

Participants

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Rheology and structural changes of plasticized zeins in the molten state (2017) Rheologica Acta

Chaunier L, Della Valle G, Dalgalarondo M, Marion D, Lourdin D, Leroy E

Fused deposition modeling of plant biopolymers: opportunities & challenges

(2018) Additive Manufacturing

Chaunier L, Guessasma S, Belhabib S, Della Valle G, Lourdin D, Leroy E

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Zein: a model material for 3D-printing biopolymer melts

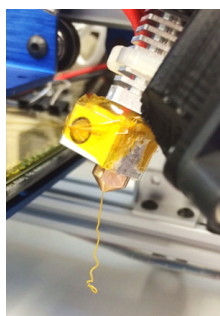
3D printing is an additive manufacturing technique that builds 3-dimensional objects based on a computer-file template. One of the most mainstream 3D printing processes is fused deposition modelling (FDM), which works by depositing a thermoplastic polymer filament layer-by-layer. To extend the range of FDM-process applications out to biomedical and pharmaceutical manufacturing, new thermoplastic materials need to be purpose-developed. All-natural biodegradable biopolymers, some biocompatible and potentially even edible, could make good candidate materials, but only with a purpose-tailored formulation.

► RESULTS

Our research has shown that zein, the seed storage protein found in maize, is suitable for 3D printing by deposition in the molten state. After hot melt extrusion with 20% added glycerol, zein protein offers thermomechanical properties that fit with FDM-process requirements, i.e. (i) high elastic modulus at room temperature ($E' > 1\text{GPa}$), and (ii) hot flowability once past its glass transition temperature ($T_g \approx 42^\circ\text{C}$). However, the hot reactivity of the plasticized zein due to the interplay of noncovalent interactions with the formation of disulphide bridges causes the melts to stiffen, which could bottleneck its workability in FDM processes. We found that long thermomechanical treatments (extrusion for 10 minutes at 130°C) lead to gelling. This reactivity stems from in-melt protein unfolding that further exposes protein sites involved in aggregation and crosslinking reactions. However, we also showed that filaments obtained via a shorter thermomechanical treatment (extrusion for around just a minute at 130°C) or by adding reducing agents that minimize the heat-driven aggregation of zein protein facilitates its melt-phase workability.

► FUTURE OUTLOOK

We intend to consolidate these findings by studying the addition of ionic liquids to zein-based materials, as they can act as both plasticizers and as active pharmaceutical ingredients (e.g. [lidocaine][ibuprofenate]) to target the pharmaceutical applications market.



Extrusion of a plasticized zein filament at the 3D-printer (FDM-process) extrusion-head nozzle outflow