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Study of a cellulose pulp-ionic liquid mixture properties for 3D printing applications

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#### PURPOSE OF THE ABSTRACT

Three-dimensional printing has been recently recognized as one of the most promising technologies being applied in a wide range of areas, such as energy, biotechnology, and medical devices due to its cost-effective fabrications, and customizable object geometry [1]. Different feedstocks are being used for 3D printing such as polymers, metals, ceramic, among others. However, the necessity to substitute plastic with more eco-friendly and renewable raw materials is increasing the research on bio-based materials, and more concretely, hydrogels, for the manufacture of 3D products. The use of cellulose in all its forms to produce biomaterials is increasing in the last few years due to its multiple advantages, such as renewability, abundance, and low cost. In this work, a blanched pulp produced from Eucalyptus globulus was mixed with 1-ethyl-3-methylimidazolium dimethylphosphate ([Emim][DMP]) to obtain a 3D printing material ink (an ionogel) for the ensuing hydrogels obtention with the desired shape.

The ink was obtained by mixing the ionic liquid (IL) and the bleached pulp (2 wt.%) at 100 °C with magnetic stirring until the pulp was completely dissolved. Then, a printability test and a complete rheological study were developed. A grid form was printed to study the printing process. The shape fidelity of the ionogel and hydrogel grids was studied using the pore factor (Pr) and the uniformity factor (U) [2]. It was also studied the integrity of the printed material, by printing a 15 layers geometrical shape. The mixture was printed using a 510  $\mu$ m needle at different flowrates from 40 to 80  $\mu$ L/min and printing velocities from 3 to 5 mm/s. The printing was done on an agar plate to improve the coagulation. Dynamic frequency and strain sweeps were performed to study the behavior of the complex viscosity and the yield stress of the mixture, respectively. The rheological properties of the ionogel after printing were also studied. Once the grid was printed, the hydrogel was obtained by placing the ionogel in water until the IL was completely removed and the integrity of the shape of the gel was also checked.

The rheological results showed that the mixture could be printable (Figure 1a,b). The viscosity decreased with frequency from values close to 1000 Pa·s to 1 Pa·s, and the mixture had yield stress, and it was close to 163 Pa. The presence of a yield stress and the shear-thinning behavior of the mixture were enough evidence for the filament formation during the printing and for the final material good stiffness [2]. Figure 2 shown a printed grid at a constant flowrate of 80  $\mu$ L/min and a printing velocity of 5 mm/s. The printability factors for these conditions exhibited good shape fidelity of the mixture with values of Pr~1.13 and U~1.03 that are in accordance with other studies [3]. In addition, hydrogels maintained their shape. Finally, the rheological properties of the ionogels after

printing showed higher G' (elastic modulus) than G'' (viscous modulus), i.e., a solid-like behavior of the gels.

This work proved the feasibility of printing an IL-cellulose mixture obtaining an ionogel with a fixed shape and, depending on the bleached pulp content, different rigidity. The possibility to replace the IL with water obtaining the hydrogel opens a new window for the formulation of biomaterial inks (hydrogels), and also ionogels, with the desirable form depending on their application.

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#### **FIGURES**







## FIGURE 1

#### Figure 1

(a) Dynamic frequency sweep and (b) dynamic strain sweep (Yield point showed with a dotted line) of the 2 wt.% cellulose pulp-ionic liquid mixture.

## FIGURE 2

Figure 2 (a) Pulp cellulose ionogel (2 wt.%) printed at 5 mm/s

and 80 uL/min and the zoom of a grid square.

## **KEYWORDS**

3D printing | Hidrogel | Cellulose | Biomaterial

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