Evaluation of a Biobased Resin with Micro- or Nanocrystalline Cellulose for 3D-Printing Application

EVALUATION OF A BIOBASED RESIN WITH MICRO- OR NANOCRYSTALLINE CELLULOSE FOR 3D-PRINTING APPLICATION

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Introduction

Stereolithography (SLA) is an additive manufacturing technology that can fabricate highly accurate components (down to 5 microns of resolution) with good thermal, mechanical, and chemical properties. Its process consists of using a light source, usually, a UV-light (with a wavelength between 360 and 405 nm) to selectively cure layer-by-layer a mixture of photosensitive liquids made of acrylates or/and epoxy-acrylates with a suitable photoinitiator.[1] Unfortunately, most of the materials commonly used to produce the resins are derived from crude oil, which, besides being non-renewable and having low biocompatibility, is a significant cause of environmental pollution [2].

In recent years, new studies started to address the lack of biocompatible and biobased materials for SLA applications. Usually, these new materials are based on vegetable oils or clinically approved polymers [3]. It is also possible to add new functionalities, or improve the mechanical properties of these new resins through the addition of fibers, fillers, or nanoparticles. However, there is still a limited variety of biobased resins. Therefore, this work aims at developing a new high-quality, environmentally friendly and biocompatible resin, suitable for 3D printing. To this aim, polyethylene glycol diacrylate (PEGDA) was first combined with increasing amounts of epoxy-acrylated soybean oil (AESO), ranging from 50 to 90 wt.%. Next, 0.15 to 2.4 wt.% of micro- or nanocrystalline cellulose was added to the optimized 20:80 (w/w) PEGDA:AESO formulation, in order to improve the mechanical properties of this latter. The photocurable resins were prepared avoiding any exposure to light and samples were printed using a Peopoly moai 130 SLA 3D printer with an easy-to-level build plate. Finally, after the printing process was over, the excess of resin was drained and washed off with isopropanol and water, then post-cured for 40 min in a UV chamber.

Results and discussion

The most important factor when developing a resin for 3D printing application is controlling its viscosity. Ideally, the viscosity needs to be lower than 5 Pa·s to avoid failures during the printing process. Unfortunately, the PEGDA viscosity increased with increasing AESO concentration, and the mixture containing 90 wt.% of AESO was too viscous for 3D printing. Thus, the maximum AESO loading was set at 80 wt.%.

It is crucial for tissue engineering that the resin can fabricate parts that sustain their form when dipped in water. As shown in Figure 1, pure PEGDA absorbed almost 40% of its weight in water over a 30 day period. The addition of 50 and 80 wt.% AESO decreased the water sorption respectively by 76% and 93% over the same test duration. This decrease could be attributed to two factors: (i) the AESO large carboxylic chains and (ii) an increase in the cross-linking density.

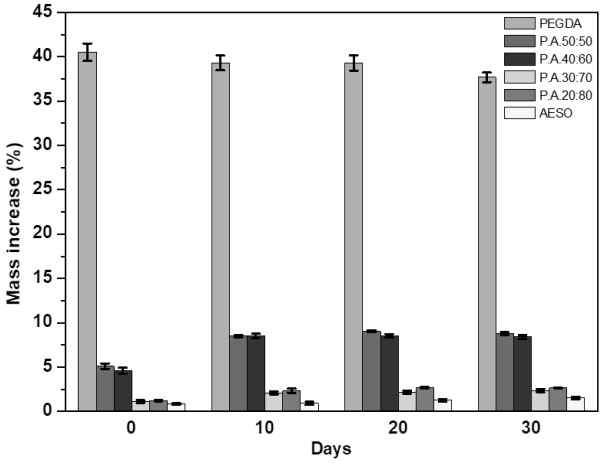

Figure 1. Swelling behavior of 3D-printed parts for 5, 10, 20, and 30 days with different AESO loadings.

Figure 2 shows the tensile test results of the 3D printed dumbbell samples with increasing AESO loadings. Pure PEGDA has a tensile strength and elongation of 0.6 ± 0.2 MPa and 2 ± 1%, respectively. The addition of AESO drastically increased both properties, which reached their maximum values of 4.4 ± 0.2 MPa and 25 ± 2.3%, respectively, when 80 wt.% of AESO was added.

The addition of MCCs and CNCs to 20:80 PEGDA:AESO mixture had opposite effects on its tensile strength and elongation at break (Figure 3). When the fillers were incorporated into the mixture, the elongation at break drastically decreased.

In contrast, there was an increase in the tensile strength by 2.3% and 59.1% when 2.4 wt.% of either MCCs or CNCs were added, respectively. This opposite behavior can be attributed to the cellulose crystalline structure.

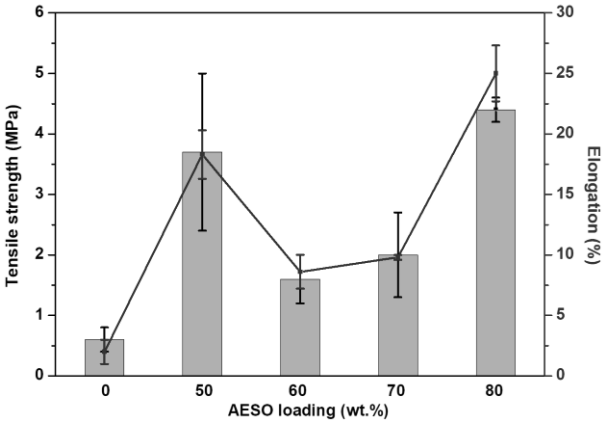

Figure 2. Variation of the tensile strength and elongation as a function of AESO loading.

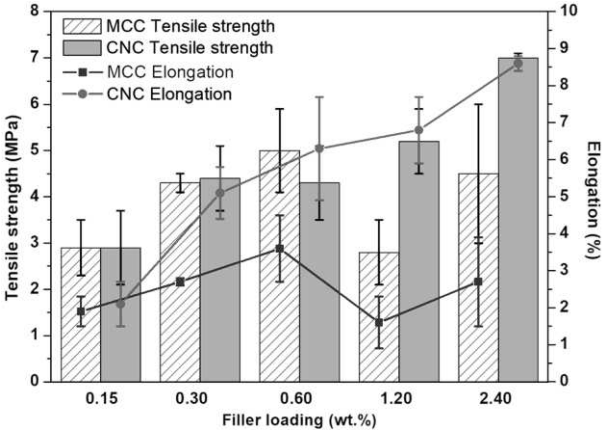

Figure 3. Influence of MCC and CNC loadings on the tensile strength and elongation at break of PEGDA:AESO 20:80 system.

The Young's modulus also substantially increased when MCCs and CNCs were incorporated. Unfilled PEGDA has a Young's modulus of 26 ± 1 MPa. As shown in Figure 4, when 0.15 wt.% of MCCs or CNCs were incorporated, the Young's modulus raised from 16.8 ± 0.17 MPa (unfilled resin system) to bout 145 MPa for both fillers. However, as the concentration of fillers further increased, MCCs-based composites achieved nearly twice the Young's modulus value of CNCs counterparts. This finding could be attributed to the differences in morphology and chemical surface structure for the two fillers, as already reported elsewhere [4].
Besides, the incorporation of the fillers at different loadings (up to 2.4 wt.%) into the resin formulation containing 80 wt.% AESO did not interfere with the 3D printing process, nor had a significant impact on the resin critical energy and depth penetration. Furthermore, the presence of the cellulose crystals, irrespective of their size, increased the wettability of the printed parts (with a lowering of the water contact angle values by ca. 34 and 43%, when 2.4 wt.% of either CNCs or MCCs were incorporated, respectively).

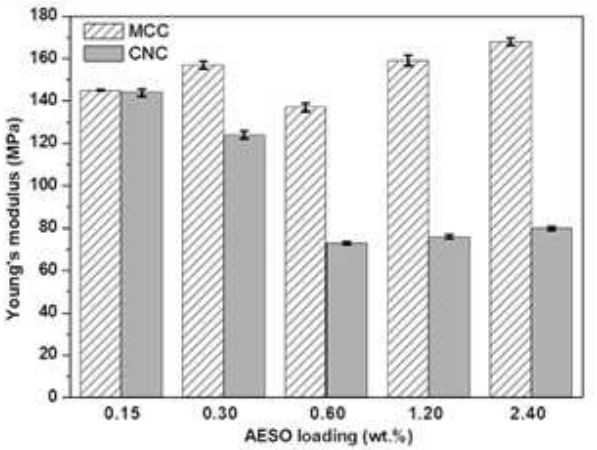

Figure 4. Young's modulus values of PEGDA:AESO 20:80 systems, containing different amounts of MCCs and CNCs.

Conclusions

In this work, a new photosensitive composite for SLA was successfully developed. The mixture containing 80 wt.% AESO achieved the best performance, showing an appropriate viscosity, good mechanical properties, low swelling deformation, high bio-content and reactivity, thus it was chosen as the reference for dispersing the fillers. The incorporation of 2.4 wt.% of CNCs and MCCs improved the tensile strength by 59%, and the elastic modulus by 890%, respectively. Furthermore, the fillers did not interfere with the 3D printing process, proving their viability for stereolithography even at high loadings.

References

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