
Extrusion and rheological behavior of zein plasticized by glycerol and an active pharmaceutical ingredient to obtain 3D printed tablets

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Zein is the major storage protein extracted from corn kernels (3-5%db). It is a natural thermoplastic biopolymer that can be extruded once properly plasticized by glycerol as standard plasticizer. Among various Active Pharmaceutical Ingredients-Ionic Liquids (API-IL), which are considered as promising compounds for future drugs because of better stability and bioavailability, [Lidocainium][Ibuprofenate] has a triple interest: (i) a plasticizing effect on biopolymers and two therapeutic roles as (ii) local anesthetic and (iii) anti-inflammatory. This opens prospects to obtain customized edible delivery systems based on zein by additive manufacturing in the molten state. To do this, the rheological properties are a key parameter of the material.

Previous work showed that the glass transition temperature (T_g) of zein can be lowered from 80 to 42°C by adding 20w% glycerol as plasticizer. The composition (Z20GLY) can be extruded at 130°C using a co-rotative twin-screws microcompounder. Its apparent viscosity determined in steady-state flow increases with residence time due to protein aggregation, from 1kPa.s to 5kPa.s after 10min. Then, for short residence time (3min), it can be 3D printed by hot melt extrusion at 130°C. The substitution of glycerol by [Lidocainium][Ibuprofenate] leads to a T_g at 60°C and to a faster increase of viscosity. Unexpectedly, in the case of a partial substitution of glycerol, the apparent viscosity increases less rapidly, especially for material Z10GLY10LI containing 10w% of each plasticizer. The evolution of its flow curve was monitored as a function of the residence time by varying the rotation rate of the screws of the microcompounder. After applying the Rabinowitsch corrections, in order to consider the shear-thinning behavior of the material according to a power law, a progressive shift was observed towards high viscosities.

Several hypotheses can explain the limitation of the thermal aggregation of the protein matrix induced by the partial substitution of glycerol by API-IL. They will be mentioned during the presentation. From a practical point of view, this work highlights the possibility of optimizing the processability of the plasticized zein by the formulation, in particular for additive manufacturing, in which the residence time during processing can vary a lot.