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# Material extrusion of plant biopolymers: Opportunities & challenges for 3D printing

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ABSTRACT

The current applications of 3D printing by Material Extrusion (ME) to biopolymers other than polylactic acid (PLA) are scarce. The present paper reflects on the benefits and challenges of using plant biopolymers in for ME. The challenges are considered on the basis of (1) a review of additive manufacturing (AM) techniques applicable to biopolymers, (2) the current material specifications required to comply with the ME processing window, and (3) modeling and optimizing the process. In parallel, the potential benefits are discussed in terms of new fields of application (such as food and biomedical) and related reverse engineering possibilities.

In both cases, an edible plant protein (zein from maize) is considered as an example. It is used to illustrate the formulation challenges for ME processability, focusing on the role of plasticizers. Finally, a reverse engineering approach is presented that combines algorithms for generating structures and deterministic finite element modeling. This enables the design of ME printable parts with a targeted structure and final properties such as controlled release during mastication for biomedical applications.

## 1. Introduction

Material Extrusion (ME) based 3D printing is now one of the most widespread processes used for the rapid prototyping and production of customized plastic parts directly from computer-aided design models [1]. Along with acrylonitrile butadiene styrene copolymers (ABS), polylactic acid (PLA) has emerged as a highly versatile material for the formulation of ME filaments, with the advantage of being biobased and biodegradable [2,3].

Among the different types of biobased polymers (Fig. 1), several other biopolymers could potentially be used to formulate ME filaments. This of course includes other biopolyesters such as polyhydroxyalkanoates resulting from fermentation [4–6], as well as other melt-processable natural biopolymers. In particular, proteins and starch can be processed as thermoplastic materials using plasticizers. They could be good candidates, with the advantage of being edible and/or biocompatible, and directly available from plant or animal sources.

With these types of biopolymers, the fields of application of ME could be considerably extended to the food, pharmaceutical and biomedical sectors [7–9]. For such applications, the finely controlled structures that can be achieved by ME processing would create new opportunities for tailor-made structures in food products, scaffolds and implants [10,11] designed by reverse engineering.

This design approach refers to mathematical concepts that help guide the manufacturing process to achieve predefined functionality objectives. This guidance is provided as a numerical framework (for example, finite element computation) that is able to predict the desired functionality. It is within this context that Computer-Aided Design (CAD) models associated with additive manufacturing can be easily transformed into finite element models. This can be viewed as an opportunity to use reverse engineering for AM, more particularly to optimize biobased products.

Examination of the biobased market shows a wide range of desired functionalities that can be defined for end products (Fig. 2). Depending on the type of application, the objective may differ widely [12–14] and, in turn, the numerical model that needs to be implemented. Structural, thermal and transfer performances can be independently or simultaneously targeted. For instance, the design of biobased end-products such as biofilms requires appropriate permeability kinetics coupled with acceptable mechanical performance [15]. In the food industry, the design of novel products combines seemingly contradictory objectives like the ability to be chewed (low fracture toughness, high

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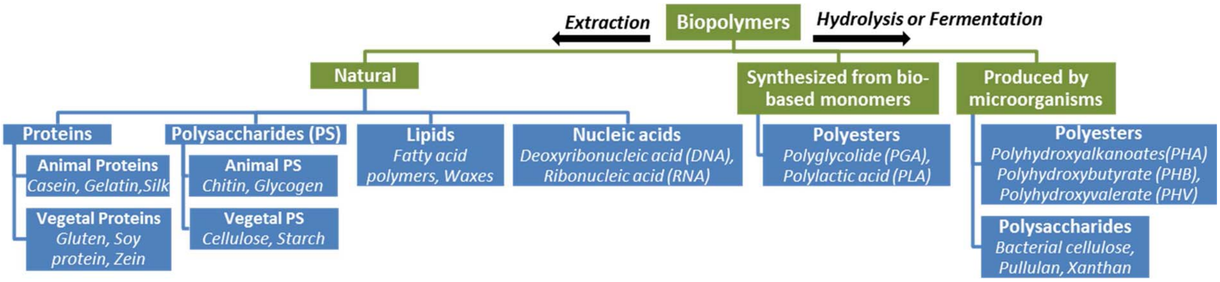

**Fig. 1.** Schematic arborescence of biopolymers and their production.

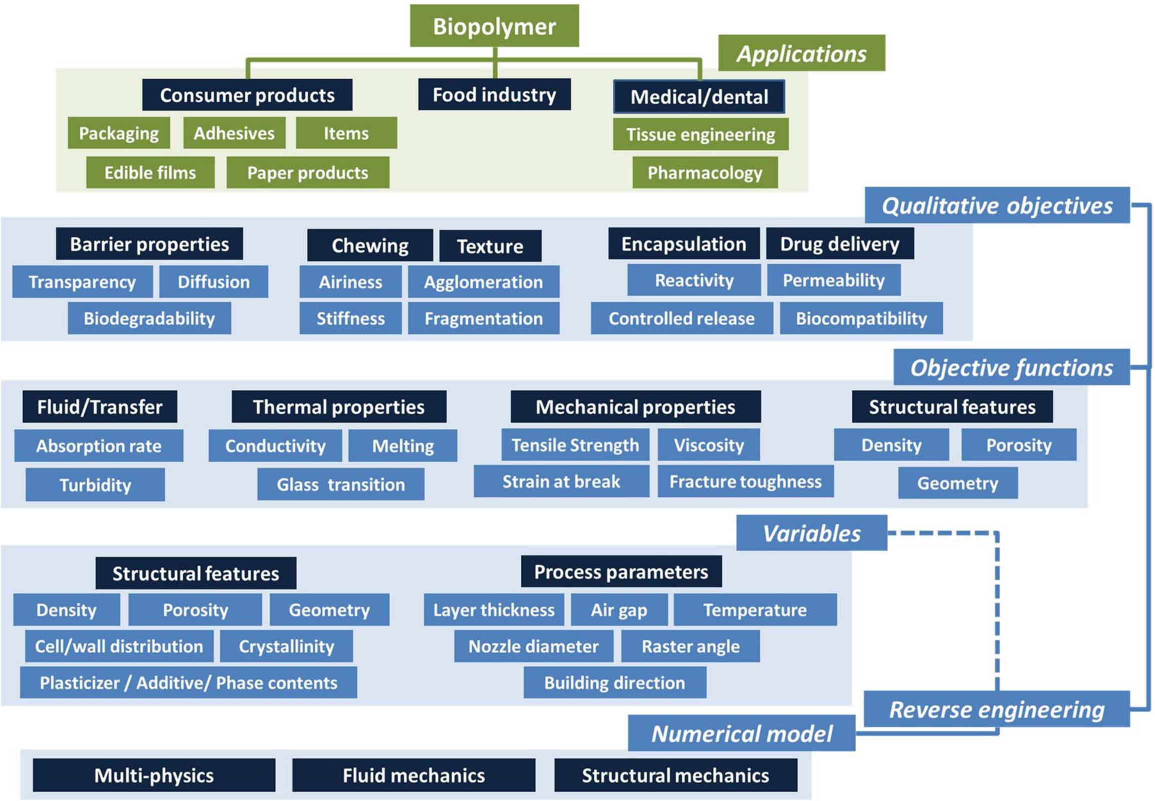

**Fig. 2.** Diagram presenting desired functionalities for a biobased product, numerical model and physics of interest.

fragmentation rate) while preserving acceptable mechanical resistance during packaging and transportation (a compromise between stiffness and strength). In the medical sector, in areas such as tissue engineering, the objective of obtaining the largest airy space possible for cell growth is coupled with a stiffness threshold for the self-holding of the biological material during cell differentiation. In order to achieve these objectives, key structural and physical parameters are generally evaluated on an experimental basis. They represent the set of quantified objective or cost functions that are optimized through the reverse engineering approach. In order to guide the objective functions to the desired state, a set of leverage variables is introduced. Variables are connected to the objectives via the numerical model that represents the physics of interest (Fig. 2). In this way, reverse engineering virtually targets the variables to meet the desired objective. In the case of drug delivery where transfer phenomena prevail [8], fluid dynamics or transfer (heat or mass) models are needed. For texturing foodstuffs [16,17], models are more concerned with structural mechanics.

The development of biopolymer 3D printing by ME could be a driving force for pushing the limits of the current state of art in design and reverse engineering. It also brings new challenges, starting with the formulation necessary to adapt the properties of these natural polymers to the ME processing window. Indeed, this process requires a complex combination of thermomechanical, rheological and self-adhesion properties that corresponds to a limited (though increasing) number of synthetic thermoplastics. Moreover, the modeling and the optimization of the process require the precise knowledge of several physical properties of the materials.

A methodic material selection and formulation approach that takes the different steps of 3D printing by ME into account is thus required. In the present paper, we consider an edible and melt-processable protein (zein from maize) as an example to illustrate both these formulation and modeling challenges, as well as the reverse engineering possibilities for biobased products. We first focus on the ME process. We show how its key steps define the specifications of the properties of the material required for processing. In light of these specifications, zein and other biopolymers are compared to currently used thermoplastics. It also makes it possible to identify the current lack of knowledge necessary for the formulation of printable compositions and the modeling of their behavior during the different steps of ME. In the second part, we present two examples of potential zein-based ME products obtained by reverse engineering for typical food and pharmaceutical applications.