Hydrogels based on poly(fructose methacrylate)

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Abstract
Fructose methacrylate monomer was synthetized by transesterification of D-fructose with trifluoroethylmethacrylate catalysed by lipase Novozym 435, and polymerized by radical polymerization in the presence of a crosslinker at different concentrations. The poly(fructose methacrylate) hydrogel presented high water swelling coefficients dependent on the crosslinking density. These hydrogels are elastomeric and resilient, and the water entrapped inside them is located in different environments as binding and free water.

Key words:
Hydrogel, glycomonomer, carbohydrate.

Introduction
Hydrogels are hydrophilic tridimensional polymeric networks with the capability for absorbing a high amount of water. They have been employed in several biomedical applications such as contact lenses, drug delivery, wound dressing, synthetic skin, cell culture, and they also find applications in areas such as hygienic products, agriculture, materials for purification and many others. Hydrogels can be prepared from glycomonomers, such as fructose methacrylate, in the presence of a crosslinker to form polymer chains with an apolar backbone and carbohydrates moieties, providing biocompatibility, biodegradability and hydrophilic features to the material. A simple and efficient route to synthesize glycomonomers is the transesterification enzymatically catalyzed. In the present work, fructose methacrylate synthesized by transesterification enzymatically catalyzed was polymerized by radical polymerization to achieve carbohydrate based hydrogels. These hydrogels were characterized by thermal and mechanical analyses and water swelling experiments.

Results and Discussion
The transesterification of fructose by trifluoroethyl methacrylate and catalyzed by Novozym 435 resulted in four isomers of fructose methacrylate (FMA) monomer (conversion of 99%): 1-methacryloyl-β-D-fructopyranose (58%), 1-methacryloyl-β-D-fructofuranose (21%), 6-methacryloyl-β-D-fructofuranose (11%) and 6-methacryloyl-α-D-fructofuranose (9%). The radical polymerization of FMA was performed in water/DMF solution using ammonium persulfate and ethyleneglycol dimethacrylate as initiator and crosslinker, respectively. Three hydrogels, Figure 1, were prepared using different concentration of the crosslinker (1.0 wt%, 0.5 wt% and 0.25 wt%). Because of the hydrophilicity of the fructose moieties, the hydrogels presented high water swelling capability inversely proportional to the crosslinking density. The water swelling is reversible and, from the highest to the lowest crosslinking density, the swelling coefficients are 320%, 420% and 595%. Stress-strain compression tests were conducted at 25°C and at a rate of 0.05 N/min. All hydrogels presented an elastomeric behavior and low mechanical hysteresis when subjected to a load and unload cycle, Figure 2a. The elastic strength of the hydrogels increased with the crosslinker concentration. The compression strains achieved at a tension of 6 kPa for hydrogels containing 1.0 wt%, 0.5 wt% and 0.25 wt% of crosslinker are 25%, 30% and 45%, respectively.

Figure 1. Hydrogels of fructose methacrylates with different crosslinker concentrations. Thermoporosimetry experiments performed on a differential scanning calorimeter (DSC) allowed investigating the ambient in the hydrogels containing water. The DSC curves, Figure 2b, shows two melting peaks (yellow and blue regions) for the water into the hydrogels. This behavior indicates that the hydrogels present a porous structure where water crystallizes in different ambient and it present characteristics of bonded and free water.

Figure 2. a) Stress-strain compression tests of the hydrogels with different crosslinker concentration. b) DSC curves showing the melting point of water inside hydrogels.

Conclusions
The hydrogels based on fructose methacrylate were successfully synthetized and showed to be a resilient elastomeric materials with high and reversible swelling capability.

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