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Abstract:

The use of 3-Dimensional (3D) printing, also known as additive manufacturing (AM), technology in food sector has a great potential to fabricate 3D constructs with complex geometries, elaborated textures and tailored nutritional contents. For this reason, 3D technology is driving major innovations in food industry. Here, we review the use of 3D printing techniques to design food materials. Our discussions bring a new insight into how essential food material properties behave during application of 3D printing techniques. We suggest that the rational design of 3D food constructs relies on three key factors: (1) printability, (2) applicability and (3) post-processing. Especial emphasis is devoted to how the advantages/limitations of 3D printing techniques affect the end-use properties of the printed food constructs.

Keywords: 3D Printing; Additive Manufacturing; food design; material properties; printability; 3D-food construct
1 INTRODUCTION

The design of food which meets the unique demand of special consumer categories, such as, elderly, children and athletes, has raised the need for new technologies usable in the processing of additives, flavours and vitamins with tailored chemical and structural characteristics, and longer shelf-life properties. Additive manufacturing (AM), also known as solid freeform fabrication (SFF), is one of these methods that involve techniques applied for building physical parts or structures through the deposition of materials layer by layer. This is also referred as a “3D printing” in a general term.

AM was originally invented to build 3D objects based on materials, such as, metals, ceramics and polymers aiming to perform the fabrication of complexes parts in a single step. In the very first studies, the fabrication of 3D objects from polymers relied on photo-polymerization processes in which ultraviolet curable polymers were used for printing layers upon layers of solid constructs (Hull, 1986; Kodama, 1981). AM technology using photo-sensitive materials is not suitable to design food. However, curable printing inks can be attractive in the field of food packaging where there is a continued need for safer, faster and cheaper inks, functional coating, and overprint varnishes. This technique can also be applied to make films and plastic containers with gas barrier coatings to protect flavour and extend the life of packaged food and beverages.

In the food sector, a relevant application of 3D printing techniques to design food constructs was firstly reported by researchers from Cornell University who introduced the Fab@Home Model 1 as an open source design 3D printer capable of producing forms using a liquid food materials (Malone and Lipson, 2007; Periard et al., 2007). The operation system of the Fab@home printers is based on extrusion processes. In subsequent years many studies were carried out in an effort to adapt AM technology to the design of food constructs (Diaz et al., 2015a; Diaz et al., 2014b; Grood et al., 2013; Hao et al., 2010a; Hao et al., 2010b; Schaal, 2007; Serizawa et al., 2014; Sol et al., 2015). This represents a challenge because AM is not easily applied to the complex food materials with a wide variation in physico-chemical properties.
The purpose of applying AM technology to print food materials does not rely on the concentration of manufacturing processes of product in a single step, but it is associated with the design of food with new textures and potentially enhanced nutritional value. This approach is achieved by the synergetic combination of the essential constituents of food (carbohydrates, proteins and fat), bearing in mind their intrinsic properties and binding mechanisms during deposition of layers. Another trend of the AM in the food sector is the design of complex structures which are not possible to design manually by an artisan, for example. This second strength generally uses sugars and other low nutritional ingredients to produce confectionary items.

In this review, we describe the current 3D printing techniques applied to design food materials. They are classified according to material supply: liquid, powder and culture of cells. The deposition of liquid-based materials can be performed via extrusion and inkjet processes. Powder-based structures are printed by deposition followed by application of a heat source (laser or hot air) or particle binder. A brief description of cell culture deposition (bioprinting) is also described, as this technique was applied to print meat analogue. Our discussions, however, are especially devoted on how the food constituents (not cell cultures) would behave during AM processes.

This review looks into three interactive factors which we consider essentials for the rational choice of 3D printing techniques in the design of food: (1) printability, (2) applicability and (3) post-processing feasibility. We emphasize that the profitable incorporation of AM technology by food industry relies on comprehensive studies of the materials properties and optimization of multicomponent systems containing carbohydrates, proteins and fat.
Depending on the fabrication principle, number of 3D printing techniques can be introduced in the food field and adapted to meet the demand of food design and materials processing. Table 1 summarizes the 3D printing techniques currently applied for food design. The processes are grouped the type of material used: liquid, powder or cell cultures. Cell culture-based systems have been applied for printing meat. Particular attention was given to the techniques involving the essential constituents of food.

Table 1

2.1 Extrusion processes

The application of extrusion processes into AM was introduced by the Fused Deposition Modelling (FDM™) method developed by Crump (Crump, 1991; Crump, 1992) and trademarked by Stratasys Inc (Batchelder, 2012). In this method a moving nozzle is used to extrude a hot-melt filament polymer as a continuous melted threat, fusing it to the preceding layer on cooling (Fig. 1a). While FDM is primarily used for prototyping plastics, the technology has been adapted to 3D food printing for few years (Fig. 1b). Depending on the materials used in extrusion processes, the binding mechanisms may happen by the accommodation of layers controlled by the rheological properties of the materials, solidification upon cooling or hydrogel-forming extrusion.

Figure 1

2.1.1 Soft-materials extrusion

In AM, soft-materials extrusion has been applied to print 3D constructs by mixing and depositing self-supporting layers of materials such as dough, meat paste and processed cheese. The viscosity of the material
is critical to be both low enough to allow extrusion through a fine nozzle and high enough to support the structure post-deposition. Rheological modifiers, or additives, can be used to achieve the desired rheological properties but must comply with food safety standards.

Periard et al. (2007) applied extrusion at room temperature to print cake frosting and processed cheese using the Fab@home Fabrication system (Periard et al., 2007). Using the same system, Lipton et al. (2010) tested a variety of recipes to print sugar cookies. Variations on the concentration of ingredients such as butter, yolk and sugar played an important role to form natively printable dough and resistant on cooking. The authors have also used transglutaminase and bacon fat as additives to make printable scallop and turkey meat-puree, respectively. The resulted meat-based products kept their shape after cooking (Lipton et al., 2010).

Extrusion-based processes have also been employed by the Netherlands Organisation for Applied Scientific Research (TNO) scientists to print a large variety of foods using essential carbohydrates, proteins, meat purees and other nutrients extracted from alternative sources, such as, algae and insects (Van der Linden, 2015). Most recently, TNO and Barilla (Italian pasta company) have presented the preparation of 3D printed pasta using classical pasta recipes (ingredients: durum wheat semolina and water, without additives) (Sol et al., 2015; Van Bommel, 2014; Van der Linden, 2015). Another example, a company called Natural Machines created Foodini Food printer which extrudes fresh food ingredients to design meals. The extruded ingredients are used for surface filling (e.g., pizza or cookie dough and edible burger from meat paste) and graphical decoration (Chang et al., 2014; Kuo et al., 2014). **Fig. 2** illustrates some examples of 3D extrusion-based techniques applied to print pasta recipe, pork puree and pizza dough.

**Figure 2**
2.1.2 Melting extrusion

Melting extrusion has so far been applied to print chocolate 3D objects, denoting a working temperature which ranges from about 28 °C to 40 °C (Hao et al., 2010a; Hao et al., 2010b; Schaal, 2007). The formulation of chocolate self-supporting layers is challenging due to the complex crystallization behavior exhibited by cocoa butter, the main structuring material in chocolate and confections. Six different crystal polymorphs have been identified for cocoa butter (Marangoni, 2003). The correct polymorph should be produced in the chocolate for its best melting, textural and shelf-life properties.

The chocolate deposition directly into a 3D object by means of extrusion was introduced by researchers from Cornell University using a Fab@home Fabrication system (Schaal, 2007). Their studies, however, did not look at the materials properties and geometrical accuracy of the extrudate. Hao et al (2010a,b) revealed the factors influencing the geometrical precision of the chocolate deposition: (1) nozzle aperture diameter, (2) optimum nozzle height from the forming bed and (3) the extrusion-axis movement (Hao et al., 2010a; Hao et al., 2010b). The expertise of the research group led by Hao enabled the foundation of ChocEdge Ltd, a spin-off company from the University of Exeter, which pioneered the commercialization of 3D chocolate printers. Fig. 3a shows an example of 3D printed chocolate by ChocEdge. Over the years, many companies applied chocolate extrusion to build 3D objects, for example, Foodini, TNO and recently 3D Systems in partnership with The Hershey Company has introduced the CocoJet™ at the 3D Chocolate Candy printing exhibit (2014) as a breakthrough 3D chocolate printer, enable to build self-supporting layers in a 3D shape, as illustrated by Fig. 3b (3DSystems, 2015).

Figure 3
2.1.3 Hydrogel-forming extrusion

The extrusion of hygrogel-forming materials is critically dependent on the polymer rheological properties and the gel forming mechanism. At first, the polymer solution should present viscoelastic characteristic, and then turn into self-supporting gels prior the consecutive layers are deposited. To prevent premature gelation of the polymer solution inside the printer, temporal control of the gelation mechanisms must be carried out. Generally, the hydrogel-forming mechanisms can be classified in three categories: (1) chemical cross-linking, (2) ionotropic cross-linking and (3) complex coacervate formation, as depicted by Fig. 4 (Kirchmajer et al., 2015). Chemical cross-linking is unlikely to be applied for food design, as many cross-linking reagents are harmful and must be completely removed from the designed structure before they are consumed. Conversely, ionotropic cross-linking has been widely applied by food industry, especially in microencapsulation processes (Bokkhim et al., 2014; Ching et al., 2015). As an example, alginate is a polysaccharide composed of mannuronic and glucaronic acid residues (negatively charged at pH values higher than 2) which are cross-linked by calcium ions, resulting in ionotropic gel. A complex coacervate hydrogel is produced when a polyanion and a polycation are bound with one another.

The use of hydrocolloids in combination with food ingredients was reported by Cohen et al. (2009) as an alternative to create printable food materials composed of starch, protein etc. in a platform of different texture and flavours. Testing solely two hydrocolloids, xanthan and gelatin, they simulated a broad range of mouthfeels. The resultant complex coacervate formed by the mixture between xanthan and gelatine has shown granularity, which was not observed when the pristine hydrocolloids were tested (Cohen et al., 2009). This behavior can be explained by the hydrogel-forming mechanism of the combination between a polycation (xanthan) and an amphoteric polymer (gelatine). Cohen et al’s study suggests that further materials developments are required to progress in the field of food design using 3D technology. For example, the combination of alginates of different guluronic/mannuronic acid ratios and pectin of high and
A low degree of esterification has potential to reveal a new printable material for food structure design. By mixing alginate and pectin at low pH values a synergistic gel is formed in absence of Ca\(^{2+}\) and at high water activity; at this condition, neither of the pristine samples would gel. To promote gel formation, both alginate and pectin chains should be partially positively charged before interacting and methylation is recommended to avoid electrostatic repulsion (Walkenström et al., 2003).

2.2 Inkjet printing (IJP)

Inkjet Printing (IJP) technology relies on the fundamental of accumulation of droplets of material deposited on-demand by ink-jet printing nozzles, as depicted by Fig. 5 (Kruth, 2007). Inkjet printers generally operate using thermal or piezoelectric heads. In a thermal inkjet printer, the print head is electrically heated to generate pulses of pressure that push droplets from the nozzle. Piezoelectric inkjet printers contain a piezoelectric crystal inside the print head which creates an acoustic wave to separate the liquid into droplets at even intervals. Employing a voltage to a piezoelectric material arouses a prompt change in shape, which in succession produces the pressure necessary to eject droplets from the nozzle (Murphy and Atala, 2014).

The technology developed by Grood et al. (2011) for dispensing a liquid onto layers can be classified as drop-on-demand deposition (Grood and Grood, 2011; Grood et al., 2013). This technology was commercialized by the name of FoodJet printing and uses an array of pneumatic membrane nozzle-jets which layers tiny drops onto a moving object. The drops together shapes a digital image in the format of a graphical decoration, surface fill or cavity deposition (FoodJet, 2015). Inkjet printers generally handle low viscosity materials; therefore, it does not find application on the construction of complex food structure. Typical deposited materials are: chocolate, liquid dough, sugar icing, meat paste, cheese, jams, gels etc (Fig. 6).

Figure 5

Figure 6
2.3 Powder binding deposition

After extrusion processes, powder binding deposition is the second most popular system in 3D food printing. This category can be divided into three sub-types: (1) Selective Laser Sintering (SLS), (2) Selective hot air sintering and melting (SHASAM) and (3) Liquid binding (LB); which have in common the powder deposition in bed. By SLS and SHASAM the layers of powder are fused together upon application of a heat source, infrared laser and hot air, respectively. In liquid binding, there is no phase change during layer solidification: a liquid binder is overprinted onto layers of powder that are accumulated consecutively, as in directed fusion (Wegrzyn et al., 2012). Liquid-binding method has been patented as 3D printing (3DP). All three techniques require an additional step for removing the unfused material at the end of construction. **Fig. 7** shows a schematic representation of SLS, LB and SHASAM technologies.

**Figure 7**

### 2.3.1 Selective Laser Sintering (SLS)

Selective Laser Sintering (SLS) applies a laser, as a power source, to sinter powder particles. A solid structure is built by directing the laser at points pre-determined by a 3D model. The laser fuses together specific areas of the particulate powder bed by scanning cross-sections. Afterwards, the powder bed is lowered by one layer thickness, a new layer of particles is deposited on top, and the process is repeated until the object is finalised. This method can be applied to generate multiple layers of food matrix each layer containing different food material components (Diaz et al., 2014b).

The interaction between the laser beam and the particles used in SLS is important to define the feasibility and quality of any SLS process (Kruth, 2007). The selection of the laser has a relevant influence on the
fusion of powder for two main reasons: (1) the laser absorptivity of materials relies on the laser wavelength and (2) the mechanism for powder densification is affected by the input laser energy density (Gu, 2012).

Although SLS has been extensively used to sinter metals, this technology was also adapted for some food designs. Based on SLS technology, using an infrared laser that heats and sinters the material, TNO has incorporated nutritional value and flavours to powder-based 3D objects. The principle relies on the powder binding as a result of the melting fat and/or sugar of the composition (Diaz et al., 2014a; Diaz et al., 2014b). **Fig. 8** illustrates examples of 3D food objects created by TNO using SLS technique.

**Figure 8**

### 2.3.2 Liquid binding (LB)

This technology has been originally patented as 3D printing (Bredt and Anderson, 1999). During the fabrication by liquid binding, a liquid binder is ejected by a drop-on-demand print head onto a thin layer of powder following a sliced 2D profile generated by a computer 3D model. The binder plays an important role of joining adjacent particles together creating, therefore, a 3D construct. This can occur due to the dissolution-fusion or cross-linking of the particle surfaces (Peltola et al., 2008).

An example of this technology applied for food design is the 3DSysystems's ChefJet printer which uses the Z-Corp inkjet process to produce a broad range of confectionary recipes including sugar, fondant and sweet and sour candy in a variety of flavours-sculptural, as can be seen by the example illustrated in **Fig. 9** (Von Hasseln et al., 2014). Recently, TNO researchers described a liquid binding-based method called Powder Bed Printing (PBP). In this method, edible 3D objects are produced by spatial jetting of food fluid (binder) onto a powder bed containing formulated food powder composed of a water soluble protein and/or a hydrocolloid (Diaz et al., 2015b).

**Figure 9**
2.3.3 Selective hot air sintering and melting (SHASAM)

CandyFab machines, a project by Evil Mad Scientist Laboratories (California, USA), use SHASAM technology to print sugar-based 3D objects. SHASAM technology uses a narrow, directed, low-velocity beam of hot air to selectively fuse together sugar powder, building a two-dimensional (2D) picture out of fused powder. At first, the powder bed is slightly lowered then a thin flat layer of particles is spread to the top of the bed, and selectively fuse the media in the new layer. The freshly printed 2D object is indeed fused to any overlapping connected areas in the previous layer. By performing this step again, a 3D object is gradually built up. Upon finishing the 3D object, the bed is brought to its initial position, disintering the manufactured model, while the unused powder is kept for use in the construction of the next object (CandyFab, 2006). **Fig. 10** illustrates an example of 3D structure made of sugar, using SHASAM technology.

Figure 10

2.4 Bio-printing

Bio-printing have been originally applied to build tissues without any biomaterial-based scaffold. This technique relies on the precise layer-by-layer deposition of biological materials and culture of living cells. The most common technologies used for deposition and patterning of biological materials are inkjet, microextrusion and laser-assisted printing (Murphy and Atala, 2014).

Considering meat as a post-mortem tissue, researchers from University of Missouri led by Prof Gabor Forgacs proposed to construct a strip of edible porcine tissue using 3D printing technology. Their technology uses multicellular cylinders as building blocks and thus depends on self-adhering cell types. Droplets of freshly prepared multicellular aggregates (the bio-ink particles) are deposited on-demand via an inkjet nozzle into a biocompatible support structure (in this case, agarose rods). The final construct is transferred to special purpose bioreactor for further maintenance and maturation to make it appropriate for use. During maturation, the
bioreactor promotes pulsatile flow and the maturing graft develops biomechanical properties (Forgacs et al., 2014; Marga et al., 2012; Norotte et al., 2009).

Figure 11

According to Marga (2012), the bio-printed meat would find acceptance by the vegetarian community which rejects meat for ethical reasons. Upon affordable price, in the future this technology would benefit the masses with religious restrictions on meat consumption and populations with restrict access to safe meat production. The bio-printing of meat, however, shows many drawbacks to overcome, most of them associated to the spatial resolution of the final construct and long maturation processes (Marga, 2012).

2.5 Advantages/limitations of AM techniques and desirable end-use properties of 3D food structures

Although AM technologies have received a lot of attention in the field of food engineering, the advantages and limitations of 3D printing techniques and their impact on the end-use properties of the materials need to be addressed to exchange, in a profitable manner, the traditional fabrication methods by processes involving AM technology. Ideally, the end-properties related to the mechanical stability of 3D printed food should match with those in conventional manufacturing processes. And, in terms of texture design and nutritional optimization, AM technology would potentially defeat traditional fabrication methods.

Both liquid deposition and powder binding bed techniques are capable to build geometrically complex structures. Liquid-based supplies, however, afford a broad range of materials and mechanisms of binding. Printable mixtures comprised of carbohydrates, proteins and fat can be prepared by tuning the material’s properties, such as, melting and glass transition temperature, gelation and viscosity. The strong interaction between layers is the main factor affecting the stability and self-supporting properties of the final construct. For example, the melting extrusion of chocolate must avoid formation of fissures when the deposited layers
are cooled down. Presence of empty spaces between layers (as result of poor interaction) not only cause fracture of the final build but facilitate the undesirable migration of fat (fat bloom) due to the creation of preferential channels.

Powder binding bed techniques have been used to print sugar structures. Especially when heat is used as power source to bind patterns of powder (SLS and SHASAM), the lack of nutritional value in the final product makes this technique less attractive than liquid-based deposition. For this reason, toughness and uniform surface are relevant end-properties of the construct. The powder patterns formed should, in theory, resist fracture upon presence of a crack. The choice of food grade binder can restrict the application of 3DP technique. In addition, weak interactions between powder and binder may lead to rough surface and unstable buildings.

Self-supporting layers, palatability and visual appeal are common desirable end-properties of the 3D food constructs designed via liquid-based deposition, powder binding deposition and bio-printing. Particularly, for the resulting material of bio-printing processes where 3D constructs of meat is designed by depositing biological material (cell cultures), visual appeal would rather relevant than liquid and powder-based AM techniques. This is because bio-printing is an unusual technique in the field of food engineering and the consideration of meat as a post-mortem tissue might cause negative effect on the acceptance of the product for consumption.

3 RATIONAL CHOICE OF 3D PRINTING TECHNIQUE BASED ON MATERIALS PROPERTIES

Originally, AM technologies were applied for building 3D objects by means of layering deposition of non-food materials, such as, metals, ceramics and synthetic polymers in processes involving the use of organic solvents, extreme temperature conditions or crosslinking agents that do not comply with food safety standards. Therefore, one of the critical challenges in the 3D food printing field has been to align food grade materials with printing processes. Three food materials property related critical factors are suggested here for the rational design of 3D food structures:
(1) Printability: This feature relies on how the properties of the material enable handling and deposition by a 3D printer and hold its structure post-deposition. The printability of liquid-based AM technologies, such as, drop-on-demand techniques is influenced by the material viscosity or rheological properties. In addition to rheological properties, 3D printing based on extrusion techniques can be affected by specific gelation mechanisms (crosslinking) and thermal properties (melting point and glass transition temperature). Properties like particle size distribution, bulk density, wettability and flowability can also exert influence on powder-based 3D printing;

(2) Applicability: AM technologies can be attractive by their capability of building complexes structures and textures. In addition, AM becomes more interesting when nutritional value is incorporated to the unique designed structures. The applicability of AM technology is also ruled by the materials properties.

(3) Post-processing: Ideally, the 3D construct of food should resist to post-processing, such as, baking in an oven, being cooked by immersing in boiling water or deep frying. In the pursuit of a cooking-resistant structures, an accurate selection of materials with appropriate physical-chemical, rheological and mechanical properties are essential.

We emphasize that printability, applicability and post-processing feasibility can be achieved by controlling the physical-chemical, rheological, structural and mechanical properties of the materials (Fig. 12). Knowledge of the essential constituents of food (carbohydrates, proteins and fat) and how their properties influence AM technology is critical to guarantee quality in the end-use product.

Figure 12

15
3.1 Essential constituents of food and their feasibility for 3D printing

As discussed earlier, the food materials should be flowable (liquid or powder) during deposition and also support its structure during or after the deposition. The flowability is achieved by plasticization and melting. The self-supporting structure can be achieved by the reverse process or by gelation by variation of temperature and/or by an additive. In a multicomponent system, variations in the fraction of proteins, carbohydrates and fat will definitely affect the melting behaviour, glassy state and plasticization of the food-materials during liquid-based and powder based 3D printing processes. It has been well reported that the plasticization phenomena by water depresses the glass transition temperature of food polymers such as starch, gluten and gelatin (Bhandari and Howes, 1999; Bhandari and Roos, 2003; Haque and Roos, 2006; Roos, 2010; Slade and Levine, 1994).

3.1.1 Carbohydrates

The Tg of food systems is strongly dependent on the carbohydrates fraction, which may vary from simple sugars (e.g., glucose) or disaccharides (e.g., sucrose and lactose) or may encompass polydisperse carbohydrate oligomers such as maltodextrins. High molecular weight polymeric carbohydrates can be unprintable without modification or addition of water or gelling agent. High molecular weight carbohydrates, such as, maltodextrins have higher Tg (for pure starch, ranging between 100 °C to 243 °C) than simple sugars, e.g. fructose glucose and fructose with Tg values at about 31 °C and 5 °C, respectively (Adhikari et al., 2000; Bhandari et al., 1997). Slade and Levine reported diverging influences of sugars on the Tg for food systems which deserves consideration for their use in AM techniques. In the presence of water and heat, when the intermolecular bonds of starches are broken down allowing hydrogen bonding sites to engage more water (gelatinization), sugar can act plasticizer in low-moisture systems, by playing a role as a co-solute with starch depressing the Tg. Control of glass transition temperature is important to make the deposited material to be set in order to support its own structure after deposition.
The crystallization state of the sugars is important in the 3D printing of chocolate by melting extrusion (section 2.3.1). Upon extrusion, in milk chocolate, sucrose and lactose must be fully crystallized. The advantages of a highly crystalline crumb are the reduced amorphous glassy sugar remained to trap fat. Consequently, less fat is necessary to adjust the final chocolate viscosity. Below the Tg, for sucrose in water, viscosity is increased enabling the growth of many crystal nuclei. By releasing fat from the amorphous sugar, the chocolate manufacture is facilitated because the overall fat required to reach the ideal viscosity is reduced (Gonçalves and da Silva Lannes, 2010).

Sugars comprise the major component of particulate systems used in powder bed binding processes (section 2.3). In this category of AM technology, the ongoing interaction between layers promoted by a heat source (laser or hot air) is based on the melting point range of the material. Parameters, such as, powder density and compressibility also deserves attention, as they have an important effect on the powder flowability inside the vessel which, in turn, contributes for the formation of patterns when the heat source is directed to the powder bed (Berretta et al., 2014; Schmid et al., 2014). Powder flowability of the sugars inside build platform together with wettability of the powders is a critical parameter for liquid-based 3D processing (section 2.3.2). The flowability plays an important role when the powder is spread and should allow building up thin layers. Low flowability leads to insufficient recoating and high flowability results in powder bed instability. Wettability of particles is also important as the volume of binder dispersed into the powder bed and also the amount of binder absorbed by the particles governs the resolution and mechanical/structural properties of the constructs. Low wetting of fine particles give rise to powder bed rearrangement and high wettability together with slow powder reaction may reduce the smallest feature size. Particle size distribution is another important parameter which may alter the powder bulk density and pore size distribution within the and consequently affects the drop penetration behavior of a water-based binder. The interactions between powder and binder can be related to adhesive forces or chemical reactions (Shirazi et al., 2015). For food design, water-based binder is probably a better alternative, as polymeric binders may give rise to undesirable non-food safety products.
Hydrocolloids are hydrophilic polymers originated from vegetable, animal, microbial or synthetic sources, which form colloidal dispersions in water. In liquid-based AM techniques, hydrocolloids may combine with food ingredients via gelation mechanism giving rise to a different rheological behavior of the mixture. This approach has been demonstrated by Cohen et al. (2010) as a potential alternative to create a wide range of simulated textures of food using only the combination of xanthan gum and gelatin with flavoring agents (Cohen et al., 2009). In powder-based AM techniques, Diaz et al. (2015) have recently reported that hydrocolloids act as a binder component of an edible powder formulation and enhance the control of the migration and flow of the liquid spray into the powder bed during printing. They suggested that the content of hydrocolloid in the powder composition should ideally lie in the range 0.1-2.0wt.%, based on the total dry weight of the composition (Diaz et al., 2015a; Diaz et al., 2015b).

3.1.2 Proteins

Food proteins are composed of a mixture of amino acids containing negative and positively charged functional groups. Proteinaceous polymers can be positively or negatively charged depending on the solution pH and the isoelectric point (pI) of the protein. At pI proteins will show aggregation. This is a very attractive feature for liquid-based AM processes ruled by the particle based-gelation and hydrogel-forming mechanisms described in the section 2.1.3. New textures can also be created by the intercalated deposition of layers of food proteins with polysaccharide materials, such as, gelatin and alginate during AM processes. The application of external stress (temperature or mechanical strength) or compounds (e.g., strong acid or base) can also be incorporated to AM technologies promoting, therefore, aggregation and denaturation of proteins as an alternative to design different textures.

Food proteins can also have their conformation changed by the addition of enzymes. Lipton et al. (2010) have tested transglutaminase as a food additive to build complex geometries out of meat. By incorporating transglutaminase to the meat puree right before printing, the material retained its rheological properties, however, a new protein matrix has been developed (Lipton et al., 2010). This behavior can be explained by
the fact that enzymes, such as, transglutaminase catalyses the formation of covalent bonds between lysine and glutamine residues in a calcium dependent reaction. Hence, the proteins present in the meat puree were enzymatically crosslinked; giving rise to self-supporting hydrogels (Davis et al., 2010). This approach brings insights to the development of 3D printed meat.

Gelatin can be one of the potential candidates for 3D printing (Diaz et al., 2015a; Diaz et al., 2015b). Gelatin, a derived protein from the irreversible breakdown of the fibrous structure of the collagen (alkali or acid treatment), is a potential candidate to be used as an ingredient of 3D printer inks. Gelatin gel possesses a unique ‘melt-in-mouth’ texture that provides appreciable mouthfeel and flavour perception. Air-dried gelatin dissolves instantaneously in warm water (approximately 40 °C) when the hydrated particles form flexible single random coils. Upon cooling, junction zones are formed by small segments of polypeptide chains reverting to the collagen triple-helix-like structure, leading to gelation (Burey et al., 2008; Ward and Courts, 1977). Gelatin exhibits Newtonian flow in dilute solution except when extended by charged groups. Hence, the used of flexible protein molecules, such as, gelatin in 3D-extrusion processes must bear in mind that charges on the molecules give rise to relevant effects on viscosity. When both positive and negative charges are present, the molecule is fully contracted at the isoelectric point and a minimum in the viscosity is observed. A change in pH in either direction alters the ionization of the functional groups and increases the preponderance of either positive or negative charges. The mutual repulsion of similar charges extends the molecule and enhances the viscosity. At pH values where the molecule depicts its maximum extension, it may be less flexible and lead to non-Newtonian behavior. The shear rate is another important factor affecting the flow of proteins like gelatin in extrusion processes. Irreversible reduction in viscosity can be observed upon shear application. And, extreme conditions of very high shear rate may lead to a non-Newtonian behavior (Kragh, 1961).
3.1.3 Fat

Fat is formed by the reaction between three fatty acid molecules (long, straight chain carboxylic acids) with a glycerol molecule to yield a triglyceride (TAG). The TAG composition and structure can affect the material formulation for AM technology and, consequently, the end-use functional properties of the material, such as melting point range, solid fat index, and crystal structure. As an example, it is well-known that the quality of meat in terms of texture, colour and shelf-life is closely related to the TAG composition. This is because the different melting points of fatty acids have significant effect on firmness or softness of the fat in meat. Colour is affected by the content of fatty acids, as solidified fat with a high melting point appears whiter than liquid fat. Shelf-life of meat (rancidity and colour deterioration) is also influenced by the composition of fatty acids, based on the fact that unsaturated fatty acids, especially those with more than two double bonds, can be easily oxidised (Wood et al., 2004). AM technology has potential to help achieving high quality meat-based products, with texture developed for special consumer categories (e.g., elderly and children), by tuning the content of TAGs throughout the deposition of layers of meat paste.

Fatty acids with larger number of carbon atoms depicts higher melting point. In an opposite way; larger number of double bonds result in lower melting point. Hence, the TAG composition can help to regulate the melting point of the deposited layers and determine their self-supporting properties prior and post-processing. Particularly in melting extrusion-based AM processes, where the mixture is melted upon application of heat and solidified by cooling. Lipton et al. (2010) optimized the content of butter fat in traditional dough recipes to avoid liquefaction of the printed structure when baked (Lipton et al., 2010). The same researchers have used bacon fat as flavour enhancer to print turkey meat puree in combination with transglutaminase additive.

In the melting extrusion-based AM technique applied to print chocolate 3D structures, it is absolutely essential to understand the mechanisms of fat crystallization and how they contribute for the manufacturing of self-supporting layers. Cocoa butter, the main structuring material in chocolate, can develop six different
polymorphic forms, noted from I to VI in increasing order of melting points (γ: -5 to +5°C; α: 17-22°C; β_2 and β_1': 20-27°C; β_2 and β_1: 29-34 °C) (Marangoni, 2003). The polymorphism of cocoa butter has a relevant impact on the organoleptic and physical characteristics of the final products (self-supporting layers, gloss and blooming during storage).

4 SUMMARY AND FUTURE DIRECTIONS

As reviewed, the design of 3D food constructs via AM technology is strongly dependent on the material properties and binding mechanisms. In recent years, great efforts have been made aiming to achieve end-properties of 3D constructs having end-use properties aligned with or more advantageous than those obtained through traditional manufacturing method. However, there are still many barriers to overcome for AM technology to be incorporated in place of traditional manufacturing fabrication processes. From our point of view, many of the challenges faced by AM technology, in the field of food engineering is attributed to (1) process productivity and (2) product innovation and functionality.

Process productivity can be achieved by enhancing the cost-effectiveness which, in turn, is closed related to the properties of the materials and speed of deposition of layers. As an example, the resolution of extrusion processes, the most common AM technique, is attained through the deposition of very thin layers. This increases the time and cost of operation; placing AM in an unfavourable circumstance in comparison to traditional manufacturing techniques. In the current scenario of substantial advance in the methods of layer deposition, this engineering barrier faced by the AM technology is likely to determine the commercialization underpinning of 3D printers.

AM is a powerful technology which shows capability to promote product innovation and functionality. We noted, however, quite a few active groups of researches in the field of AM exploring this feature. Most of the 3D food printers are used to build geometrically complex structures without nutritional value. To
aggregate value to the final product or design novel textures, correlations between materials properties and factors influencing a rational design of food structures need to be addressed.

We reinforce that materials properties play important role on the achievement of printability, applicability and resistant-constructs upon cooking post-processing. Foreseeing and understanding how the essential constituents of food (carbohydrates, proteins and fat) behave during AM processes bring useful insights into the AM of food structures which will help future research into the optimization of printable multicomponent mixtures.

ACKNOWLEDGMENT

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with position coordinates for movement of tool, instructions for exchange of capsule holders, and adjustment of heating device. NATURAL MACHINES LLC (NATU-Non-standard).


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applying edible binders to regions of the successive layers of the food material. 3d Systems Inc (Thde-C) 3d Systems Inc (Thde-C).


**Table 1:** List of 3D printing techniques applied for food design.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Principle</th>
<th>Binding Mechanism</th>
<th>Application</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Supply: liquid</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soft-materials</td>
<td>Extrusion and deposition</td>
<td>No phase change, accommodation of layers controlled by rheological properties of</td>
<td>Frosting, processed cheese, dough, meat puree</td>
<td>(Chang et al., 2014; Kuo et al., 2014; Lipton</td>
</tr>
<tr>
<td>extrusion</td>
<td></td>
<td>material</td>
<td></td>
<td>et al., 2010; Periard et al., 2007)</td>
</tr>
<tr>
<td>Melting extrusion</td>
<td>Extrusion and deposition</td>
<td>Solidification upon cooling</td>
<td>Chocolate, confection</td>
<td>(Hao et al., 2010b; Schaal, 2007)</td>
</tr>
<tr>
<td>Hydrogel-forming</td>
<td>Extrusion and deposition</td>
<td>Ionic or enzymic cross-linking</td>
<td>Xanthan gum and gelatine</td>
<td>(Cohen et al., 2009)</td>
</tr>
<tr>
<td>Extrusion</td>
<td></td>
<td>No phase change, accommodation of layers controlled by rheological properties of</td>
<td>Chocolate, liquid dough, sugar icing, meat paste, cheese, jams, gels</td>
<td>(Grood and Grood, 2011)</td>
</tr>
<tr>
<td>Ink Jet Printing</td>
<td>Drop-on-demand deposition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Supply: powder</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid binding</td>
<td>Powder binding and binder drop-on-demand deposition</td>
<td>Adhesive forces or chemical reactions between powder and binder</td>
<td>Chocolate</td>
<td>(3DSystems, 2015; Diaz et al., 2015a; Diaz et al., 2015b; Von Hasseln et al., 2014)</td>
</tr>
<tr>
<td>Selective Laser</td>
<td>Powder binding and heat</td>
<td>Sintering and melting of sugar/fat</td>
<td>Sugar, Nesquik</td>
<td>(Diaz et al., 2014a; Diaz et al., 2014b)</td>
</tr>
<tr>
<td>Sintering</td>
<td>source (laser)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hot air sintering</td>
<td>Powder binding and heat</td>
<td>Sintering and melting</td>
<td>Sugar</td>
<td>(CandyFab, 2006)</td>
</tr>
<tr>
<td>and melting</td>
<td>source (hot air)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Supply: cell</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bioprinting</td>
<td>Drop-on-demand deposition</td>
<td>Self-assembly of the cells</td>
<td>Meat</td>
<td>(Forgacs et al., 2014; Marga, 2012)</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

**Figure 1:** Schematic diagram of 3D food printing extrusion processes.

**Figure 2:** Examples 3D printing technique based on soft-material extrusion: (a) pasta recipe (Van der Linden, 2015), (b) pork puree (Van Bommel, 2014) and (c) pizza dough. Image (c) was reproduced with permission of Natural Machines from data available at https://www.naturalmachines.com/press-kit/.

**Figure 3:** Examples of 3D printing technique based on melting extrusion: chocolate constructs printed by (a) ChocEdge and (b) 3DSystems (3DSystems, 2015). Image (b) was reproduced from data available at http://www.chocedge.com/creations.php.

**Figure 4:** Schematic illustration of hydrogel-forming mechanisms: chemical cross-linking, ionotropic cross-linking and complex coacervate formation. Adapted of (Kirchmajer et al., 2015).

**Figure 5:** Schematic diagram of Inkjet printing technology.

**Figure 6:** Examples of 3D printing technique based on inkjet technology: (a) graphical decoration, (b) surface filling and (c) cavity deposition. Images (a), (b) and (c) were reproduced from data available at http://foodjet.com.

**Figure 7:** Schematic diagram of Powder Binding technologies (SLS and LB).
Figure 8: Examples of 3D printing technique based on SLS technology: (a) Sugar, (b) Nesquik and (c) Curry Cube, Paprika Pyramid, Cinnamon Cylinder and Pepernoot Pentagon constructs printed by TNO (Van Bommel, 2014).

Figure 9: Example of 3D printing technique based on LB technology: 3D chocolate structure. The image was reproduced from the data available at http://www.3dsystems.com/culinary/gallery.

Figure 10: Example of 3D printing technique based on SHASAM technology. Image reproduced with permission from Windell H. Oskay, www.evilmadscientist.com.

Figure 11: Schematic illustration of bio-printing technology applied to construct meat.

Figure 12: Parallel between materials properties and factors to consider for the rational design of 3D food structures.
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RESEARCH HIGHLIGHTS

1) 3D food printing technologies overview
2) Design of new textures and tailored nutritional content
3) Design of complex geometries of food structure
4) How 3D printing techniques are influenced by material properties?
5) Relation between advantages/limitations of 3D printing techniques and the end-use properties of 3D printed food
6) Rational choice of 3D printing technique to design food