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# Plasticized Protein For 3D Printing By Fused Deposition Modeling

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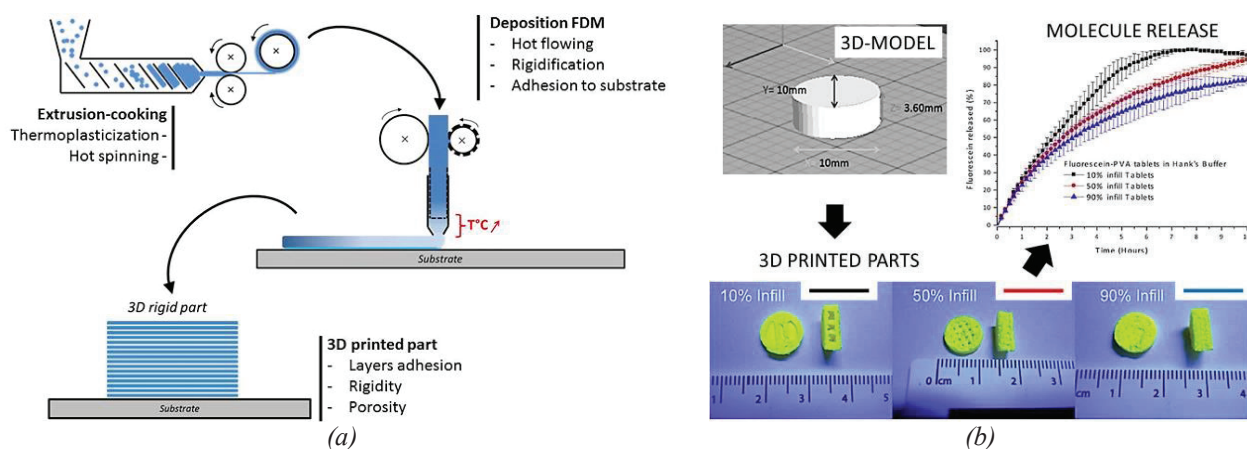
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**Abstract.** The developments of Additive Manufacturing (AM) by Fused Deposition Modeling (FDM) now target new 3D printable materials, leading to novel properties like those given by biopolymers such as proteins: degradability, biocompatibility and edibility. Plasticized materials from zein, a storage protein issued from corn, present interesting thermomechanical and rheological properties, possibly matching with AM-FDM specifications. Thus commercial zein plasticized with 20% glycerol has a glass transition temperature ( $T_g$ ) at about 42°C, after storage at intermediate relative humidity (RH=59%). Its principal mechanical relaxation at  $T_\alpha \approx 50^\circ\text{C}$  leads to a drop of the elastic modulus from about 1.1 GPa, at ambient temperature, to 0.6 MPa at  $T_\alpha+100^\circ\text{C}$ . These values are in the same range as values obtained in the case of standard polymers for AM-FDM processing, as PLA and ABS, although relaxation mechanisms are likely different in these materials. Such results lead to the setting up of zein-based compositions printable by AM-FDM and allow processing bioresorbable printed parts, with designed 3D geometry and structure.

## INTRODUCTION

Additive Manufacturing (AM), or 3D printing, is the set of processes for the realization of an object layer by layer from a digital three-dimensional model [1]. It is thus opposed in principle to usual machining where the final part is obtained by removing material from a bulk. The main additive manufacturing processes were initiated for rapid prototyping of synthetic polymers and metals from the 1980s [2]. They allow now the making of functional finished parts. Applications can be found in different fields as for the production of prostheses or matrices for cells growth, in the biomedical field [3], elements of tooling or complex mechanical parts [4], or even foods [5]. The main advantage of additive manufacturing is the short transition from the design to the realization of parts. Furthermore, a reverse engineering approach is applicable with AM techniques, where a finished part with certain final characteristics (e.g. mechanical, porosity) can be obtained by 3D printing from a digital model providing the desired properties [6]. Additive fabrication techniques are particularly of interest in the medical field, especially in tissue engineering. They allow realizing porous matrices, or obtaining architected materials close to the natural structures of the targeted tissue, for obtaining implantable devices [7, 8]. The geometry and porosity of finished 3D printed parts, assessable by 3D-imaging techniques such as X-ray tomography per example, are directly controlled by the process for printable materials with well-defined rheological and thermal properties, without any mold. This

contrasts to other deposition methods of porous materials, like electrospinning, used in the biomedical field, for the production of cell culture media [9]. Regarding polymers, one of the widespread techniques is the Fused Deposition Modeling (FDM). It is based on the deposition layer-by-layer at high temperature of a molten thermoplastic polymer (e.g. ABS and PLA), through a nozzle, on a solid substrate. Initially, the thermoplastic material is shaped as a filament, obtained by a previous extrusion step and which allows the feeding of the 3D printer where a viscoelastic form allows the molten material to flow and to adhere on the substrate for the first layer (Fig.1-a). The deposited material must solidify quickly, by lowering its temperature below its glass transition temperature,  $T_g$ . The upper layers of the deposited material must adhere to the previously deposited layer so as to obtain a finished solid part. The FDM 3D printer allows movement in a (x, y) plane during the deposition of a given layer and provides more or less material during stages of acceleration or stop, respectively, following the pattern of the 3D digital model. So as to create an upper layer at the end of a completed one, the nozzle is moved to an upper position on the z-axis. In the case of FDM applied to the pharmaceutical field, the manufacture of materials with specific porosity (e.g. variable density, or deposition patterns during filling) allows to produce innovative 3D printed medicines for the controlled release of active constituents. As an example, in a printed part made from PVA, 100% fluorescein, taken as a model molecule, can be released under simulated physiological conditions in less than 6 hours with 10% density of the printed filling, while more than 10 hours are required for 50% or more (Fig.1-b) [10].



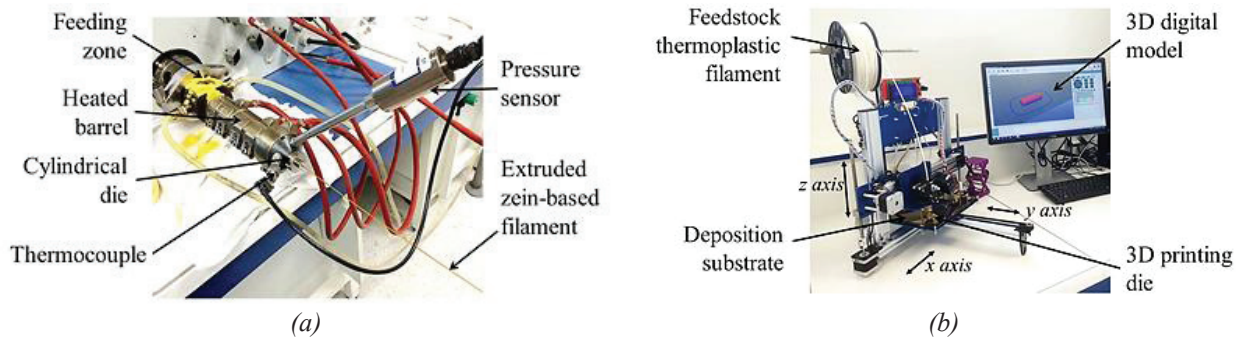
**FIGURE 1.** Scheme of the main steps and characteristics of additive manufacturing by Fused-Deposition Modeling, FDM (a). Drugs models from soluble polyvinyl alcohol (PVA), 3D printed by FDM: impact of the porosity of the printed filling on the release kinetics of a control molecule (fluorescein) based on Goyanes et al. [10] (b)

Now, FDM should be improved, in particular by the increase of speed and print resolution. Progresses should also involve the development of new 3D printable materials targeting adequate behavior for FDM like rheological properties, adhesion ability and mechanical properties [11]. Biopolymers are good candidates to obtain 3D printed parts with novel properties, such as biodegradability, or biocompatibility. The present work focuses on a vegetal protein : zein, a corn storage protein which represents about 5% of its dry weight and is part of the prolamins family [12]. It is a by-product of starch and bioethanol production, used as a water barrier in food or pharmaceutical industries and for the production of degradable plastics [13]. Its amino acids sequence, rich in apolar residues (>50%), leads to hydrophobic properties. Interactions with polar compounds are possible, because its structure presents glutamine turns. Then, zein can be thermoplasticized after blending with polar plasticizers as glycerol, triethylene glycol, or even hydrophobic fatty acids, and submitted to a thermomechanical treatment, like extrusion [14, 15]. For a content of 22% glycerol (w/w), it presents a glass transition temperature,  $T_g$ , at about 60°C, and a storage modulus,  $E'$ , at about 1GPa, in ambient conditions [16]. Plasticized zein, added with paracetamol, has been recently considered as extruded-molded caplets for controlling drug release [17]. Thus, this protein is a promising compound for processing as a molten thermoplastic biopolymer, in the case of Fused Deposition Modeling, to obtain tridimensional structured parts presenting a defined porosity, which could be used for the controlled release of bioactive molecules. The present work proposes to investigate 3D printing abilities of plasticized zein and understand structure-properties relationships possibly leading to 3D printed parts with targeted structure and mechanical properties.

## MATERIALS AND METHODS

### Raw Materials and Their Processing (Extrusion & 3D-Printing by FDM)

Zein from corn (Ref.Z3625) and glycerol were purchased from Sigma-Aldrich (F-38, Saint-Quentin Fallavier). The moisture content was determined by thermogravimetry after 2hr at 130°C (TA Instruments, F-78 Guyancourt). Zein and its plasticized compositions were obtained after blending with 10% (Z10GLY), 20% (Z20GLY) and 30% glycerol (Z30GLY), based on the zein weight. Samples were extruded using a SCAMIA single-screw device (F-91 Crosne) equipped with a 200 mm long barrel (screw L/D=10) and a cylindrical die ( $\text{Ø}_{\text{die}}=1.7\text{mm}$ ). The screw speed was 20 rpm and temperature was set at  $T_{\text{die}}=130^\circ\text{C}$  (Fig.2-a), leading to an average flow rate at  $Q\approx 2\text{g/min}$ . A 3D Printer (ORDBot-Hadron,  $\text{Ø}_{\text{die}}=0.5\text{mm}$ ) and standard synthetic polymers as feedstock filaments for 3D printing by FDM (*i.e.* Acrylonitrile Butadiene Styrene -ABS- and Polylactic Acid -PLA-) were purchased from eMotion Tech (F-31 Toulouse) with a printed volume about  $20^3\text{cm}^3$ , Figure 2-b.



**FIGURE 2.** Extrusion of a thermoplasticized zein-based filament (a). FDM 3D Printer, ORDBot Hadron, here presented with PLA filament feedstock ( $\text{Ø}_{\text{filament}}=3\text{mm}$ ) (b)

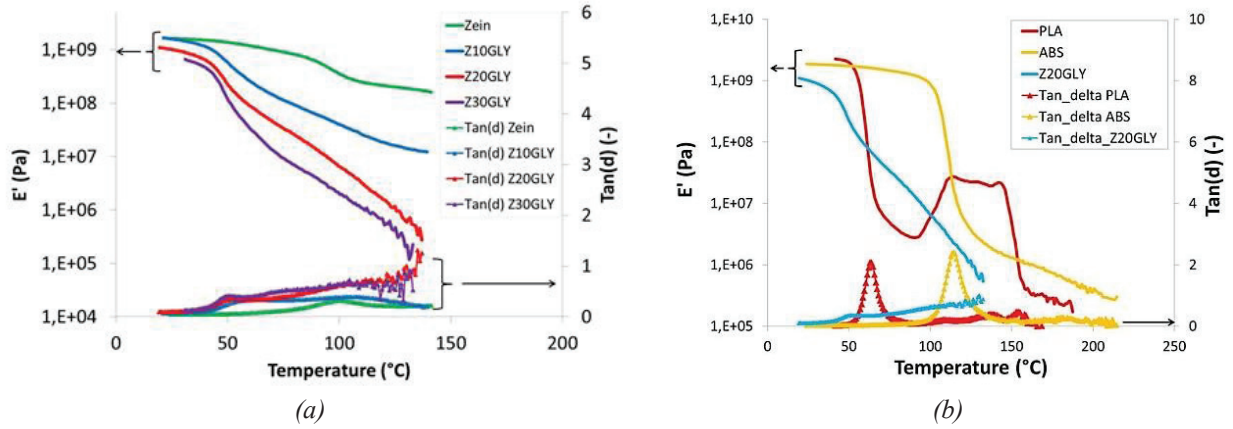
### Glass Transition Temperature and Thermomechanical Properties of Zein-based materials

To determine the glass transition temperature, thermograms were recorded with an automated differential scanning calorimeter DSC (Q100, TA Instruments, F-78 Guyancourt). Each specimen (10 mg) was placed into a sealed stainless-steel cell. Measurements were performed at 3 °C/min from 10 to 140 °C during a second scan, to previously delete any thermal event due to aging during storage. Extruded cylindrical samples ( $\text{Ø}\approx 1,75\text{mm}$ ), cut in 20mm long specimen, were submitted to Dynamic Mechanical Analysis, DMA (DMA-50N-O1dB, Metravib, F-59 Lyon). The mechanical active length, between the grips, was 10 mm and extrudates were characterized in a tensile mode at 1 Hz, with a strain set at 0.1% and heating rate of 3 °C/min, up to 160°C.

## RESULTS AND DISCUSSIONS

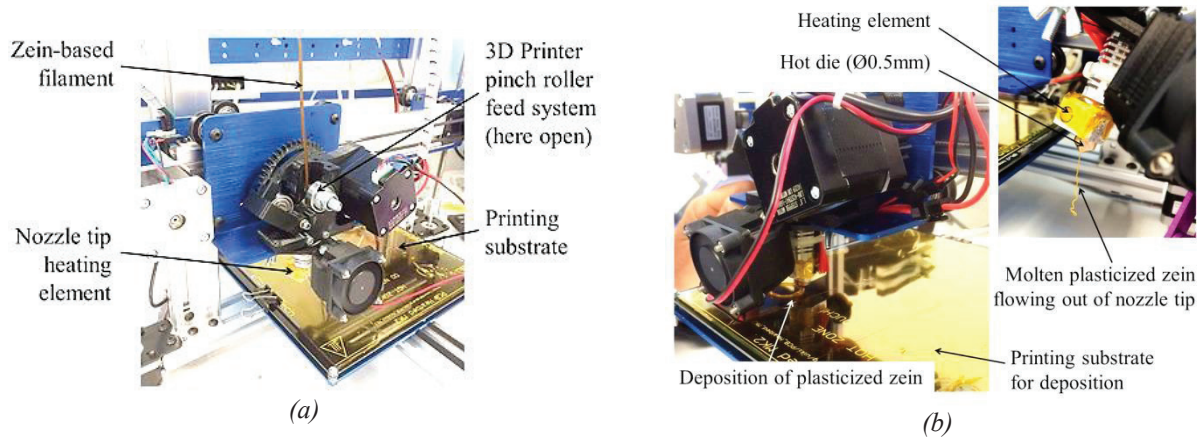
Commercial zein presents a moisture content at  $\text{MC}=5\%$  (total wet basis) and  $T_g=88^\circ\text{C}$ . When plasticized with 20% glycerol,  $T_g$  decreases to  $42^\circ\text{C}$  which leads to interesting thermomechanical properties. Indeed, the storage modulus decreases from  $E'=1.1\text{ GPa}$  at  $20^\circ\text{C}$  to less than 0.6 MPa at  $130^\circ\text{C}$ , after the principal mechanical relaxation linked to its glass transition temperature, at  $T=50^\circ\text{C}$ , as shown by the peak on the  $\tan\delta$  curve, Figure 3-a. Z10GLY and composition without plasticizer do not present such an important decrease of storage modulus, preventing their flowing in molten state above  $T_g$ , for their application in 3D printing by FDM. Z30GLY displays lower mechanical properties at ambient conditions ( $E'< 1\text{GPa}$ ) than Z20GLY, but similar values at high temperature. Thus, extrudates based on 20% glycerol are of interest to test 3D printing of zein-based materials by FDM technique. Although mechanisms are different, by comparison of the thermomechanical properties of Z20GLY to those of standard synthetic polymers, the loss of mechanical strength at high temperature allows to evaluate its printing temperature at  $T_{\text{printing}}\approx 120^\circ\text{C}$ , whereas  $T_{\text{printing}}>180^\circ\text{C}$  for PLA and  $T_{\text{printing}}>220^\circ\text{C}$  for ABS. In these

conditions, each considered material is over its relaxation temperature, *i.e.* above  $T_g$  for amorphous Z20GLY or ABS ( $T_g=115^\circ\text{C}$ ), or above its melting temperature as in the case of PLA ( $T_{\text{melting}}=160^\circ\text{C}$ ).



**FIGURE 3.** Evolution of the elastic modulus and the damping factor  $-\text{tan}\delta$  of zein-based thermoplastic filaments (a). Thermomechanical behavior of the plasticized zein with 20% glycerol (Z20GLY), PLA and ABS filaments : evolution of the elastic modulus and the damping factor  $-\text{tan}\delta$  (b)

Even if the mechanical strength is below the one of standard rigid polymers for 3D printing, like PLA and ABS which present moduli above 2GPa, it is large enough to launch trials on FDM 3D printer (Fig.4-a and -b). The expected mechanical properties of printed parts are lower than the ones obtained with standard synthetic polymers.



**FIGURE 4.** Feeding of the FDM-3D Printer with zein-based rigid filament containing 20% glycerol (Z20GLY) (a). Molten thermoplasticized zein (20% glycerol) flowing through the die and deposition of 2 superimposed layers (b)

## CONCLUSIONS AND MAIN PROSPECTS

The tridimensional printing of plasticized zein by Fused Deposition Modeling was demonstrated for the first time. The thermomechanical properties of a composition containing zein with 20% glycerol, allow the feeding, the melt flowing and the rigidification of printed parts at small scale. This result has now to be extended to a larger production of thermoplasticized zein-based filament to print 3D parts of larger size. Besides this technical achievement, the structural characterization of plasticized zein, especially at molecular scale, should help to ascertain its structure-properties relationships relevant to the Fused Deposition Modeling in order to open the field of new applications for 3D printing of biopolymers.

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