for potato cubes prepared from different cooking methods (microwaved and boiled) as well as raw potato cubes at time 0 (initially before drying) and after being freeze-dried for 6, 12, 24, 48 and 72 hours on an STS FTIR spectrometer. Spectra were recorded in the range of wavenumber 349 to 4000 cm^{-1} by an MCT detector cooled with liquid nitrogen. The samples were blended with KBr and pressed into tablets before measurements. Spectra were collected at a resolution of 4 cm^{-1} and at an average of 35 numbers of scans per sample.

2.4. *X-Ray Diffractometer (X-RD)*

The XRD patterns of all samples were tested using a Bruker D8 Discover (AXS GmbH, Germany) with Cu radiation at a wavelength of 1.5406 Å. Measurements were obtained at room temperature with a scanning rate of 0.02°/1 s and a diffraction angle range of 5 to 80° (2-theta range), where theta was the angle of incidence of the X-ray beam on the sample. The diffraction patterns were analyzed using EVA software. XRD of frozen raw potato cubes (before being lyophilized) was carried to compare the main effect of changes at the long-range level.

2.5. *Scanning Electron Microscopy (SEM)*

Scanning electron microscopy (SERON SCI2100) was used to visualize the surface structure of all potato samples (raw, microwaved and boiled; initially and after different intervals of drying). The samples were first subjected to vacuum in a vacuum chamber to be dehydrated and avoid their swelling under the microscope. Samples were then mounted on circular aluminum stubs with double-sided adhesive tape followed by 20 nm gold prior to observation. The SEM experiments were carried out at 15KVx4.0K.

3. Results and Discussion

3.1. Scanning Electron Microscopy (SEM)

SEM micrographs were used to identify microstructural changes between RP, MP, and BP initially and after the different stages of freeze drying. Before lyophilization (at $t=0$), RP was observed to contain aggregations of intact starch granules with an oval shape and smooth surfaces of various sizes (5- 100 μm) (Fig. 1), which is a typical appearance of native potato starch granules (Szymońska, Krok, Komorowska-Czepirska, & Rebilas, 2003; Yadav, Guha, Tharanathan, & Ramteke, 2006; B. Zhang et al., 2014). After a few hours (6 and 12) of lyophilization, the number of starch granules in RP decreased, and they appeared to be embedded within the potato matrix. This decrease in number could be the result of starch granule fracturing and the leaching out of starch molecular chains under the sublimation effect of freeze drying. Moreover, as freeze drying proceeded (12, 24 and 72 h), the starch matrix appeared to become increasingly dried, fragile and torn, with the development of large cavities inside the structure that were mainly formed by the pop-up release of water vapor. Major changes in the structural conformation of RP starch were observed after 24 hours of lyophilization, including ruptured cell walls, a decreased number starch granule, and a starch matrix that appeared to be dried, fragile and torn, with formation of large cavities inside the structure that were mainly formed mainly by the pop-up release of water vapor. At the last stages of drying (72 hours), the intact starch granules observed

decreased in number (more granules were torn or puffed and starch leaked to the exterior). Additionally, the starch matrix appeared to be more dried and fragile, and irregular cracks formed inside the matrix due to the highly induced stress due to drying on RP. The starch granules also appeared to be rough, with visible scratches. Similar results were observed by Zhang et al. (2014) while studying the effect of freeze drying on potato starches. Furthermore, the presence of some starch granules, even at a smaller size, in RP samples after intensive lyophilization for 72 hours indicated the effective strength of the molecular bonds present in raw potato tubers. On the other hand, SEM micrographs illustrated considerable structural differences between RP, MP and BP starting from $t=0$. It was clear that MP and BP starch granules had undergone gelatinization (complete absence of starch granules) under the effect of heat treatment and cooking. As the time of lyophilization increased, cells with a large number of cell wall cracks, fissures and fragments were more frequently observed in BP because conventional treating causes surface gelatinization in granules without disrupting the cellular structure (Bouchon & Aguilera, 2001), while microwave treatment induces marked changes of the morphological structure of potato starch granules because microwave energy affects the water molecules in the crystalline regions of starch granules and enhances rupture (Xie, Yan, Yuan, Sun, & Huo, 2013). Additionally, some pores were formed upon freeze drying of both MP and BP, but these pores were smaller in size than those formed in RP24. Wang et al. (2017) similarly reported that the large cavities that were induced by freeze drying were reduced in size when samples were previously treated by microwaving or boiling. Moreover, it should be noted that MP6 and BP6 appeared to undergo an ordering process and starch re-association after the initial gelatinization and subsequent water removal and drying. This process can be explained by the fact that freeze drying not only caused the removal of water molecules, keeping some binding sites free, but also inducing a more compacted internal structure, which facilitated more physical cross-linking between starch helices (amylose and amylopectin intermolecular bonding), resulting in a reinforced network that tended to resemble the original structure (a starch-like granule). Yet, this process was more profound in BP6 as the appearance of edgy-like granules was clearly observed. This phenomenon was reported for microwaved heat-moisture modified starch (dried starch) in previous studies, where it was stated that upon water removal, dispersed starch molecules go through a re-association process (Chen et al., 2017; J. Zhang, Chen, Liu, & Wang, 2010). With the increased lyophilization time, its effects (starch ordering and re-association) became more intensified in both MP and BP, with a clearer appearance of intact-like granules that had more edgy and rough wall surfaces. Subsequent drying of these edgy granules caused some tearing of the surfaces in MP24 and BP24. At the last stages of drying (48 and 72 hours), a brittle polymer morphology that appeared to be highly compactable was found in both MP and BP samples, in addition to some irregular crack formation, even along the restructured granule surface. However, SEM images revealed differences in the reconstruction of the starch structure of BP samples, in which the structure was always denser, more compact and more organized.

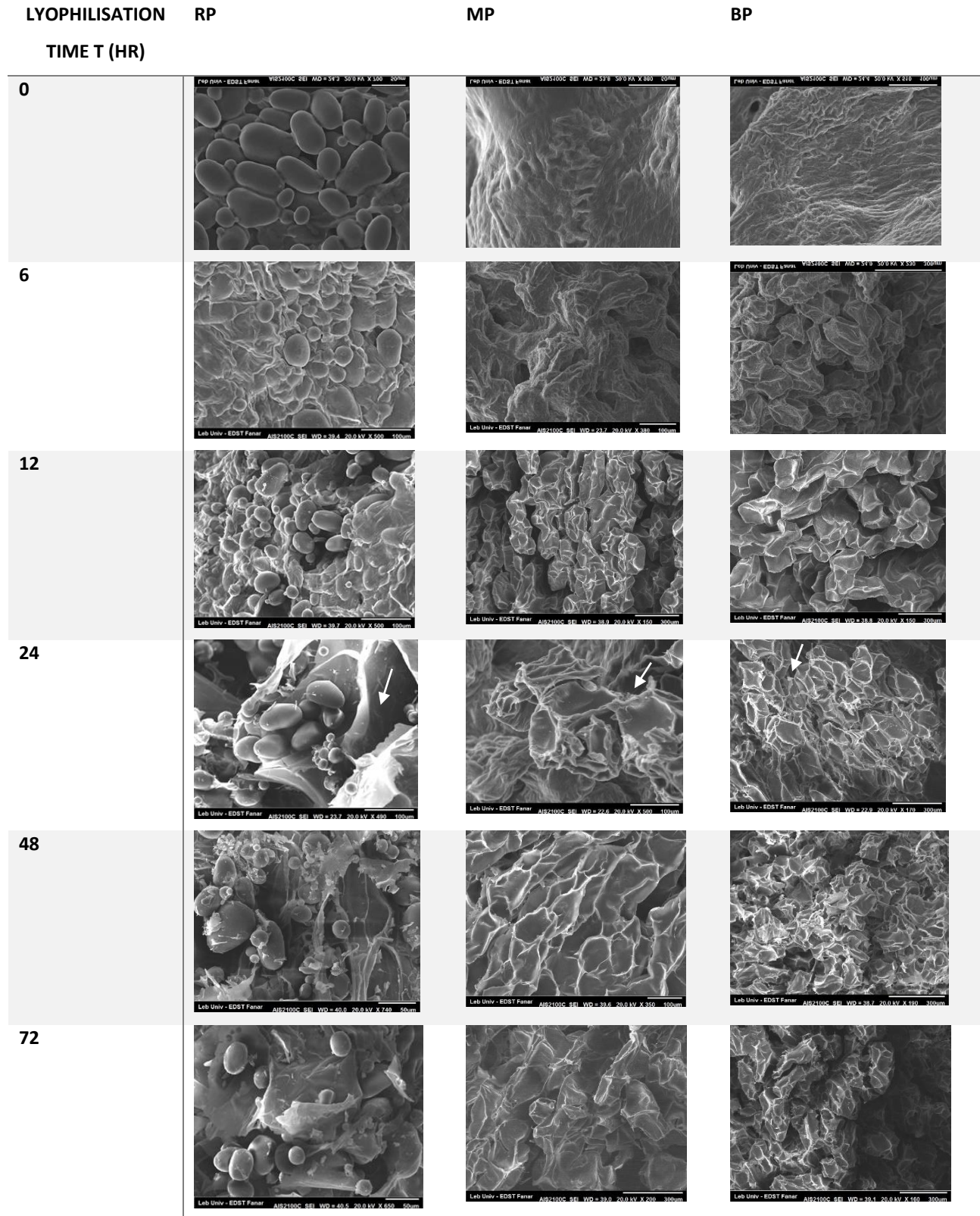


Figure 1. SEM micrographs of raw potato (RP), microwave potato (MP) and boiling potato (BP) at t_0 (initially before lyophilisation) and after 6, 12, 24, 48 and 72 hrs of lyophilisation respectively. *arrows correspond to the cavities induced inside the structure of potato due to lyophilisation.

3.2. Fourier transform infrared spectroscopy (FTIR)

Initially at $t=0$, the FTIR spectra of RP, BP and MP showed that the 3 samples had the same characteristic peaks, but with differences in their intensities (Fig. 2a), which revealed that microwave heating and boiling did not change the type of chemical groups in starch molecules nor produce new ones (no difference in the short-range order of starch). Similar results were reported by Fan et al. (2012), who studied the effect of microwave heating and traditional heat drying on rice starch. The peaks of the 3 samples were at 3500 cm^{-1} (OH vibration), 2900 cm^{-1} (CH_2 stretching), 2100 cm^{-1} (free water content not directly bound to starch), 1650 cm^{-1} (water molecules absorbed in the amorphous region of starch and stretching vibration of C=O band), 1412 cm^{-1} (CH_2 bending and $-\text{COO}$ stretch), 1160 cm^{-1} (vibration of the glycosidic C-O-C bond as well as the whole glucose ring), 1048 cm^{-1} (ordered crystalline structure), 1022 cm^{-1} (amorphous structure), 930 cm^{-1} (vibration of α 1-4 skeletal glycosidic bond), 715 cm^{-1} and 668 cm^{-1} (C-C stretch), and 632 cm^{-1} (assigned for skeletal modes of pyranose ring) (Fig. 2) (Cael, Gardner, Koenig, & Blackwell, 1975; Dankar et al., 2018; Fan et al., 2012; JAO & KO, 2002; Kačuráková & Mathlouthi, 1996; Olsson & Salmén, 2004; Ramazan Kizil, Joseph Irudayaraj, & Seetharaman, 2002; Sekkal, Dincq, Legrandb, & Huvenne, 1995; Sevenou, Hill, Farhat, & Mitchell, 2002).

Moreover, initially ($t=0$), RP had a higher intensity for all peaks compared to those of BP and MP, mainly due to the processing effect that was applied to the latter two samples (Fig. 2a), which caused some alterations in the inter and intra-molecular hydrogen bonds between starch molecules and subsequently influenced the IR absorption intensity (Fan et al., 2012). The major effect was at 2100 cm^{-1} since the water present at this peak was mostly in the free form (Dankar et al., 2018), which made its evaporation easier and faster under the heat effect, leading to small intensity peaks within the MP0 and BP0 spectra compared to the same high intensity peak recorded for RP0. Furthermore, a resemblance between the FTIR spectra of BP and MP was initially noted and during the different stages of freeze drying, following a similar trend in the decreased intensity order of peaks (Fig. 2, 3, 4). When the two spectra were superimposed, very few differences in intensity were found, implying that MP and BP initially had a similar internal structural at the molecular level (short-range order, chain conformation and double helical order). Moreover, a slight shift in the axis of peaks between RP0, MP0 and BP0 was observed within the range of the structural conformation of starch $1400\text{--}400\text{ cm}^{-1}$ (finger print region), which is sensitive to any changes. For example, the peak at 715 cm^{-1} (assigned to C-C stretch) in RP0 shifted to 615 cm^{-1} in MP0 and that at 668 cm^{-1} (assigned for skeletal modes of pyranose ring) shifted to 579 cm^{-1} in the BP0 and MP0 spectra (Fig. 2a). In fact, this slight shift revealed the effect of the processing heat treatment applied to MP and BP, which was reflected through the physical differences confirmed by SEM images, as stated by other authors (Fan et al., 2012; Siemion, Jabłońska, Kapuśniak, & Koziół, 2004).

Additionally, the dried spectra for MP and BP were detected after 6 hours of lyophilization, which were repeatable for the rest of the drying time points (Fig. 1b). This effect was previously observed in SEM images after 6 hours of lyophilization in dried samples of MP and BP. In fact, the fast drying process of both MP and BP samples was mainly due to the pre-heat treatment (microwaving or boiling) of potato tubers, partially disrupting the strong network interaction between starch molecules, rendering them more susceptible to further treatments, such as freeze drying, thus facilitating the rapid evacuation of water molecules from the treated

samples. The strong interaction network that is persistent between starch molecules in the RP sample (amylose-amylopectin, amylopectin-amylopectin intermolecular hydrogen bonds) makes it harder to obtain a dried spectrum by freeze drying, which takes a 24 hrs, as shown in SEM images (Fig. 1). It was observed that after 24 hrs of lyophilization, the FTIR spectra of the 3 samples were perfectly aligned (Fig. 3b), which means that RP24 reached the same chemical structure as those of BP24 and MP24. Therefore, 24 hours was determined to be the time required for the removal of free water surrounding the starch molecules in raw potato tuber, and the structure remaining for the potato samples was the main integral skeletal structure of starch with strongly bound water.

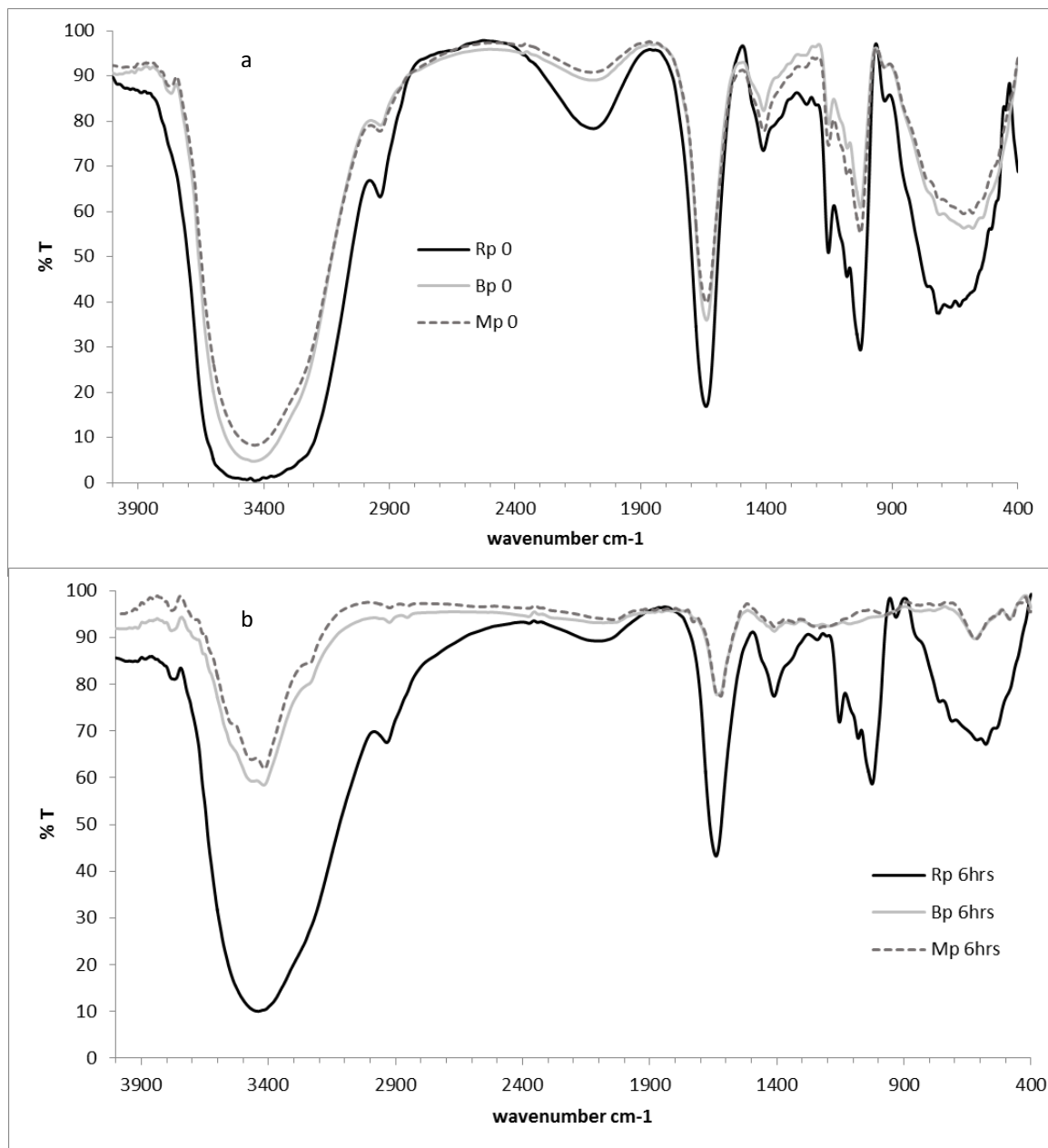


Figure 2. FTIR spectra for RP, BP and MP initially before freeze drying and (a) and after 6 hours of freeze drying (b).

Indeed, the effect of freeze drying on the starch structure of potato samples was revealed through FTIR spectra, most importantly within $1400\text{-}400\text{ cm}^{-1}$ (range of conformational changes), not only by the large decrease in the intensity of peaks but also through the absence of some peaks, such as the 715 cm^{-1} peak recorded by RP0 and 1022 cm^{-1} peak in MP0 and BP0, and the narrowing and shifting of others. For example, spectra peak shifts were observed in MP and BP from $t=0$ (initially) to after 6 hrs of lyophilization at the following positions: 930 cm^{-1} to 970 cm^{-1} (vibration of alpha 1-4 skeletal glycosidic bond), 597 to 485 cm^{-1} (skeletal modes of pyranose ring), and 615 to 620 cm^{-1} (C-C stretch). For RP, a shift was observed from 632 cm^{-1} (skeletal modes of pyranose ring) at $t=0$ to 575 cm^{-1} at $t=12$ hrs and 485 cm^{-1} at $t=24$ hrs, and from 668 cm^{-1} (C-C stretch) at $t=0$ to 620 cm^{-1} at $t=24$ hrs. Actually, the two peaks recorded at 620 and 485 cm^{-1} could be assigned as characteristic peaks of dried skeletal starch, as these two peaks were found to be present in all of the dried starch spectra at different drying times within RP, MP and BP. It should be noted that this shift was accompanied by a narrowing of the peaks as well, which is indicative of a decrease in the number of respective conformations as well as increase of polymer ordering as a result of the compact structure induced by freeze drying (Fan et al., 2002).

Therefore, the differences in the starch conformational structure between RP, MP, and BP were only detected initially (a shift in the modes of the starch pyranose ring) when water molecules were present, whereas after dehydration, all samples resembled each other, whether they were previously heat treated (MP, BP) or not (RP), possessing the same peaks at 620 and 485 cm^{-1} corresponding to C-C stretching and the skeletal modes of pyranose ring, respectively. Hence, water responsible for highlighting the differences between the three potato samples, and upon its removal, the initial structure of the starch diminished, even without being exposed to any further treatment.

Although the three samples had similar peaks after being dried for 24 hours, some modulations and shifts along the X-axis within the two peaks in the range of $1022/1048\text{ cm}^{-1}$ (responsible for the amorphous and crystalline order, respectively) were observed, indicating that there were some differences in the long-range order of starch between the three samples. For example, at $t=24$ hrs, RP had a peak at 1020 cm^{-1} that shifted towards an amorphous structure, whereas MP and BP had peaks at 1072 cm^{-1} (a more ordered structure) (Fig. 3b), as also shown in the XRD patterns at higher intensities.

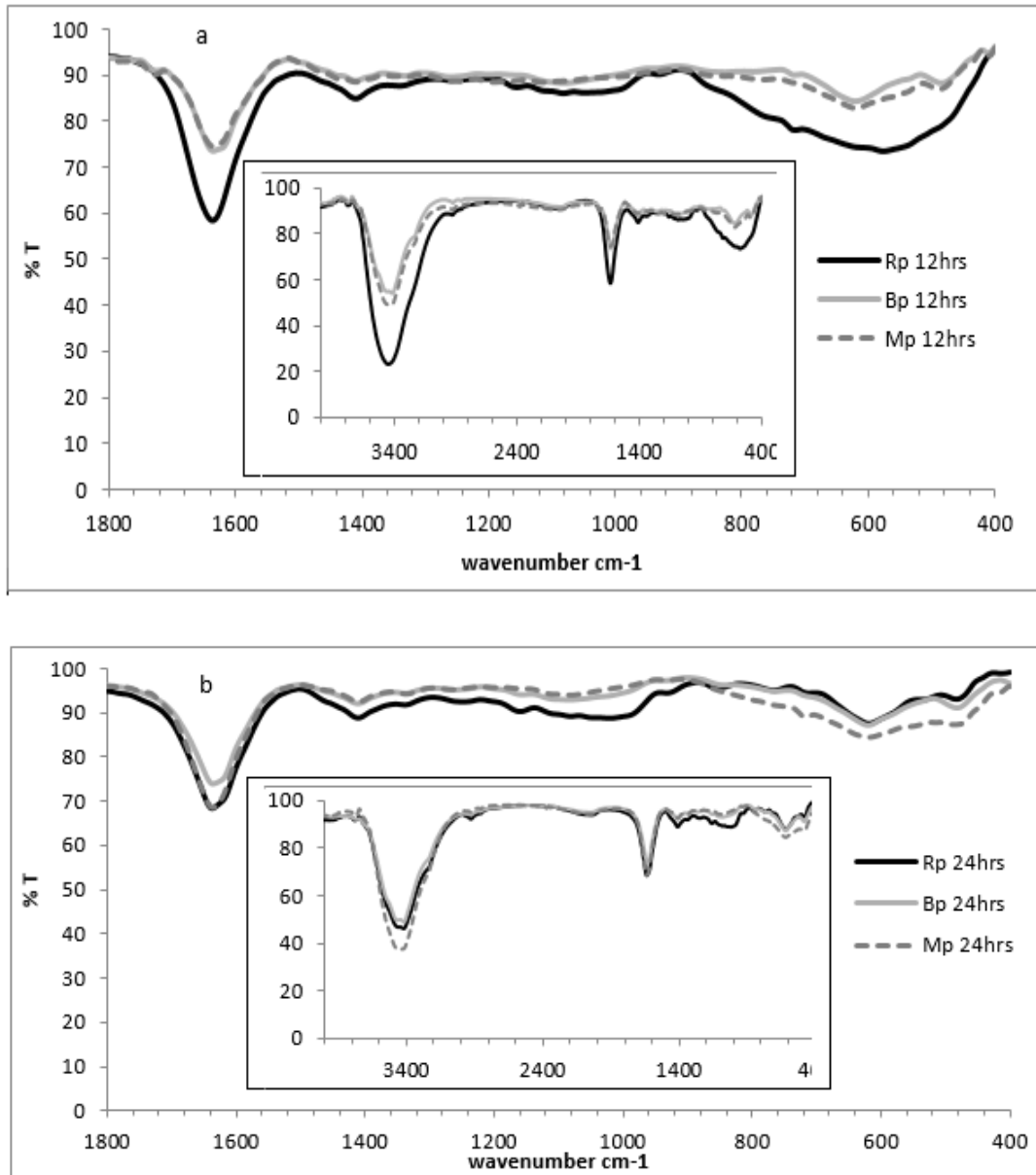


Figure 3. FTIR spectra for RP, BP and MP after 12 hours (a) and 24 hours (b) of lyophilization.

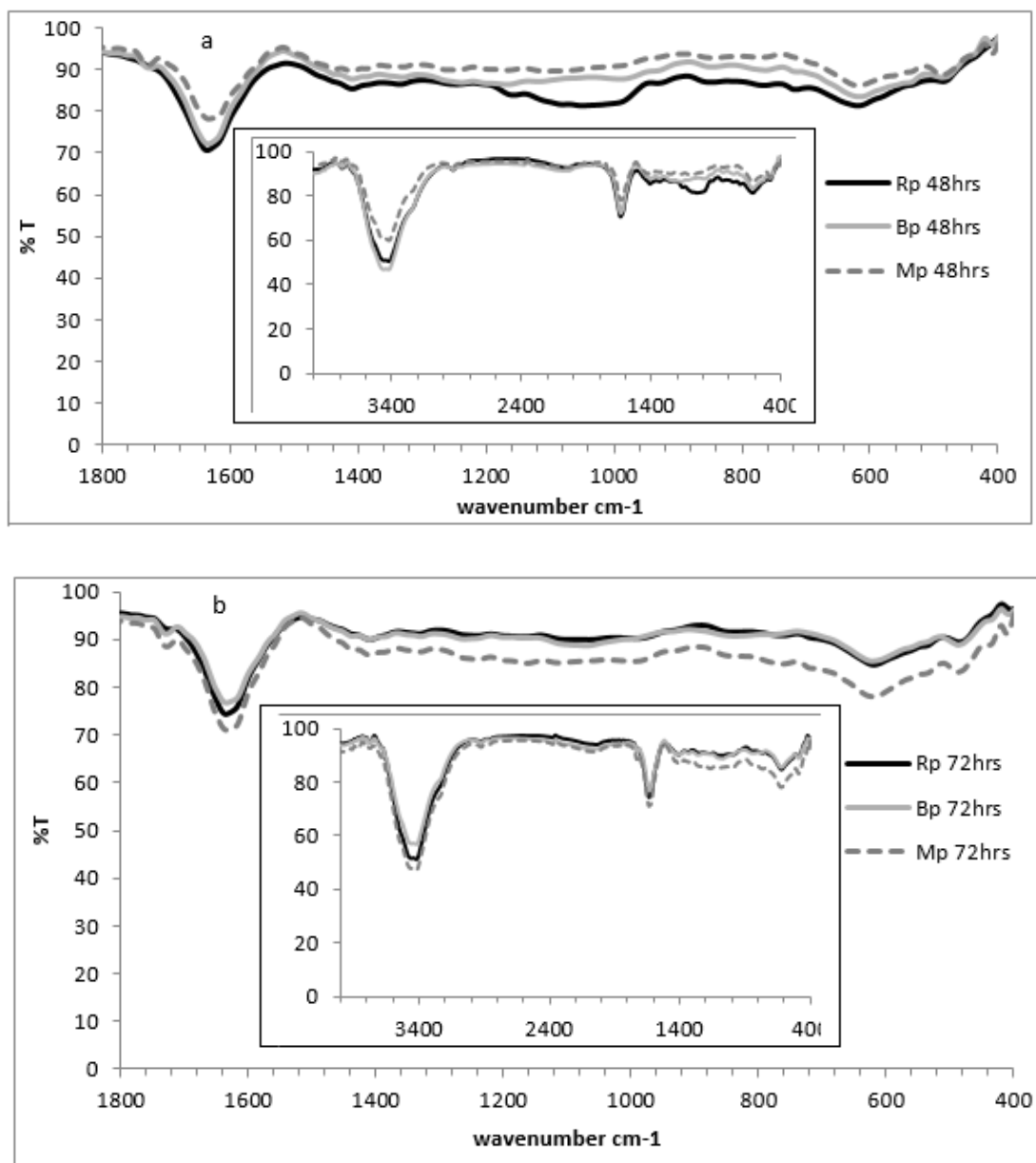


Figure 4. FTIR spectra for RP, BP and MP after 48 hours (a) and 72 hours (b) of lyophilization.

3.2. X-ray Diffraction (XRD)

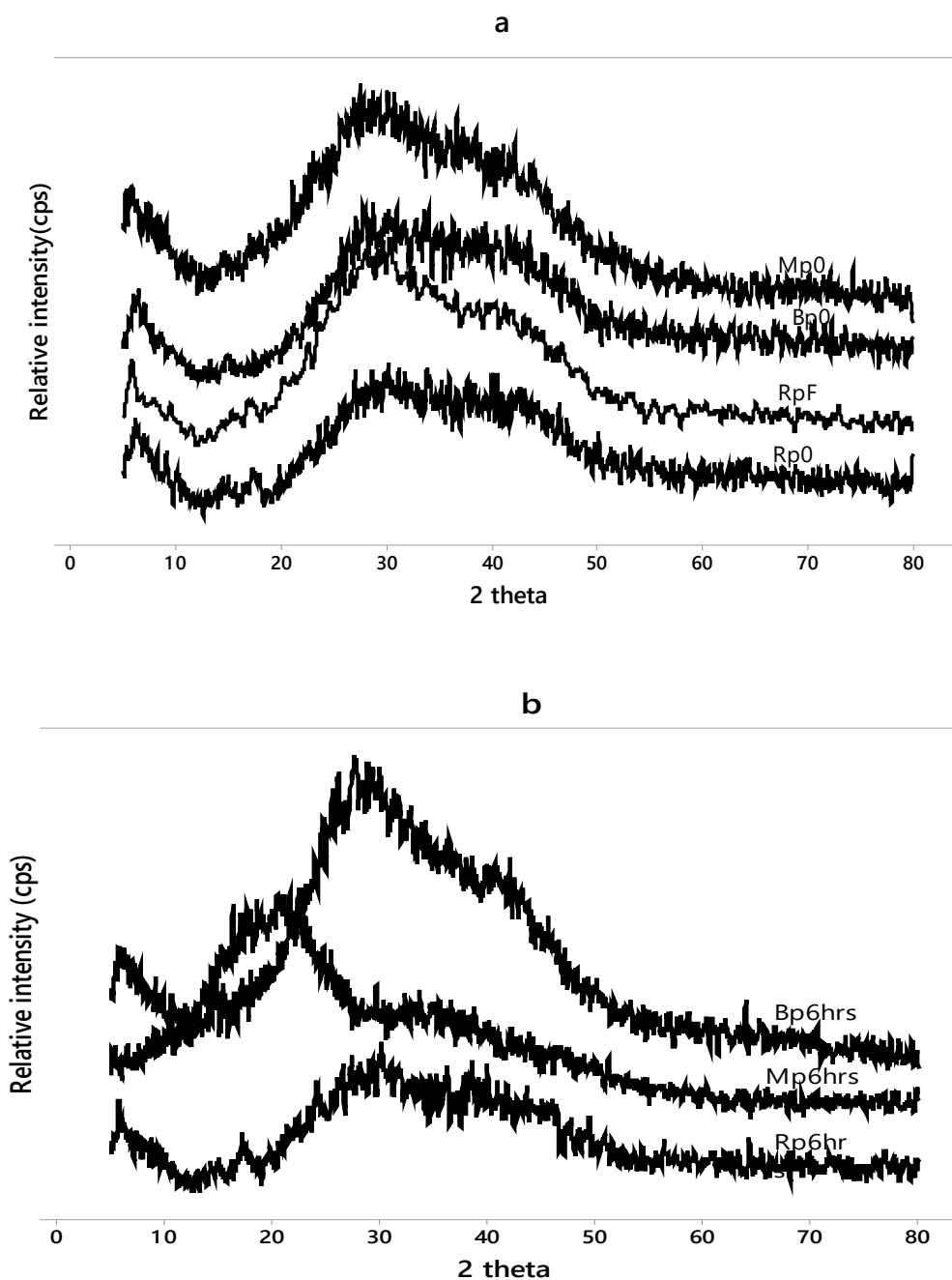
In agreement with previous IR results, the comparison between XRD figures at different lyophilization times indicated that the internal structural order increased after lyophilization for all samples (the peaks became sharper with higher intensities), although it was observed that freezing also promotes increased starch ordering, as shown in RPF (Fig. 5a); yet, drying increased the order in starch molecules (as revealed with the higher

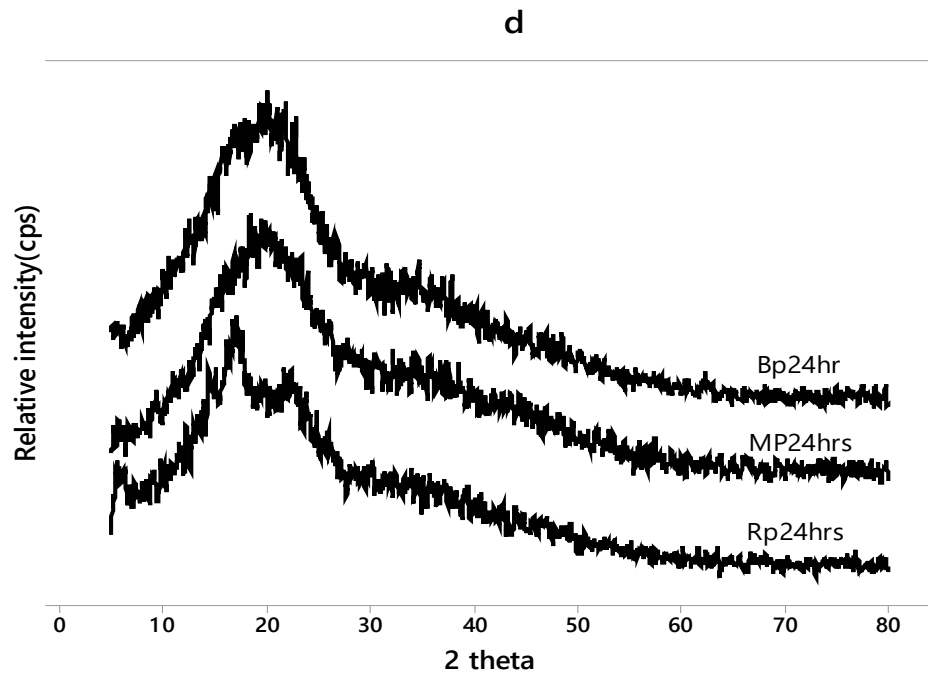
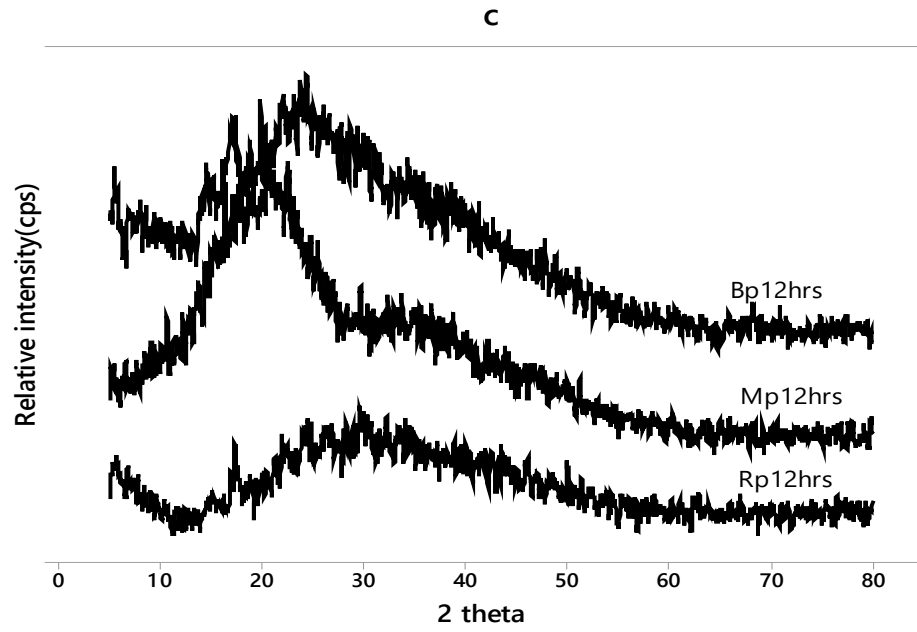
intensity peak in RP24) (Fig. 5c). Similar results were found by Chen et al. (2016), who stated that freeze-drying techniques increased the range ordering and relative percent of crystallinity of starch in yam flours, and Wang et al. (2017), who found that the crystallization of gelatinized foxtail millet starch during the freeze-drying process that resulted from starch retro-gradation was sensitive to decreased temperatures. Additionally, Van et al. (1994) showed that changes in the FTIR band intensities resulted from changes in specific conformations, such as the long-range ordering and crystallinity, which were related to the quick decrease in the FTIR intensities of MP6 and BP6 and increase in their corresponding XRD peaks. However, it was also observed that for MP after 6 hrs of lyophilization, all of the XRD patterns were similar in shape, with slight differences in intensity, as if they were superimposed above each other, whereas for RP, similar XRD patterns were observed after 24 hrs of lyophilization (Fig. 5). Therefore, these results confirm the previous hypothesis that MP at 6 hrs becomes dried while RP takes more time (24 hrs) to dry. Moreover, a shift in the 2-theta angle was detected after 24 hrs of lyophilization in RP and after 6 hrs in MP, supporting the hypothesis and revealing that a reconstruction of the starch structure molecules had occurred after these freeze drying times, in which MP6 and RP24 were considered to be dried samples. On the other hand, BP also showed an increase in the XRD peak after 6 hrs of lyophilization, indicating an increase in the ordering of the structure, which was also revealed by the narrowing of the FTIR peaks at BP6 and MP6. Nevertheless, this result does not coincide with the other peaks found in BP at the other drying stages, although they showed similar patterns with similar intensities. Yet, a shift in 2-theta angle was detected after only 12 hrs of lyophilization. It should also be noted that BP0 and BP6 expressed the same axis level of the 2-theta angle. Actually, the increase in intensity of the XRD peak was related to the increased ordering in the structure of BP, while the shift in 2-theta angle was due to a deeper change at the level of the unit cell dimensions, leading to the rearrangement of the planes of the molecules (more reconstruction of the starch structure), as detected in the long-range level rather than short-range order, mainly due to the rearrangement of double helical structures to a more ordered phase.

Comparing MP, BP and RP after the same duration of lyophilization, the XRD patterns revealed that at $t=0$, MP and BP had higher levels of peak intensity compared to that RP, with MP recording the highest peak height (Fig. 6). According to Wang et al. (2017), cooking reduces the moisture content within the millet, leading to the transition of amorphous complexes into a crystalline type at a lower moisture content. In fact, MP and BP had a lower moisture content, as revealed by the less intense FTIR spectra, compared to RP. Additionally, MP recorded slightly lower intensity peaks (related to the water content) compared to those of BP as a result of the higher energy input driven by microwave heating, which leads to faster water evaporation and, consequently, the occurrence of more V type crystals (more intense peak) within the MP sample (Wang et al., 2017).

Furthermore, a spotted change was observed in the XRD pattern of RP24 that was characterized by the appearance of two peaks that corresponded to native potato starch (low B-type crystallinity) at 2-theta = 17 and 22 (Srikanlaya, Therdthai, Ritthiruangdej, & Zhou, 2017) and that gradually increased until the end of the freeze drying stages. This change indicated that some transformation occurred in the RP structure starting from 24 hours, such as the tendency of RP to return to its original structure after being deprived of water molecules (dried), which agrees with the previous observations.

Indeed, the subsequent changes in the recorded intensity levels of the scattered XRD patterns within MP, BP and RP can be directly attributed to changes in the conformational order (long-range order), which can be explicitly explained in the SEM images. In this way, the peak intensity of BP is larger than that of MP after 6 hours of lyophilization, and this trend persists throughout the rest of the drying stages (Fig. 6). This difference is mainly due to the clearer rearrangements and ordering of starch into a granule-like structure within the BP sample as well as the appearance of a more compact and denser structure compared to that MP, as shown in the SEM images. On the other hand, the lower intensities of the XRD pattern displayed by RP compared to those of MP and BP can be ascribed to the scattering of starch granules (also torn up) inside the starch matrix in an unorganizable non-ordered fashionable way, as was observed in the SEM images (Fig. 1).





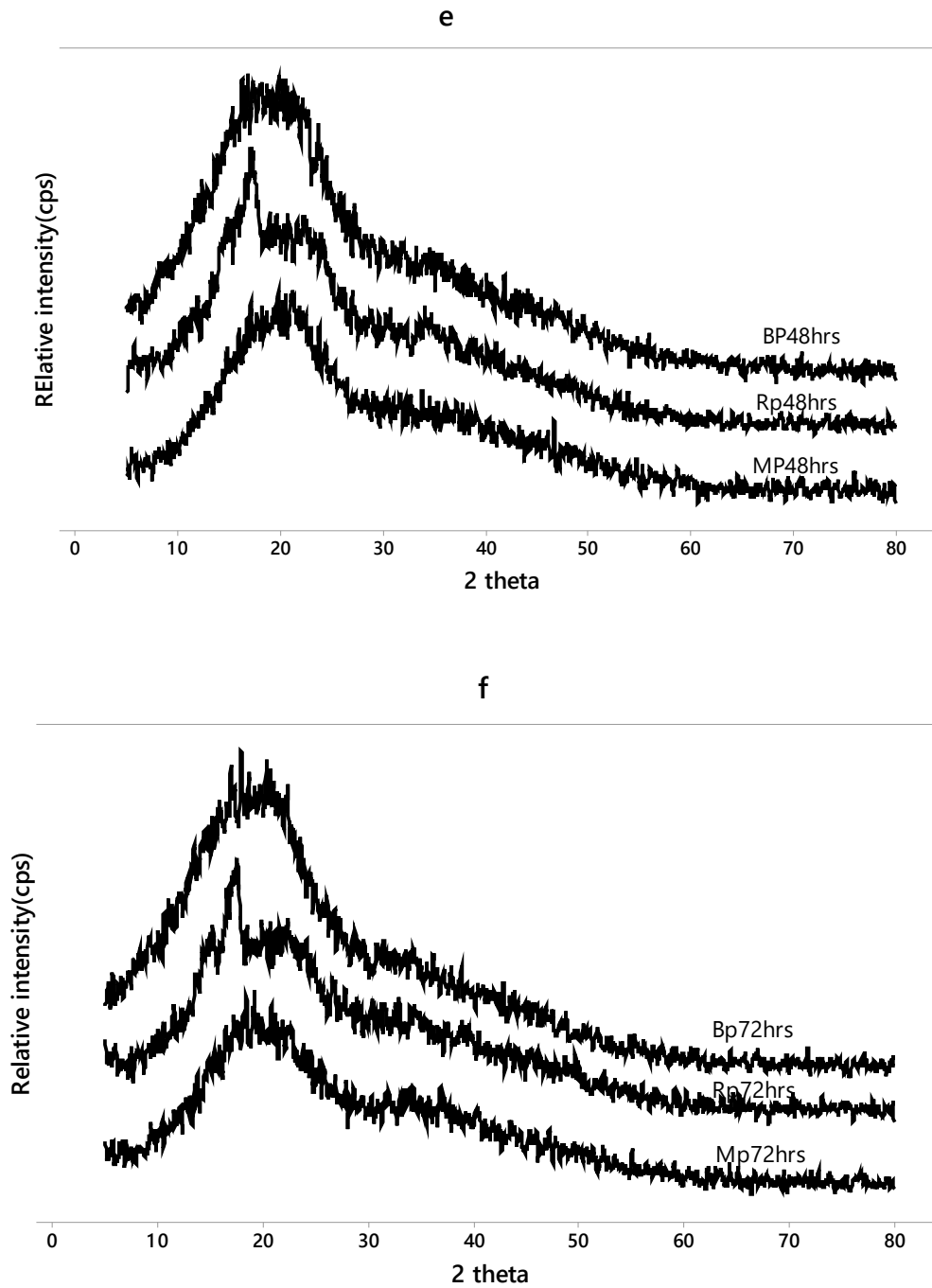


Figure 5. XRD patterns of RP0, BP0, MP0 (initially before freeze drying) and RPF (after freezing) (a), and XRD patterns of RP, BP and MP after the respective hours of lyophilization, 6 hours (b), 12 hours (c), 24 hours (d), 48 hours (e) and 72 hours (f).

4. Conclusions

The rearrangement and re-association of starch molecules from gelatinized and leached starch recoiling towards a granule-like structure were clearly observed in SEM images for both MP and BP samples under the effect of freeze drying.

The presence of smaller sized starch granules in RP samples after intensive lyophilization for 72 hours indicates the presence of some water molecules strongly bound to starch in raw potato tubers.

Heat treatment induced peak shifting among the RP, MP and BP spectra in the finger print region ($1100\text{--}400\text{ cm}^{-1}$), indicating the presence of some changes at the level of starch helical structure, as was also detected through the SEM figures.

Temperature triggered microstructural modifications in potato tuber, but water was the main contributor, leading RP to have similar chemical characteristics as those of dried MP and BP after being totally dried and without being exposed to any heat treatment (the effect of temperature was negligible or removed without water).

Two important peaks were found for dried skeletal starch of potato samples at 485 cm^{-1} and 620 cm^{-1} .

Sample freezing increased the order of starch molecules; however, the XRD peaks of all of the samples tended to increase more after freeze drying, with some shifting in 2-theta due to re-arrangement and ordering at the microstructural level.

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▪ Chapter 9

Influence of rheological properties, mechanical characteristics and cooking treatments on 3D printing potato samples

- *This chapter has been submitted as:*

Dankar, I., Pujolà, M., EL Omar, F., Haddarah, A., Sepulcre, F. (September, 2018). Influence of rheological properties, mechanical characteristics and cooking treatments on 3D printing potato samples, *Journal of food engineering*

Influence of rheological properties, mechanical characteristics and cooking treatments on 3D printing potato samples

Abstract

This paper studied the rheological, microstructural and 3D printing characteristics of potato tubers with different added substrates (olive oil, butter, alginate, agar and carrots) and after being applied to different cooking methods (microwave (MP) and boiling (BP)). MP samples recorded lowest moisture content with more aggregated and densely concentrated starch granules compared to BP, consequently leading to higher levels of mechanical and rheological properties and better stable printed products. The relatively low mechanical and rheological properties of BP resulted in over dough deposition during extrusion and hence in deformed final printed products with inaccurate dimensions and submissive details. The high increase in the mechanical properties, viscosity, yield stress and thixotropy exerted by agar addition on MP, retarded 3D printing with non-continuous layer deposition and a final rough surface. The shapes printed using MP-butter resulted in smooth printing and an excellent self-supporting structure with a creamy surface due that butter was able to increase the mechanical characteristics, yield stress and thixotropy of MP a lot of while maintaining a similar viscosity value as that of MP for continuous extrusion. Using carrots provided fairly good printability and an option of widening the applicability of 3D food printing to more customized, colorful nutritive products.

Key words: Microwaved, Boiled, viscosity, thixotropy, optical microscopy, additives

1. Introduction

3D printing, additive manufacturing technology, is a digitalized process that aims on producing innovative shapes, by extruding a layer above layer according to a predefined cross sectional area till the whole 3D model is formed. Moreover, 3D food printing possesses many advantages in comparison with conventional food processing technique, such as customized food structures, widening available food sources, simplifying and enhancing food production process as well as creating personalized food nutrition for an individual person (Dankar et al., 2018b; Liu, Zhang, & Bhandari, 2018a). The latter being of great importance, where in the previous research, the attempt was to optimize the printing of mashed potato puree combined with different food additive in order to obtain innovative shapes that could be personalized for elderly or people facing mastication problems (enhancing their sensory perception), along with children in order to promote them the concept of a more healthful snack instead of sweets and sugars. All the newly published research in the field of 3D food printing focuses on optimizing and characterizing the properties of the printed substrate for achieving best printability. For instance, Hamilton et al. (2017) and Severini et al. (2017) analyzes the rheological properties of commercially breakfast spreads, Vegemite and Marmite and cereal based snacks enriched with edible insects respectively to study their compatibility with extrusion 3D printing. Yang et al. (2018) assessed the rheological and mechanical properties of lemon juice gels after combining them with different

percentages of potato starch, and studying their influence together with the printing parameters on the quality of the printed product. While Liu et al. (2018) investigated the effect of the addition of different gums on the rheological, microstructural and 3D printing characteristics of mashed potatoes.

Based on this, the selection of the different additives to be added to the printed substrate is vitally important which critically affects the rheological, mechanical and microstructure properties of the substrate, consequently affecting the feasibility and the final resolution of the printed shape. Hydrocolloids such as agar and alginate are frequently used to enhance the structure, texture and stability of food, by binding to water molecules, preventing their penetration inside the starch granules and developing an interconnected network with starch molecules. On the other hand, fat additives as Butter and olive oil are known to act as lubricants in food materials, augmenting smoothness texture, flavor and surface creamy appearance (Lurueña-Martínez, Vivar-Quintana, & Revilla, 2004; Prindiville, Marshall, & Heymann, 2000). Other highly consumed vegetables, such as carrots could be integrated in the printing material such as to escalate the nutritive density and colorful ambience of the final printed product.

The objectives of this study were to (1) investigate the effect different cooking methods (microwave and boiling), and (2) various added substrates on the rheological, microstructural and mechanical properties of potato tubers while (3) correlating these characteristics with 3D printing behavior using an extrusion based 3D printer.

2. Materials and methods

2.1. Sample preparation

Fresh potato tubers (*Solanum Tuberosum* L cv Kennebec) acquired in local supermarket, were selected, washed thoroughly and then subjected to two different treatments; Microwaved heating and boiling respectively. During cooking, potato tubers of around 500g were used as a whole after doing some punching insertions using a knife. For microwaving, a potato tuber was cooked at a full power (700 W for 7 minutes), whereas for boiling, potato tuber was set in a beaker filled with distilled water and left to boil for around 25 minutes. Different substances that are usually incorporated during cooking such as (olive oil, butter, alginate, agar and carrot) were then added separately at 1% w/w on the basis of weight of each type of cooked potato tubers; microwaved potato (MP) and boiled potato (BP). Carrots as an exception were added at a ratio of 1/3 of potatoes (carrots were boiled when added to BP and microwaved when mixed with MP).

2.2. Microscopic Observations

In order to compare the structure and the alignment of the starch particles between raw, microwaved and boiled potato, a thin film from each of potato tuber was spread on a glass slide and stained with diluted Lugo's Solution then examined under a Compound Light Microscope (Better images were taken at 10x magnification).

2.3. Dry matter content

The dry matter content of raw, microwaved and boiled potatoes was determined by a gravimetric method (AOAC method 931.04) and expressed as g.Kg^{-1} via detecting the difference between the weight initially

of these samples and after being placed in an oven at a temperature around 75°C for 24 hours. Measurements were held in duplicates.

2.4. Mechanical characteristics

The mechanical characteristics of the different blends were tested, including firmness, consistency and cohesiveness using the Textural Analyzer (TA.XT Plus, Stable Microsystems, Godalming, UK) coupled with a back extrusion cell and a 35 mm disc. Samples up to 40 mm were placed in a standard-size cylinder. During the test, the disc penetrates a distance of 30 mm at a speed of $2\text{ mm}\cdot\text{s}^{-1}$, after which the probe returns to the original position. The peak in the positive area is taken as a measurement of firmness (kg). The area under the curve up to this point refers to consistency (kg.s). The maximum negative force is taken as an indication of cohesiveness (kg) (Dankar et al., 2018c). Each sample was replicated at least 3 times.

2.5. Steady Rheological Measurements, Thixotropy, Yield Stress

The rheological measurements were performed in a Viscometer (HAAKE Rheostress, Barcelona, Spain) controlled with commercial computer software (HAAKE RheoWin 4 Job and Data Manager Software). Samples were analyzed for their flow properties using a concentric rotating cylinder sensor (SV2). After loading samples were rested for 2 minutes prior to testing. Steady rotational tests were performed to study the flow behavior, thixotropy and yield stress. Hysteresis loop test was performed to give an indication whether the sample is thixotropic and to determine the degree of thixotropy. The shear rate was increased logarithmically from 0.1 to 10 s^{-1} during the first 30 secs, then was maintained at 10 s^{-1} for 30 secs, and finally was decreased logarithmically again to 0.1 s^{-1} during 30 secs. Consequently, the viscosity (η) and the shear stress (τ) were recorded, as well as the yield stress for each sample. Accordingly, a quick drop of viscosity as a response of increase in shear stress and shear rate was registered. Yield stress was estimated as the point in which viscosity as a function of the shear stress ($\eta = f(\tau)$) changes abruptly (Tabilo-Munizaga & Barbosa-Cánovas, 2005). The temperature of the rheological tests was set constant at $20 \pm 0.1^{\circ}\text{C}$. Results were reported as the average of three replicates (a new sample was loaded for each repetition).

2.6. 3D Food Printing conditions

A RepRap BCN3D+ printer (designed by CIM Foundation, Spain, Barcelona) coupled (100 mL volume and 4 cm diameter) was used to 3D print the potato purees. The 3D printing process is based on extrusion and works through the principle of joining materials layer-by-layer to make a final 3D object. The code for the desired 3D object is transferred through an SD card from a CAD program (CURA 15.02.01). Speeds set in the CURA program were as follows: travel speed= $100\text{ mm}\cdot\text{s}^{-1}$, infill speed= $40\text{ mm}\cdot\text{s}^{-1}$, printing speed= $40\text{ mm}\cdot\text{s}^{-1}$, flow %= 100 and retraction speed= $40\text{ mm}\cdot\text{s}^{-1}$.

2.7. Statistical Analysis

Statistical analyses of the data were conducted on Minitab 18 (Minitab Inc. Coventry, UK). Data concerning textural characteristics were tested for significant differences ($p < 0.05$) using analysis of variance, one-way ANOVA and Tukey's HSD comparison test.

3. Results and Discussion

3.1. Microscopic observations

Images of the optical microscopy for raw, microwaved and boiled potatoes are shown in Figure 1. Observations had shown separate clusters of small round oval starch granules that are scattered around the polygonal parenchyma cells in raw potato (Fig. 1c) compared to the enlarged aggregates of well-defined (no cell rupture) extensively swollen starch granules that occupied nearly the entire parenchyma cell volume in MP and BP (Fig. 1a, b). Similarly, Ormerod et al. (2002) found that upon cooking potato starch cells increase relatively in their size compared to RP. This extensive swelling in granules is due to starch gelatinization under the effect of heating which aids in the absorption of the starch granule to the cellular water and in its respective swelling to form a gel. Moreover, more dispersed swollen starch granules with less intense blue color were observed in BP compared to the denser highly pigmented dark blue aggregates with a higher level of intercellular cohesion observed between starch granules in MP. In fact, this could be attributed to the differences in the rate of heating or the method used for cooking (microwaved or boiling) (Moorthy, 2002). For instance, (Anderson, Gekas, Lind, Oliveira, & Öste, (1994) reported that during boiling a high uptake of water from the liquor to tuber occur while at the same time soluble starch such as amylose would also leach out of the cells. This might explain the less intense blue color observed in BP since the percentage of the relative concentration of starch per unit area of the cell would become less. Furthermore, the more separated cells revealed in BP microscopic images could be linked to the destruction of the pectin cells in the cellular wall and the middle lamella of the potato tissue and the loss of some of the amylose starch during boiling in which both are responsible for the intercellular cohesion of the cells, and it was found that these pectic substances are more reduced during boiling than other cooking methods (Andersson et al., 1994; Hughes, Faulks, & Grant, 1975).

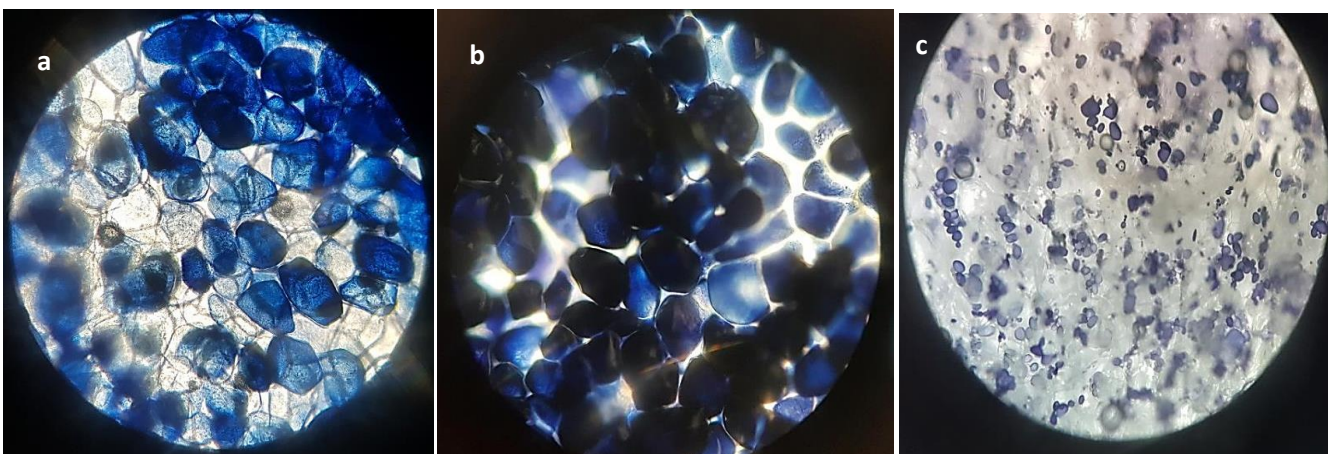


Figure 1. Microscopic observations (10x) of (a) boiled potato, (b) microwaved potato and (c) raw potato stained with Lugol's iodine solution.

3.2. Moisture content

The water content present in starch governs the internal microstructure and affects its textural and rheological properties (Singh, Kaur, Ezekiel, & Guraya, 2005). Results showed that BP possessed the highest moisture content of 82.28% while MP had the least moisture content of 70.48% and it was reported that a stronger gel is formed under restricted water content (Liu, Zhang, & Bhandari, 2018a) which explains the variations in the mechanical characteristics and viscosity values obtained between BP and MP in the below sections. Actually, this difference in moisture content could be explained by the fact that during boiling, water would penetrate inside the potato tuber and increase the relative percentage of moisture content inside whereas the higher energy input that is applied during microwaving aids in faster rate of water evaporation from potato and therefore in recording lower levels of moisture content. Similarly, Yang, Achaerandio, & Pujolà (2016) studied the effect of the intensity of different cooking methods on the physical and nutritional quality of potato tubers from various cultivars and found that baking and microwaving led to higher dry matter content compared to boiling and which is due to the water losses that occur during processing. Moreover, the high percentage of moisture content recorded by BP is one of the reasons that aids in the swelling and separation of starch granules as observed in BP microscope figure (Fig. 1a).

3.3. Mechanical properties

3.3.1. Effect of cooking method on mechanical properties of potato tubers

The results of statistical analysis showed a great significant difference ($p < 0,05$) among the firmness, cohesiveness and consistency of the MP and BP samples, with MP alone possessing much higher values of 0.52 kg firmness, 6.42 kg.s consistency and 0.49 kg cohesiveness compared to that of 0.14 kg firmness, 1.64 kg.s consistency and 0.11 kg cohesiveness for BP (Table 1). These results are in agreement with those found by Yang et al. (2016), who reported that different cooking treatments resulted in varying textural properties with microwaving being able to provide firmer structures compared to boiling. This could be linked to the fact that the higher moisture loss recorded by MP and the presence of denser

aggregated cells with higher intercellular cohesiveness observed under the microscope (Fig. 1 b) provided those properties of MP to be much firmer and more cohesive and consistent. In contrast, the high moisture content of BP as well as its dispersed cell arrangement (Fig. 1a) contributed to its less firm, cohesive (cohesiveness is inversely related to the distance between the adjacent cells) and low consistent mechanical properties. Likewise, Singh et al. (2005) linked changes in textural characteristics between potatoes from different cultivars to their respective cellular arrangement, in a way that potato cultivars that showed a more closely packed cell alignment were much harder and cohesive compared to those that showed loose cell arrangement and that were found to possess lower textural properties with less hardness and cohesiveness. Moreover, Srikanlaya et al. (2017) reported that the hardness and consistency of microwaved bread was higher than that of oven heating due to the high moistures loss obtained during microwave baking. In addition, Andersson et al. (1975) related firmness and cohesiveness to the stability of the pectic substances in the cell wall and the middle lamella, and since these substances are more

destroyed during boiling, this could be another reason why lower firmness and cohesiveness values were detected within BP samples.

3.3.2. Effect of type of additive on the mechanical properties of boiled and microwaved potato tubers

As stated above, initially MP possessed higher mechanical properties than BP. Therefore, even after the addition of the different substrates, the range of the mechanical properties of all MP samples persisted to be higher than that of BP's. However, within each type of cooked potatoes some deviations in the mechanical properties were recorded according to the type of substrate added. For instance, in MP, agar showed its forte ability to produce the highest increase in textural properties (firmness (1.54 kg), consistency (18.40 kg.s) and cohesiveness equal to (1.55 kg)). Moreover, alginate and butter were found to be the second additives that induced the highest elevation on the textural properties of MP (no significant difference was detected between microwaved potato with alginate or butter), followed by the addition of 1/3 carrots and 1 % olive oil (Table 1). In fact, MP and MP+1% olive oil showed no significant difference ($p < 0,5$) among their mechanical characteristics values. In a previous study conducted on the effect of different food additives on the mechanical properties of commercial potato puree, agar was also found to be the additive that produced the highest increasing effect on the mechanical properties followed by alginate. This was attributed to the conveyed network structure that occurred between polysaccharide chains and the large-sized long additive molecules (agar and alginate), though this effect was more pronounced with the agar additive because it has a higher effect of creating a stronger network between the glucan chains, enhancing the particle-particle surface contact and consequently leading to an increase in the firmness, consistency and cohesiveness of potato sample (Dankar et al., 2018 a; Huang, Kennedy, Li, Xu, & Xie, 2007). Moreover, the two fat substrates that were added to potato (butter and olive oil) showed a different effect on the mechanical properties of potatoes. In fact, this difference could be related to variations at the level of the chemical composition and physical properties of each substrate. All the chemical bonds present in butter are saturated and hence the molecule had a higher ability to form hydrogen bonds interactions with the starch molecules compared to olive oil that is chemically unsaturated (possessing some double bonds) and thus had less sites for interactions and a more disrupting effect. Moreover, butter structure is more compact while oil is lighter and more flexible. Thus, upon butter addition continuous interactions of starch granules-fat clusters are induced along with flocculation of fat globules which creates a dense strong network system characterized by high levels of mechanical properties compared to the loose system with less connected clusters that is formed upon the addition of olive oil to potatoes (Buldo & L., 2012; Rønholt, Mortensen, & Knudsen, 2013). Domínguez et al. (2016) reported the ability of olive oil in producing softer textures in pate with less hardness and cohesiveness due to increasing the ration of unsaturated to saturated fats in meat. Likewise, the different added substrates exerted the same effect on the mechanical properties of BP in a similar trend as well, but with less recorded ranges compared to MP as stated before, except for the addition of 1/3 carrot ratio where no significant difference was detected between mechanical properties of BP and BP+ 1/3% carrot whereas in MP the addition of 1/3 carrots elevated its firmness and cohesiveness. This can be attributed that in the latter case carrots were microwaved as well, hence most of the moisture

content was sucked out of the material leaving more a dried matter which upon addition to the MP would be relatively elevating the percentage of solid matter per material and consequently causing this increase in the textural parameters values.

Table 1 Mechanical characteristics values of firmness (Kg), consistency (Kg.s) and cohesiveness (Kg) of potato tubers with different types of food additives and after being applied to two methods of cooking microwaving (MP) and boiling (BP)

Samples	Firmness (Kg)	Consistency (Kg.s)	Cohesiveness (Kg)
MP+1% agar	1.54 ± 0.10 ^a	18.40 ± 1.73 ^a	1.55 ± 0.06 ^a
MP+1% alginate	0.80 ± 0.03 ^b	9.87 ± 0.04 ^b	0.73 ± 0.04 ^b
MP+1% butter	0.77 ± 0.02 ^b	9.16 ± 0.30 ^{b,c}	0.72 ± 0.01 ^b
MP+ 33% carrot	0.63 ± 0.04 ^c	7.55 ± 0.11 ^{c,d}	0.61 ± 0.05 ^c
MP+1% olive oil	0.58 ± 0.01 ^{c,d}	7.09 ± 0.31 ^{d,e}	0.55 ± 0.05 ^{c,d}
MP	0.52 ± 0.03 ^{d,e}	6.42 ± 0.65 ^{d,e}	0.49 ± 0.004 ^{d,e}
Microwaved carrot	0.51 ± 0.02 ^{d,e}	6.08 ± 0.36 ^{d,e}	0.47 ± 0.04 ^{d,e}
BP+1% agar	0.43 ± 0.008 ^e	5.51 ± 0.14 ^e	0.42 ± 0.02 ^e
BP+1% alginate	0.27 ± 0.008 ^f	3.35 ± 0.11 ^f	0.24 ± 0.007 ^f
Boiled carrot	0.23 ± 0.01 ^{f,g}	2.70 ± 0.24 ^{f,g}	0.19 ± 0.01 ^{f,g}
BP+1% butter	0.19 ± 0.003 ^{f,g,h}	2.30 ± 0.06 ^{f,g}	0.17 ± 0.006 ^{f,g,h}
BP	0.14 ± 0.004 ^{g,h}	1.64 ± 0.09 ^{f,g}	0.11 ± 0.006 ^{g,h}
BP+33% carrot	0.12 ± 0.006 ^h	1.44 ± 0.07 ^g	0.09 ± 0.005 ^h
BP+1% olive oil	0.11 ± 0.01 ^h	1.36 ± 0.09 ^g	0.09 ± 0.003 ^h

*Values are mean ± standard deviation (n=3) Different letters (a-h) in the same column represents statistical differences (p<0.05)

3.4. Effect of cooking treatments and additives insertion on Rheological characteristics

3.4.1. Viscosity

Rheological starch properties with different food additives and after being applied to different cooking treatments were studied through the behavior of viscosity curves. Flow curves (Fig. 2) of all potato samples had exhibited an exponential decay of shear viscosity versus shear rate indicating a non-Newtonian, strong shear thinning behavior in agreement with several authors, and which is beneficial to be extruded through a nozzle (Dankar et al., 2018a, c; Yousefi & Razavi, 2016). Comparing figures 2a

and 2b, the first thing to be spotted is the huge difference between the viscosity axis ranges of MP samples (500-3500 Pa.s) versus that of BP (100-900 Pa.s). Moreover, MP alone recorded an initial viscosity of ~1250 Pa.s which is almost 10 times higher than that recorded by BP alone (~170 Pa.s). This again demonstrates the advanced internal structure and stability of all MP samples compared to that of BP and which could be directly linked to the lower moisture content, more compacted structure and higher mechanical characteristics recorded by that of MP samples. In this sense, Andersson et al. (1994) related cohesiveness to the viscosity, in a way that the lower the intercellular distance is, the more cohesive the product and the higher is its viscosity, in agreement with the microscopic observations (Fig.1).

Additionally, only agar combined with MP showed a distinct viscosity shape than other samples (Fig. 2a), stated by an initial increase in viscosity till a peak then followed by an abrupt decrease whereas other samples demonstrated an instant decrease in viscosity. This could be explained by the fact that agar with MP had formed a forte gelling network that is durable to breakdown. Therefore, upon applying the shear rate initially, the viscosity tends to increase due to its permanence and more particle-particle contact interaction; till it reaches a maximum strength above which it cannot hold up the applied shear rate anymore, this peak represents the viscosity value of agar with MP which corresponds to ~3300 Pa.s.

Furthermore, the effect of additives on the type of cooked potatoes can be linked by comparing Fig. 2a and 2b. It was observed that the different food additives had a more pronounced effect upon their addition to BP. Such that agar increased the viscosity of BP up to ~462% which is around 4 times more than when added to MP (an increase of ~164%). Likewise, alginate and butter exerted a high increasing effect on the viscosity of BP up to ~150% and ~87.5% respectively compared to a moderate increase of ~20% and ~12% respectively when added to MP. Even the decreasing effect of olive oil was more persistent in BP (~43% decrease) compared to (~20% decrease) in MP.

Actually, this effect reflects the internal stability of each type of cooked potatoes, and proves more that MP possessed a strong stable internal structure that is more resistant to modifications even when a profound hydrocolloid such as agar was added, whereas BP had presumably an unstable structure characterized by more weakening interactions due to boiling and which makes it more flexible and susceptible to high degrees of alterations (Ormerod et al., 2002; Yang et al., 2016).

Another thing to be noted and which was observed previously in mechanical characteristics part is the effect of carrots incorporation to potatoes, in which carrots when added to MP exhibited a slight viscosity increase (~12%) whereas when added to BP, a slight decrease in the viscosity (~31%) was detected. In fact, this could be due to the method in which carrots were cooked, when added to BP carrots were boiled as well, this means a more disintegration of the internal structure and an increase in the relative moisture percentage per material, therefore inducing a lower viscosity.

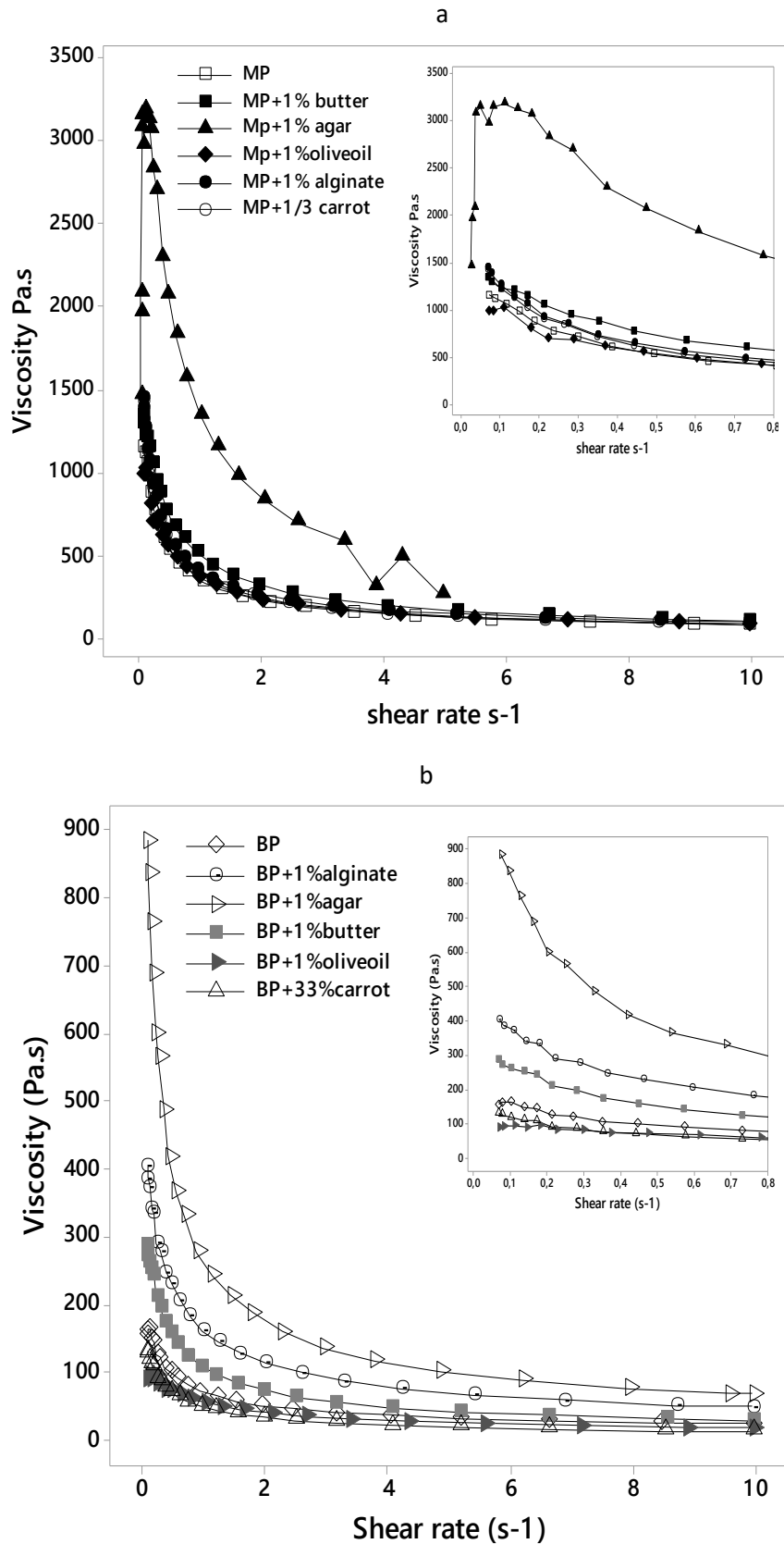


Figure 2. Typical flow curve of potato tubers with different additives (a) Microwaved and (b) Boiled. Inset: flow curves at a shear rate below s⁻¹.

3.4.2. Yield stress

Figure 3 showed viscosity versus shear stress of some studied potato samples representing their yield stress, which is an important critical stress parameter, below which the material is fully elastic and above which the structure breaks and flows (Sun & Gunasekaran, 2009). When the critical stress level (in Pa) was reached (~1250 MP+1%agar, ~330 MP+1%butter, ~280 MP, ~42 BP, ~200 BP+1%agar, ~80 BP+1%butter and ~34 BP+1%olive oil), the viscosity rapidly decreased for all samples (Fig.4). This abrupt decrease is characterized by a change in microstructure in which starch granules were unable to absorb more energy without being deformed (Tabilo-Munizaga & Barbosa-Cánovas, 2005). The yield stress results of the rest of the samples are shown in Table 1.

In fact, the higher scattered formation of starch granules in BP as revealed in Figure 1, acquired a reduced fraction of force for cellular separation which is revealed through the much lower yield stress values expressed by BP samples compared to that of MP (Fig. 3). Comparing the effect of additives on potatoes from different cooking treatments, it was revealed that agar was the additive able to present the highest yield stress, such that increasing it up to 5 times more in both MP and BP. Likewise, butter increased the yield stress around 1.2 and 2 times more in MP and BP respectively. This lengthening in yield stress is attributed to a stronger network formation within the internal microstructure of starch and that is created upon the addition of agar and butter and that provides starch with the property of being more resistant to deformation. In a previous work, Dankar et al. (2018a), it had been reported that potato puree with hydrocolloids and especially agar at 1 % exerted the highest yield stress ~1000 Pa and which is comparable to that exerted by MP+1% agar (~1200 Pa), and it was linked that both molecules (starch and agar) are polysaccharide, which upon their mixing, provided starch with better texture and appearance. On the other hand, butter presents a tendency of forming a continuous starch-lipid complex network that is stiff and stable due to the re-crystallization ability of butter (reversible binding via Vander Waals forces within the fat crystal network re-form to some extent) which enhances the re-solidification effect (a higher ratio of solid versus liquid fat), and that is the primary cause of inducing a higher consistent and stable product (Rønholt et al., 2013; Srikanlaya et al., 2017; Wright, Scanlon, Hartel, & Marangoni, 2008).

Conversely, olive oil reduced the yield stress of both BP and MP from (~42 to ~34 Pa) and from (~280 to ~245 Pa) respectively, indicating the ability of olive oil to penetrate within the starch molecule due to its flexibility, weakening the extent of bonding within the starch molecules (repulsion between the intermolecular starch chains) and producing a less resistant internal microstructure of starch to deformation in the shear stress region preceding the yield stress, while carrot addition maintained a similar yield stress to each of the cooked tubers MP or BP.

Nevertheless, alginate exposed different mode of actions according to the cooked type of potatoes in a way that it increases the yield stress of BP up to ~120 Pa (3 times more) but decreases that of MP a little down from ~280 to ~260 Pa, despite its ability to increase the viscosity of both BP and MP. This difference in the mode of action of alginate can be explained by the higher pronounced effect of alginate on the viscosity of BP as well (150 % increase), compared to a slight 20% increase in MP and which is again related to the more compacted structure exposed by MP that stimulates more the repulsive effect

between the phosphorous groups on potato and the anionic charges on alginate, creating a less continuous network characterized by less stability and reflected through a slightly lower yield stress values. Likewise, Liu et al. (2018) reported that the addition of anionic gums such as Xanthan to potato decreased its internal strength due to the repelling forces between the negatively charged gum and the anionic chain structures of potato starch.

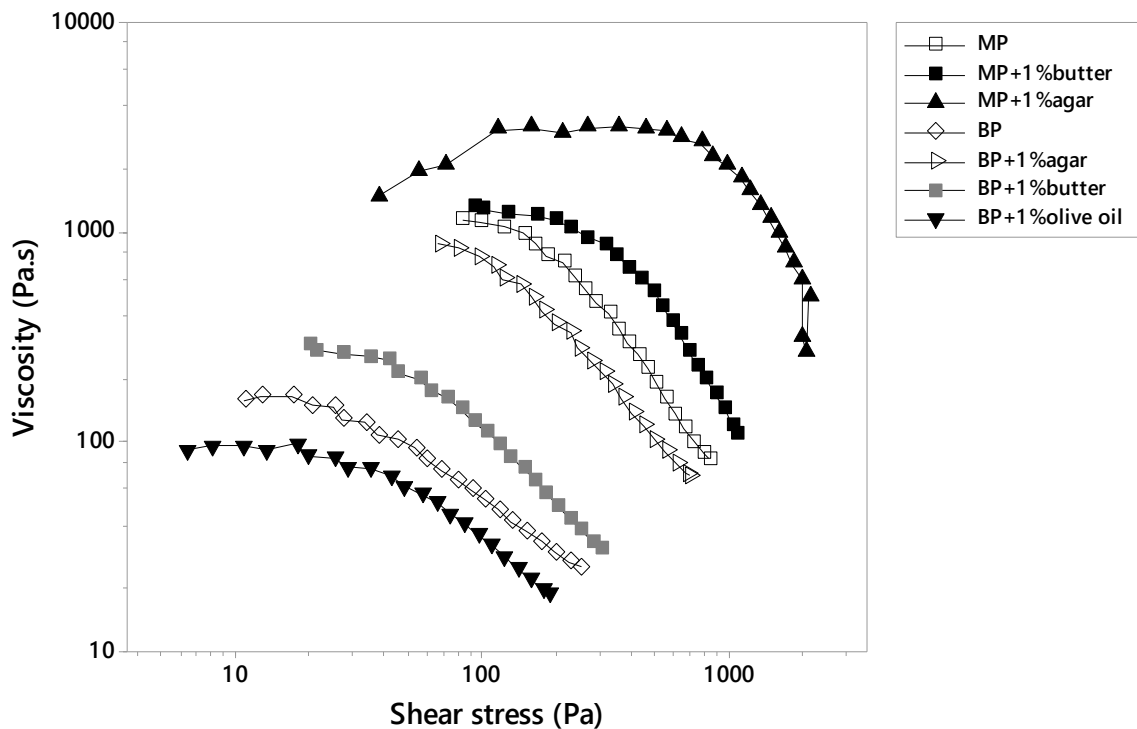


Figure 3. Measurement of the yield stress of microwaved (MP) and Boiled (BP) potato with different additives based on the stress ramp method.

3.4.3. Thixotropy

Flow curves obtained for the thixotropy of the potato samples are presented in Figure 4; the values for the thixotropic areas are expressed in Table 2. All potato samples exhibited hysteresis loop but at varying areas, indicating that all samples possessed thixotropic behavior. In a way that upon applying a work (increasing shear rate) stretching of the bonds between microstructural elements occurred, then after ceasing the work and decreasing the shear rate backward, the recovery of the internal bonding and the initial state of the material is achieved to some extent based on the stability of the material. Again, all MP samples possessed higher thixotropic areas than that of BP, it is assumed that the bigger the hysteresis loop area, the more energy is required to destroy the internal structure of the material responsible for the flow time dependence (Tárrega, Durán, & Costell, 2004), which is an implication of a stronger internal stability of the material its self and this complements perfectly with the upper discussed parts. Among the substrates added, agar also represented its ability to produce the highest thixotropic areas for both BP and

MP, followed (in decreasing order) by alginate, butter, BP alone, olive oil and carrots concerning boiled potato samples. As for the MP, samples can be classified based on the decreasing order of their hysteresis loop area as follows; MP-agar<MP-butter<MP-alginate<MP-olive oil<MP alone= MP-carrot. In fact, the major difference in the flow effect of the substrates added to the type of cooked potatoes was detected at the level of both alginate and butter. Butter effect was much enhanced in MP than in BP. Generally, butter exhibit a strong thixotropic nature, marked by a high ability of holding potential energy for the network under low stresses, which might explain why butter effect is more prominent on the yield stress and thixotropy than on viscosity. This thixotropic behavior in butter is defined by a well formed hysteresis area in Fig. 4a, in which after work applied, some of the original firmness is recovered and that could be explained by the action of two types of bonds that governs the fat crystal network and thus the lipid starch complexes. While increasing the shear rate, primary (irreversible bonds) contributing to network stiffness and secondary (reversible bonds) would be disrupted, after ceasing the shear rate effect; secondary reversible bonds recover slowly via recrystallization, yet the material may not return exactly to its original structure (Wright et al., 2008). Moreover, when presented in a more compact structure, a higher surface contact would be established between fat crystals and starch molecules, therefore inducing more its thixotropic behavior along the sample and that is characterized by a higher hysteresis loop within MP+1% butter compared to that of BP.

Another important thing that is indorsed while comparing thixotropic areas is that MP with olive oil had possessed a higher hysteresis loop than MP alone although olive oil had proven its ability to decrease the viscosity and yield stress of MP. This could be explained by taking in to consideration that hysteresis loop area is also dependent on the energy that is required to restore the material to its original state, and based on what has been hypothesized before that olive oil had the ability to penetrate within the starch molecule and cause drastic deformations within the intermolecular structure and which are enhanced under the application of shear rate, Hence a higher energy would be required in the way back to reform the original state and which is illustrated by a bigger hysteresis loop area (Table 2).

Table 2: Values of Thixotropy and Yield stress of potato tubers with different types of food additives and after being applied to two methods of cooking microwaving (MP) and boiling (BP)

Microwaved potato samples	Thixotropy (Pa.s ⁻¹)	Yield Stress (Pa)	Boiled Potato samples	Thixotropy (Pa.s ⁻¹)	Yield Stress (Pa)
MP alone	2231.00	280	BP alone	458.64	42
MP+1%butter	4633.50	330	BP+1%butter	744.97	80
MP+1%olive oil	2885.25	245	BP+1%olive oil	412.73	34
MP+33%carrot	2866.00	280	BP+33% carrot	371.73	40
MP+1% agar	1.40e+04, 87	1250	BP+1%agar	1791.67	200
MP+1%alginate	2972.00	260	BP+1% alginate	1105.78	120

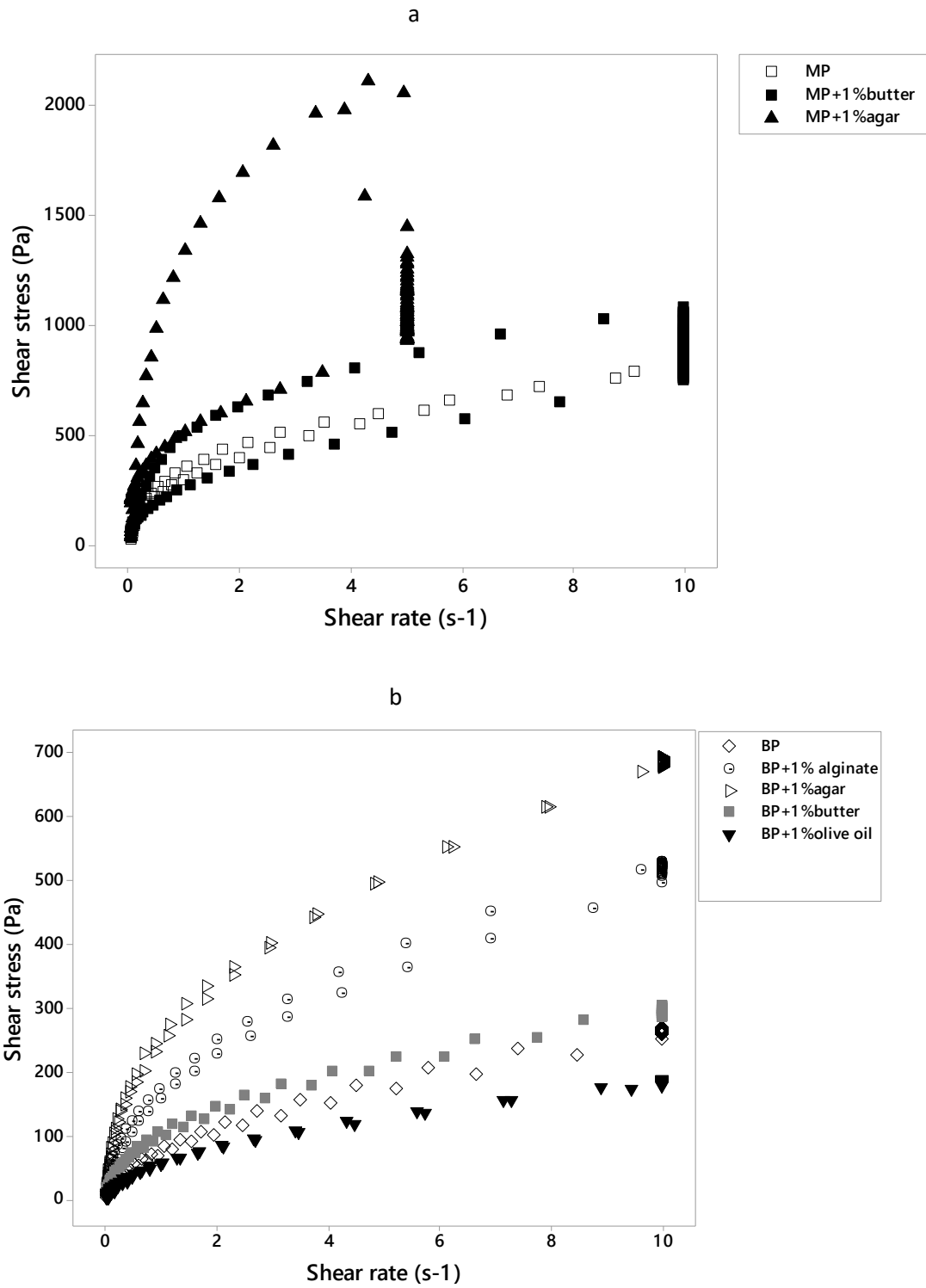


Figure 4. Measurement of the thixotropic hysteresis loop of microwaved (MP) (a) and Boiled (BP) (b) with different substrates.

3.5. Effect of the mechanical and rheological properties of the substrate on the feasibility of 3D printing

An ideal potato paste for 3D printing should have a well-defined network, sufficiently high mechanical strength and critical rheological properties; in a way that food material's viscosity should be low enough at high shear rates (pseudo-plastic) to be easily extrudable from a small nozzle tip while at the same time ensuring strong internal material structure in order to reform rapidly once deposited and to minimize shape deformation under the hydrostatic pressure of consecutive layers (pertinent information can be attained from yield stress and thixotropy) (Godoi, Prakash, & Bhandari, 2016; Liu, Zhang, & Bhandari, 2018a). These characteristics comply more while printing with MP samples since they possess generally a higher mechanical strength which provided them with a tremendous self-supporting performance post deposition and with the ability to preserve the printed shape over time (Liu, Zhang, & Yang, 2018). Yet, some differences in the aspects of printing were spotted among MP samples as summarized in Table 3. The addition of 1% agar to MP produced a very strong paste (viscosity= 3200 Pa.s, yield stress=1250 Pa and thixotropy= 8713 Pa.s⁻¹) which retarded extrusion printing, making it difficult to maintain a continuous flow, resulting in some broken deposited lines and some defected points in the final targeted shape, although the extruded layers were firm, precise and sturdily aligned above one another. Conversely, olive oil addition produced a malleable paste (decreasing viscosity and yield stress of MP), which was characterized by smooth continuous printing. However, the resulted product was less stable and exhibited some spread-ability post printing compared to other MP samples, details of the printed shape were less expressed and almost submissive as well, which is due to the lubricant soothing effect exerted by olive oil as described above. Moreover, the incorporation of 1/3 carrot, 1% alginate and 1% butter to MP produced samples with similar viscosity ranges and which had proven to be applicable in providing smooth extrusion and stable printed products but with different degrees of stability and this has been related to differences at the level of yield stress and mechanical characteristics values. In a way such that the lower mechanical characteristics values recorded by MP+1/3 carrot make it more susceptible to deformation upon removal post printing compared to the other two latter samples, whereas the high yield stress value displayed by butter enhanced the self-supporting of the printed material and increased its resistant to deformation, providing as well a creamy surface texture and attractive appearance. It has been reported that the type of fat presented in butter had the ability of both acting as a lubricant in the system (maintaining a proper viscosity), easing the flowing of the material out of the nozzle and also creating starch-lipid complexes that are stiff and stable (increasing yield stress and enhancing self-supporting behavior). Similar results have been conducted by Lille et al. (2017) who analyzed the effect of fat on printing performability by comparing between skimmed milk powder, whose printability was sticky and hard to semi-skimmed milk powder, which resulted in smooth printing with very good precise product. Furthermore, Table 3 illustrates that the printability of the control (MP alone) provided stable product but whose fill in was not properly maintained, due to some fluctuations in the thickness diameter of the extruded layers. In fact, this could be attributed to the relatively low thixotropic value expressed by MP (had the lowest thixotropic value among other samples).

On the other hand, BP samples resulted generally in softer pastes (an overall lower mechanical and rheological characteristic values), consequently resulting not only in a smooth continuous extrusion but also in an overflow of sample deposition which is not favorable to maintaining the shape of products. Although the overall shape of BP samples was likely maintained, most of the printed pattern details were hampered. Additionally, the lack of enough firmness and consistency of the material resulted in an unstable bottom supporting layer that was compressed due to its poor ability to resist the gravity of the consecutive extruded layers, leading to the observed increase in diameter and decrease in relative height of the targeted printed product (Fig. 5) (Liu, Zhang, & Bhandari, 2018a; Severini, Azzollini, Albenzio, & Derossi, 2018). Actually, this printing behavior was observed among all BP samples but to a less extent when 1% agar was imparted, since agar showed its high ability of elevating the internal stability of the material by enhancing the mechanical values, viscosity, yield stress and thixotropy of BP sample (around 5 times more as discussed above). The mode of action of agar on BP was also revealed by producing a product with better dimensional printing accuracy and with a less tendency of fluctuation and variation in the diameter thickness of the extruded layers.

Moreover, it was spotted that all BP printed samples had a fluffy surface texture compared to a firmer one in MP products and this is directly related to all the above analyzed characteristics in which BP had a higher moisture content, relatively further distributed particles, lower mechanical characteristics).

Based on these observations, it can be related that the best printing was achieved for MP+ 1%butter and MP+1% alginate which correspond to the following respective ranges of: firmness (0.77-0.80 Kg), consistency (9.16-9.87 Kg.s), cohesiveness (0.72-0.73 Kg), viscosity (1400-1500 Pa.s), Yield stress (260-330 Pa) and Thixotropy (2972-4634 Pa.s).

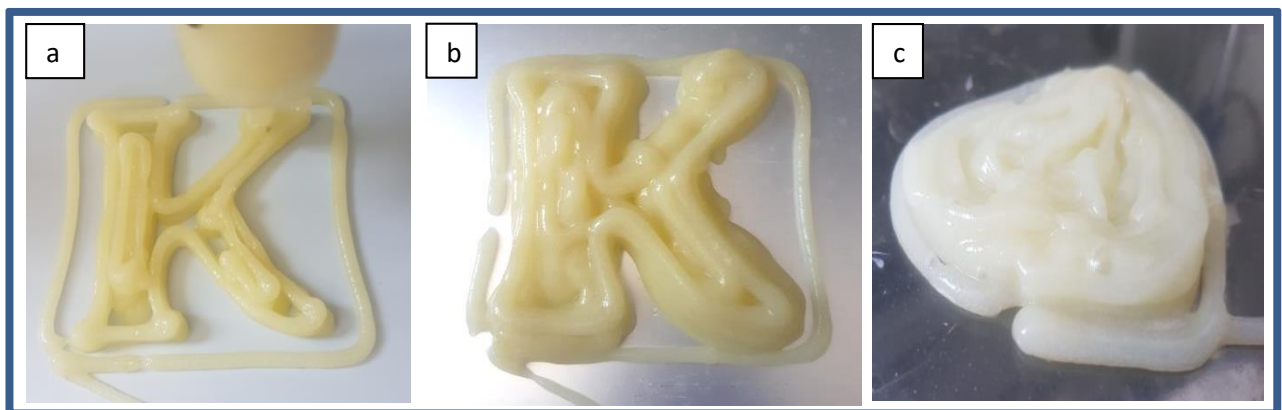




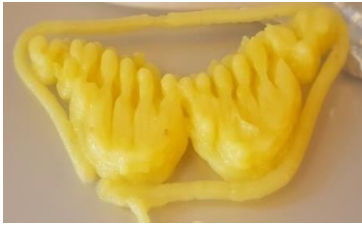
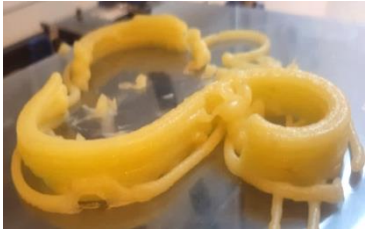


Figure 5. 3D printed shapes of BP samples with 1% agar (a), 1% butter (b) and 1% alginate (c).

Table 3: Effect of additives in microwaved potato samples feasibility during 3D printing

Microwaved potato samples with	Printed product	Advantages	Disadvantages
Alone		<ul style="list-style-type: none"> Stable end product Smooth extrusion Withstand the printed shape over time 	<ul style="list-style-type: none"> Fill in of the shape not 100% ensured
1% Butter		<ul style="list-style-type: none"> Smooth continuous extrusion Creamy surface Proper arrangement of above layers Retaining structure integrity Withstand the printed shape over time Removable 	
1% Olive oil		<ul style="list-style-type: none"> Soft lubricant surface Smooth continuous extrusion 	<ul style="list-style-type: none"> Details are submissive Less precise printing Less stable end product Spreads after printing Non-hand able post printing
1/3 Microwaved carrot		<ul style="list-style-type: none"> Soft surface Smooth continuous extrusion Hold up the weight of the up deposited layers Stable product 	<ul style="list-style-type: none"> Works better with flat-base support product Poor printing in fine-thin base supported product Sticky Susceptibility to deformation upon removal
1% Alginate		<ul style="list-style-type: none"> Stable end product with clearly observed details Layers coincide perfectly Smooth surface Withstand the printed shape over time Hand-able post printing 	<ul style="list-style-type: none"> Some plugging while extruding due to alginate coagulation ability
1% Agar		<ul style="list-style-type: none"> Easily hand-able post printing Precise definite dimension of layers Great resistance to compressed deformation Highest stable structured product for a long time post deposition 	<ul style="list-style-type: none"> Poor fluidity Retarded extrusion Non continuous flow Rough surface structure

4. Conclusions

Microwaved and boiled potato samples possessed swollen gelatinized starch granules compared to raw potato, yet microwaved potato revealed a structure of more aggregated and densely concentrated starch granules. Moreover, the lower moisture content expressed by microwaved potato provided a higher inter-cohesive starch network, subsequently leading to higher values of mechanical and rheological properties.

Additives incorporated exerted advanced modifications on the rheological properties of boiled potato, possessing a higher tendency of inducing an increasing effect (butter, alginate and agar) or a decreasing effect (olive oil).

Proper extrusion through a syringe nozzle is linked with shear-thinning pseudo-plastic ability and which all the potato samples possess. While the shape stability and self-supporting ability post-printing is linked with a strong enough yield stress, thixotropy and mechanical characteristics of the paste and which were much more profound within the microwaved potato samples.

Boiling potato samples showed poor printability, characterized by over deposition of the material and resulted in printed products with abominable dimensional printing accuracies along with hampered printed details. Whereas, microwaved potato samples possessed relatively good printability, however, the best printability was accounted with 1%butter; possessing a perfect combination of an average viscosity and a high enough yield stress and thixotropic values as well as integrated mechanical characteristics, which all combined together helped in retaining a strong self-supporting system and maintaining end stability of desired printed product, with a smooth elegant surface.

This paper reflects the basic potential of developing colorful nutritive products for customers.

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- **Chapter 10; General Discussion**

Keywords: Commercial potato, Food additives, Yield stress, Viscosity, Mechanical properties, Microscopy

3D printing is a precise digitalized process, whereby it is important to monitor several aspects to ensure its proper feasibility, starting from the printed substrate to the process parameters which should be in total accordance such as a closed loop of a specific key and locker.

Therefore, in this thesis mashed potatoes were first mixed with different food additives (agar, alginate, lecithin and glycerol) at different concentrations (0.5, 1 and 1.5%) in order to characterize the substrate property at the first place and analyze and compare how each additive would affect the yield stress, viscosity, thixotropy, mechanical properties as well as the internal microstructure of potato puree (since starch as described previously is susceptible to modifications), and based on the obtained results, try to figure out how to relate them to the process parameter of the 3D printer to assure the best printing outcome.

From all the above performed experiments, it was observed that agar and alginate had their forte ability of enhancing the viscosity and yield stress of the potato puree based on their respective used concentration and which is favorable for food technological processing. On the other hand, lecithin and glycerol produced a decreasing effect on the yield stress, thixotropy and viscoelastic properties of potato puree with this effect being enhanced at higher concentrations and therefore providing a less stable product. These results were confirmed through the SME values obtained, which were the highest for extruding puree with agar followed by alginate and the least for extruding puree with lecithin and glycerol, indicating that agar and alginate had induced more structural integrity and consistency to potato puree compared to a more disrupted one when lecithin and glycerol were added as revealed by the SEM figures. Similarly, it was related that the addition of hydrocolloids, such as carboxy-methyl cellulose, xanthan or carrageenan increase the internal strength when added to sweet potato puree, whipped cream and carrots, respectively since their relatively large molecular size, give them the ability to form conveyed network structure with the polysaccharide chains (Huang, Kennedy, Li, Xu, & Xie, 2007; Sharma, Kristo, Corredig, & Duizer, 2017; Truong & Walter, 1994; Zhao, Zhao, Yang, & Cui, 2009). On the other hand, many works illustrated that lecithin and glycerol additives have emulsifying effects and hence an ability to lessen the structural integrities of foods such as waxy maize starch, cocoa spread cream, cassava starch and dark chocolate (Afoakwa, Paterson, Fowler, & Vieira, 2009; Souza et al., 2012; Koushki & Azizi, 2015; Yang et al., 2016). Again, the values of mechanical energy confirmed these results, such that agar and alginate only showed significant difference in their textural values among other samples with their effect being higher at their respective increased concentrations.

Key words: 3D printing, Optimization, Process parameters, Commercial potato purees, Shape design, Color

Combining these data, it was predicted that additives that enhanced the stability of potato puree would have a better performance while 3D printing. Actually, this was confirmed during the 3D printing trials where first of all some process parameters (nozzle size, critical nozzle height) were optimized in accordance with the printed substrate. 4mm nozzle diameter and 1 cm nozzle height were established as the ideal values for providing printing with high precision and quality. Printing with other substrates would definitely require changing the process parameters as stated by several authors (Hao et al., 2010; Yang, Zhang, Bhandari, & Liu, 2018). Concerning the effect of the type

of printed substrate, only agar and alginate were able to provide end products with many build up layers and that hold up their shape properly post deposition. Yet, it was observed that not only the type of the substrate affects the stability of the end product but also the design geometry of the targeted printed object, such that while printing more flat shapes (with few layers) potato puree and puree with lecithin and glycerol behaved pretty well providing smooth continuous extrusion and a decent shape at the end. Besides, it is also important to highlight that when agar percentage was increased to 1.5%, difficulties in printing were faced such as retarded extrusion, broken deposited lines and improper filling due to the high gelling strength that is exerted by agar at 1.5%, this effect was also observed but to a little extent with alginate 1.5% and agar 1%. Furthermore, it was proved that the 3D printing process had no effect on the color parameters (luminosity, chroma and hue) of any of the printed samples and that those printed innovative shapes could serve as a nutritive appealing meal for people facing mastication problems as well as healthful snacks for children.

Key words: Structure conformation, long range ordering, short range ordering, XRD, FTIR

In addition, it was important to inspect the reason behind obtaining those rheological and mechanical values for the different potato blends, by conducting a further deeper investigation at the molecular level (applying FTIR and XRD) to understand better the effect of each food additive on potato puree. It was found that although potato puree consists primarily of amorphous starch (lost crystallinity); its XRD pattern is compatible with the presence of a V-type starch structure. It was also revealed that additives interact with starch at the molecular level, disrupting the OH bonds and altering the starch conformation. Small molecules such as glycerol and lecithin can enter the starch granules and induce a more intense effect on the structure as their respective concentrations increase by either suppressing the starch structure (e.g., as exerted by glycerol) or stimulating a more ordered structure upon the addition of lecithin. In contrast, long polymeric molecules such as agar and alginate interact partially via the surface of the starch granules or with just one part of the starch and thus partially modify the conformation of potato starch structure, which confirms the previous deductions from the rheological properties part.

Furthermore, an interesting remark was detected from the FTIR spectra, where it was found that the skeleton formed by the amylose/amylopectin is somehow hidden in the dehydrated potato flakes, but which was covered almost completely upon the addition of water such as to complement that of an original raw potato FTIR spectra. Hence, this proves that water molecules have a central role in the maintenance of the starch structure conformation. To verify more this hypothesis, task four was developed in order to make sure after what time of water reduction is the starch conformation altered (using this time potato tubers) and to identify whether the starch structure is modified more by the effect of the water removal or the heat treatment (microwaved and boiling).

Key words: Potato tubers, Starch structure, Lyophilization, Heat treatment, Scanning electron microscopy (SEM)

Findings showed that microwaved (MP) and boiled (BP) potato were more susceptible for water evaporation by freeze drying expressed via the following microstructural changes only after 6 hours of lyophilization; 1- obtaining an IR spectrum with much lower intensities (dried spectrum) compared to the initial spectrum, 2- undergoing a

major transformation from gelatinized swollen starch to some recoiling towards a dried starch granule that is almost the same size as that represented by RP initially (SEM figures), 3- exhibiting an increase in the intensity of their respective XRD patterns. These quick and major transformations are due to the fact that BP and MP have been previously subjected to temperature processing which had helped in losing the strong network connection between starch molecules and therefore helped in the escaping and evaporating of water (Fan et al., 2012), with this evaporation being detected at a higher rate within the MP samples (lower intensities were recorded for some FTIR peaks corresponding to water presence inside the structure at 3500 cm^{-1} , 2100 cm^{-1} and 1650 cm^{-1} respectively, also a higher increase in the peak of the XRD pattern initially compared to other samples). Wang et al. (2017) demonstrated that the high energy delivered by microwave heating facilitates the occurrence of more V-type crystals. Whereas raw potato (RP) proved relatively a very strong inter-connected amylose-amylopectin network, described by their ability to persist strongly bound water even after applying high rate of lyophilization (72 hours), some starch granules were still clearly observed under the SEM figures. Moreover, RP took around 24 hours to reach a dried stage that was characterized by some ruptured granules embedded within leached starch matrix, an FTIR spectra that resembles in intensity that of BP and MP, possessing two peaks at 485 cm^{-1} and 620 cm^{-1} and that were assigned as a distinctive for a dried potato starch spectra, and also an increase in the intensity of the XRD pattern accomplished with some shifting in peak, indicating that some molecular transformation and rearrangements are taking place within the matrix. Therefore, it was concluded that water removal to a certain extent (till achieving a dried sample) sublimates the effect of the heat processing treatment, being the major contributor in the modifications of the starch structure.

Key words: Potato tubers, Microwaved, Boiled, Food additives, Rheology, Mechanical properties, 3D printing

As a result, and based on the knowledge that starch characteristics highly relay on the present water content, it was important to take this point into consideration while developing the further experimental part, sine the amount of water present inside the sample will then define the starch characteristics which consequently affects the quality of the 3D printing process and the final 3D printed product. Thus, MP and BP have been used as the two basic samples for the 3D printing trials while adding to each different food substrates at 1% concentration with respect to the weight (butter, olive oil, alginate and agar) except for carrots which were added at a ratio of 1/3 of the respective potato weight, again to evaluate the properties of a blended substrate on the feasibility of 3D printing.

It was detected that generally MP samples showed higher intense aggregations of starch granules and lower moisture content levels (as detected before within the FTIR-XRD experiment), which consequently resulted in recording higher values of mechanical and rheological (viscosity, yield stress and thixotropy) properties (around 3.5 times more) compared to BP. Similar results were obtained by (Andersson, Gekas, Lind, Oliveira, & Öste, 1994; Yang, Achaerandio, & Pujolà, 2016; Srikanlaya, Therdthai, Ritthiruangdej, & Zhou, 2017; Liu, Zhang, & Bhandari, 2018). This made MP samples much favorable for 3D printing in providing more stable structure compared to a deformed non-well expressed design printed by BP samples. As for the effect of the substrate, it was detected that agar with MP had formed very strong entanglement networks recording the highest values for mechanical properties (significantly different from the other samples) as well as highest viscosity, yield stress and thixotropy, however this

forte ability of agar had induced some distractions while printing, a very high force was required for the extrusion of MP+1% agar out of the nozzle, the flow was non-continuous, detachable and rigid surface structure was obtained at the end. Likewise, many authors reported the un-easiness of the flow of the printed material with deposited detached lines out of the extruder when possessing high viscosity values (Hamilton, Alici, & Panhuis, 2017; Liu, Zhang, Bhandari, & Yang, 2017; Liu, Zhang, & Bhandari, 2018; Liu, Zhang, & Yang, 2018; Yang et al., 2018). Note that the mechanical values detected by MP+1% agar were higher than that when 1% agar was added to mashed potatoes and more comparable to the 1.5% agar addition range, this again explains why both samples (MP+ 1% agar) and (mashed potatoes+1.5% agar) showed some similarities in their behavior during the 3D printing process.

As for the other incorporated substrates, alginate and butter had no significant difference among their mechanical characteristics, yet some differences were inspected in their rheology. Alginate showing a little higher viscosity (illustrated by some plugging of the nozzle while extrusion), while butter exposing a higher yield stress and thixotropy, giving butter such a property of a high ability of retaining structure integrity and maintaining sample stability. In fact, many authors have illustrated that for best 3D printing, substrate should possess relatively low viscosity for smooth flow of the material while also exhibiting strong enough yield stress and thixotropy for ensuring the stability of the design post deposition (Liu, Zhang, & Bhandari, 2018; Yang et al., 2018; Zhang, Yang, & Liu, 2018). On the other hand, olive oil addition decreased both the viscosity and the yield stress of MP (Domínguez, Agregán, Gonçalves, & Lorenzo, 2016), exhibiting a smooth continuous flow while 3D printing, but also resulting in printed products with submissive details (the low value of yield stress retarded the ability of retaining the structural integrity and thus of expressing properly the fine details of the printed structure).

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- **Chapter 11; General Conclusions**

Repercussions on rheological properties:

- Commercial potato puree samples prepared from mashed potatoes and combined with different food additives at different concentrations possessed all non-Newtonian, shear-thinning behavior, which is favorable for the flow behavior through a syringe during extrusion 3D printing.
- Generally, agar and alginate demonstrated their capacity to moderately affect and stabilize more potato puree, while having an exclusive effect of acting either as an increasing or decreasing agent on viscosity according to the concentration, suggesting that alginate and agar are good and helpful options to be used in food technology processes such as 3D food printing. While, glycerol and lecithin showed strong and destabilizing effects on potato puree
- Proper extrusion is linked with shear-thinning pseudo-plastic ability and which all the samples (boiled potato and microwaved potato) combined with different additives (1% butter, 1% olive oil, 1% agar, 1% alginate, 1/3 carrot) possess.
- The cooking processes affect the rheological properties. Microwaved samples expressed higher values than boiled potato samples in terms of viscosity, yield stress and thixotropy.
- Generally, the ability of agar to produce a high gelling network was reflected by inducing the highest rheological properties among other additives for each of the microwaved and boiled potato samples.
- Olive oil acted as an emulsifier and showed a tendency of decreasing the viscosity and yield stress in both microwaved and boiled samples.

Effects on the molecular structure

- The effect of food additives on the molecular structure of potato puree prepared from commercial potato powder was investigated. Although potato puree primarily consists of amorphous starch (lost crystallinity), its XRD pattern is compatible with the presence of a V-type starch structure.
- Additives interact with starch at the molecular level, disrupting the OH bonds and altering the starch conformation. Small molecules such as glycerol and lecithin can enter the starch granules and induce a more intense effect on the structure as their respective concentrations increase by either suppressing the starch structure (e.g., as exerted by glycerol) or stimulating a more ordered structure upon the addition of lecithin.
- In contrast, long polymeric molecules such as agar and alginate interact partially via the surface of the starch granules or with just one part of the starch and thus partially modify the conformation of potato starch structure.
- Using FTIR, it was found that the skeleton formed by amylose and/or amylopectin is somehow hidden in the dehydrated commercial potato flakes but can be recovered to a great degree by adding water to the original raw potato starch structure.
- Upon applying the lyophilization process on potato tubers (raw and cooked), the rearrangement and re-association of starch molecules from gelatinized swollen starch towards a dried granule-like structure were clearly observed in SEM images for both microwaved and boiled potato samples.

- The presence of smaller sized starch granules in raw potato samples after intensive lyophilization for 72 hours indicates the presence of some water molecules strongly bound to starch in raw potato tubers.
- Two important peaks were found for dried skeletal starch of potato samples at 485 cm^{-1} and 620 cm^{-1} .
- Temperature triggered microstructural modifications in potato tuber, but water was the main contributor, leading raw potato (without being exposed to any heat treatment) to have similar chemical characteristics as those of dried microwaved and boiled samples after being totally dried (the effect of temperature was negligible or removed without water).
- Microscopic images showed that both boiled and microwaved samples possessed swollen gelatinized starch granules compared to raw potato, yet microwaved samples revealed a structure of more aggregated and densely concentrated starch granules.

Mechanical properties and printing conditions

- While performing 3D printing trials with puree samples (mashed potatoes + additives), it was found that the best extrusion conditions for 3D-printed potato purees were achieved with a 4 mm nozzle size and a 0.5 cm critical nozzle height using a printing substrate of potato puree mixed with alginate (0.5 to 1.5%) or agar (0.5, 1%) to provide the finest resolution of stable end products with many built-up layers.
- The optimal mechanical characteristic values for obtaining a good quality of 3D printed potato purees combined with additives falls within the following ranges: firmness of 0.94-2.10 kg, consistency of 11.6-26.5 kg.s and cohesiveness of 0.9-2.1 kg.
- 3D printing process does not affect the color of potato samples. Also, all printed samples showed good firmness values that fit well within the range of the maximum lingual pressure (20-40 kpa). These results will serve us to endorse the use of 3D printing with potato puree or other foods in innovative designs to produce a good substitution for the unappealing meals delivered to people facing mastication problem or promote healthy snacks for children.
- The lower moisture content expressed by microwaved samples developed an advanced inter-cohesive starch network, subsequently leading to higher values of mechanical and rheological properties.
- The shape stability and the self-supporting ability post-printing was linked to strong yield stress and mechanical characteristics of the paste, which were much more profound within the MP samples.
- All MP samples possessed relatively good printability, however, the best printability was accounted for MP+1%butter; possessing a perfect combination of an average viscosity (1400 Pa.s) that ensured smooth continuous extrusion through the nozzle and a high enough yield stress and thixotropic values (330 Pa and 4634 Pa.s respectively) as well as integrated mechanical characteristics, Firmness (0.77 Kg), consistency (9.16 Kg.s) and cohesiveness (0.72 Kg) which all combined together helped in retaining a strong self-supporting system and maintaining end stability of desired printed product, with a smooth elegant surface.

- All BP samples showed poor printability, characterized by over deposition of the material and resulted in printed products with abominable dimensional printing accuracies along with hampered printed details.

Future perspectives

- This paper reflects the basic potential of the promising tool of 3D printing, being able to link between the advanced applied technology and the food processing sector, such as developing customized colorful nutritive products for customers.
- This technology if transferred to Lebanon could be applicable in many hotels and restaurants and sure it would cause a great technological revolution by producing products of high degree of freedom in terms of designs and combined nutritive ingredients.
- 3D food printing is much intriguing and fun and could be used to create food museums such as the chocolate museum in Barcelona that is grabbing a lot of tourists monthly and thus could be an important way of increasing local income.