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Methacrylate-terminated F127/PAA hydrogels for 3D printing

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Introduction

Pluronic F127 is a triblock copolymer, formed by a hydrophobic poly(propylene oxide) (PPO) block enclosed by two hydrophilic poly(ethylene oxide) (PEO) blocks, which has been considered for 3D printable resins due to the gelation capacity, surface adhesion and biocompatibility.[1,2] F127 presents PEO blocks with terminal hydroxyl groups which can be modified with methacrylate groups to facilitate covalent cross-linking during the 3D printing process to form hydrogel networks for biomedical applications such as cartilage replacement. Methacrylate terminated F127, F127-MA, can be combined with poly(acrylic acid) (PAA) in order to prepare 3D printed hybrid hydrogels with enhanced Young´s Modulus and compressive strength.

Objectives

The aim of this work was to synthesize methacrylate-terminated Pluronic F127 using a microwave-assisted reaction and to investigate the potential of this material for light-assisted 3D printing of biomedical devices.

Methodology

The methacrylate-terminated F127 synthesis was based on the work of Van Hove et al. [3] Briefly, Pluronic F127 was reacted with a 8-fold molar excess of methacrylic anhydride in a microwave-assisted reaction according to **Fig. 1**. After a 5 min reaction, the resulting polymer was dissolved in THF and reprecipitated in hexane to remove excess methacrylic anhydride.

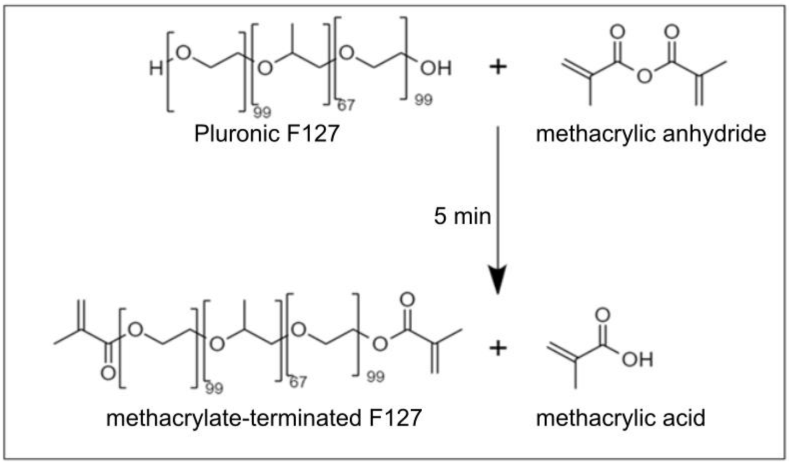

Fig. 1. Microwave-assisted and solvent-free reaction of F127 with methacrylic anhydride to generate methacrylate-terminated F127.

In order to prepare 3D printable resins, acrylic acid (AA) and Irgacure 819 were homogenized under magnetic stirring and added to an F127-MA solution in an ice bath. Afterwards, Sudan I was added to the solution prior to the 3D printing process which was performed in a DLP 3D printer (MoonRay Model D75) (**Fig. 2**). A resin with analogous composition was also prepared using unmodified F127 and N,N'-methylenebisacrylamide (MBAm) as a cross-linking agent (**Table 1**).

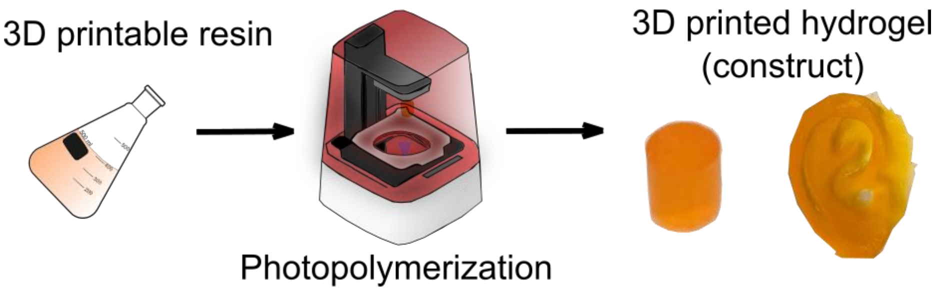

Fig. 2. Schematic representation of the 3D printing process by the photopolymerization of the resin inside a DLP 3D printer. Resins are orange because of the presence of Sudan I, a photoabsorber which enhances the 3D printing fidelity to the computational model.

Table 1. Composition of the 3D printable resins (wt %).

3D printable resin	F127	F127-MA	AA	MBAm	Irgacure 819	Sudan 1
PAA/F127/MBAm-0.26	20	-	30	0.26	0.08	0.01
PAA/F127-MA	-	20	30	-	0.08	0.01

Results and Discussion

Proton nuclear magnetic resonance (^1H NMR) (**Fig. 3**) allowed estimating a methacrylation degree of 70% for the microwave-assisted formation of F127-MA. The signals found at 1.88, 5.69 and 6.03 ppm confirmed the insertion of methacrylic groups on the chain ends of Pluronic F127, as shown by the numerical peak assignment to the chemical structure.

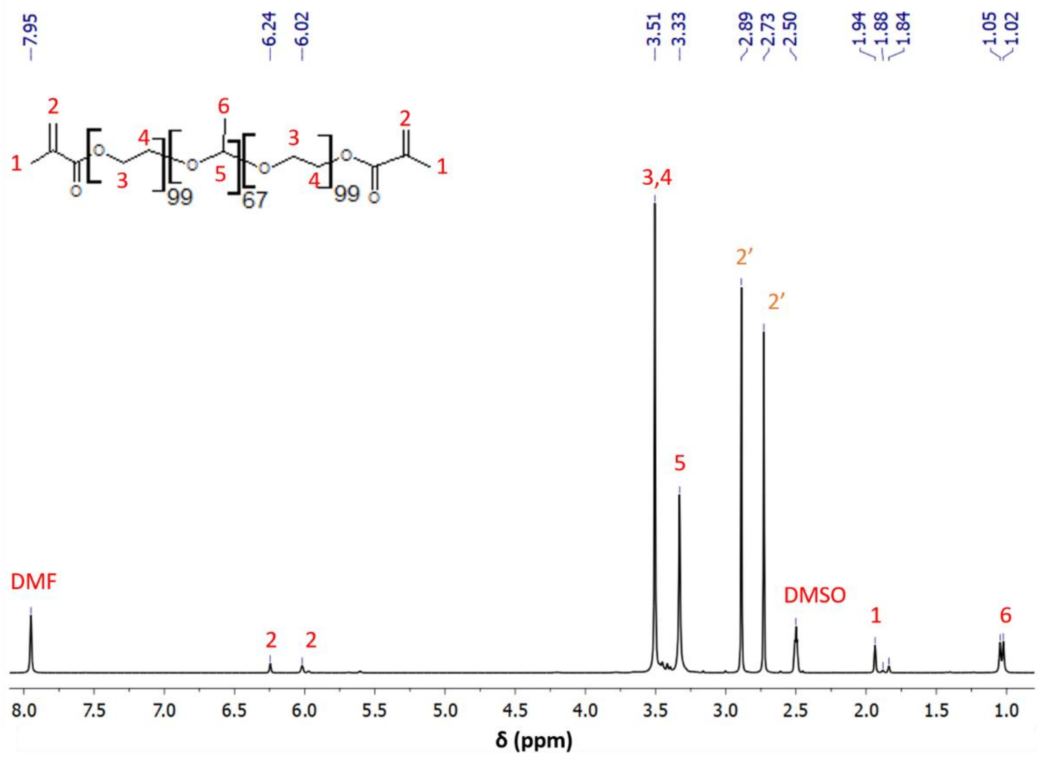

Fig. 3. ^1H NMR spectra of the F127-MA resin after 5 min of reaction. Signals assigned to F127-MA are indicated by the red figures. Orange figures refer to excess methacrylic anhydride.

The results so far obtained, confirm the feasibility of synthesizing a photo cross-linkable F127-MA resins for 3D printing in a solvent-free process. Self-standing constructs with high fidelity to the computational model were obtained without the addition of MBAm or other cross-linkers.

The compressive strength of a construct containing 30% PAA and 20% F127-MA was evaluated in a texturometer and compared to a 3D printed hydrogel containing 0.26 wt% MBAm, 30 wt% PAA and 20 wt% F127. **Fig. 4** shows that F127 methacrylation significantly enhances the Young's modulus of the constructs.

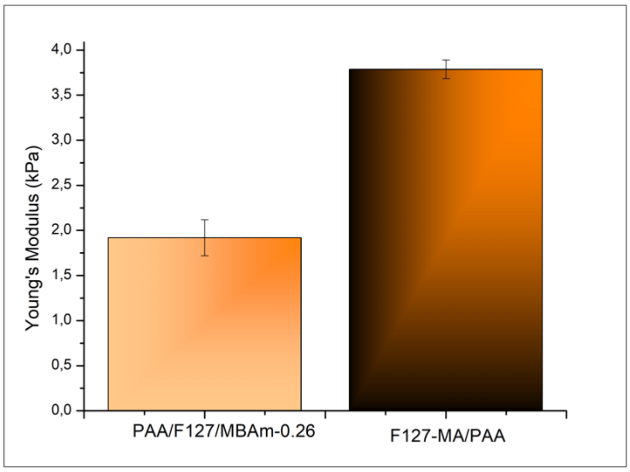

Fig. 4. Young's Modulus of PAA/F127 and PAA/F127-MA hydrogels obtained by the slope of the loading curve in the linear region of a compression test in a texturometer.

Conclusion

PAA/F127 and PAA/F127-MA hydrogels can be 3D printed with fidelity to 3D models using Digital Light Processing 3D printing technology in solvent-free microwave-assisted synthesis. F127-MA can be used as a macrocross-linker and leads to an increase in the hydrogel compressive strength, which makes it a promising material for biomedical applications such as cartilaginous tissue replacement.

Acknowledgements

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