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INVESTIGATION OF EPOXY-ACRYLATE SOYBEAN OIL AS A BIO-ENHANCER FOR 3D PRINTING APPLICATION

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Introduction

Stereolithography (SLA), one of the earliest additive manufacturing technologies, employs photosensitive resin systems and a light source with emission wavelength between 350 and 405 nm. This way, it is possible to print high detailed parts in a layer-by-layer process, reaching resolutions down to 5 μm [1]. Besides, nowadays SLA represents nearly half of the additive manufacturing market, and it is proving to be an economical technique to produce highly accurate parts having good thermal, mechanical and chemical properties [2].

The photosensitive resin systems employed for SLA generally combine liquid acrylates and epoxy monomers/oligomers, in the presence of suitable photoinitiators [3]. Unfortunately, most of the current suitable resin systems derive from crude oil, which raises many environmental issues, such as CO₂ emission, plastic waste and materials toxicity. To address the lack of biobased photocurable resins, here we investigated the suitability of epoxy-acrylate soybean oil (EASO), a derivative from soybean oil, as a component of formulations for 3D printing purposes. To this aim, different amounts of EASO (ranging from 10 to 50 wt.%) were added to a standard, commercially available resin system for SLA (namely, Peopoly Moai standard clear resin (PY)), aiming at investigating the effect of the introduction of the biobased EASO on the overall thermal, mechanical, and structural properties of the obtained 3D printed parts. PY, as indicated by the supplier, is a mixture of urethane acrylate (30–50 wt.%), bisphenol A ethoxylate diacrylate (30–50 wt.%) and benzophenone as photoinitiator (5 wt.%). The 3D printing process was carried out using a Peopoly Moai 130 SLA 3D-printer, equipped with an easy-to-level build plate. Then, the printed parts were carefully removed from the build platform, washed three times with isopropanol and water, in order to remove any unreacted monomer, dried in the dark for 1 day, and finally placed in a UV oven for the post-curing step.

Results and discussion

Figure 1 shows the rheological behavior of the resin formulations containing different amounts of EASO monomer. The viscosity of the prepared mixtures increased with increasing the EASO loading; however, the observed viscosities did not affect the range of linear viscoelastic behavior of the mixtures,

which fully satisfied the viscosity requirements for SLA applications.

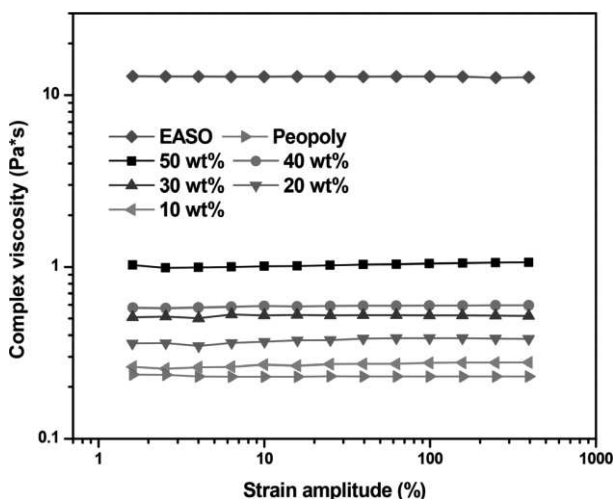


Figure 1: Variation of PY resin viscosity as a function of EASO loading (viscosity curves of neat PY and EASO are also included)

Visual tests were performed to compare the printing quality of the UV-cured formulations containing PY and different amounts of EASO. As shown in Figure 2, three boat prototypes were printed with 0, 10, and 50 wt% of EASO (Samples A, B and C, respectively): a good printing quality and smooth surfaces, which are worthy indications for commercial suitability, were achieved.

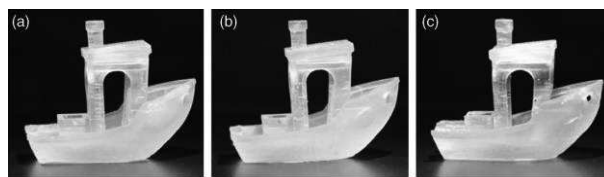


Figure 2: Digital images of 3D printed boat prototypes (48x 24.8x38.4 mm³). Boat (a) was printed with pure PY resin and boats (b) and (c) with the formulations containing 10 and 50 wt.% of EASO, respectively.

Figure 3 shows the results of the tensile tests performed on 3D printed dumbbell specimens containing different EASO loadings. It is noteworthy that unlike pure PY, for which the average tensile strength is about 50.3 MPa, the addition of just 10 wt.% of biobased monomer determines a drop down of this parameter (by about 50%), which further decreases

up to ca. 15 MPa for the system containing the highest EASO loading. These findings can be ascribed to the network loosening of plant-based resins, as already reported in the literature [4]. However, when the biobased resin content does not exceed 30 wt.%, the mechanical behavior is very similar to that observed for crude-oil based resin systems, as also indicated by the stiffness of the obtained 3D printed parts (Figure 4).

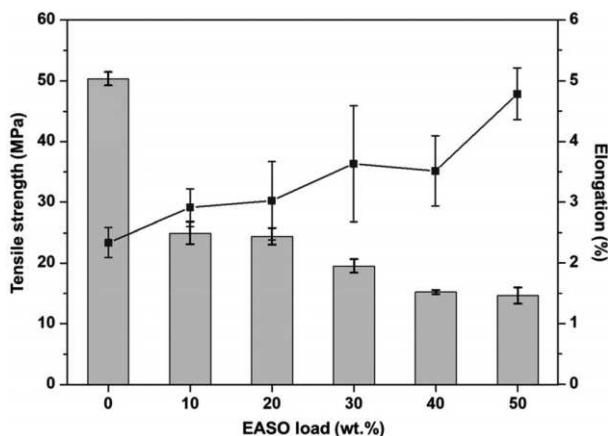


Figure 3: Variation of the tensile strength (gray bars) and elongation (blue squares) as a function of EASO loading.

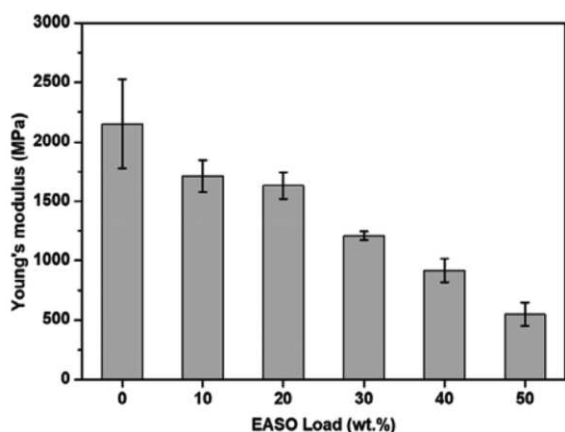


Figure 4: Young's modulus for 3D printed samples containing different EASO loadings.

Despite the decrease of the tensile strength, EASO was responsible for a significant increase of the ductility of the 3D printed parts, which increased by about 108% with respect to that of pure PY, for the formulation containing 50 wt.% of the biobased monomer.

As far as the thermal and thermo-oxidative stability of the 3D printed formulations is considered, the results of thermogravimetric analyses clearly indicated a very limited effect of the EASO loading on the overall thermal behavior, as witnessed by the minor changes of degradation onset and T_{max} values [5].

Conversely, increased amounts of the biobased monomer in the 3D printed formulations promoted an overall increase of the wettability, as shown in Figure 5. Indeed, unlike PY that is quite hydrophobic, EASO is highly hydrophilic.

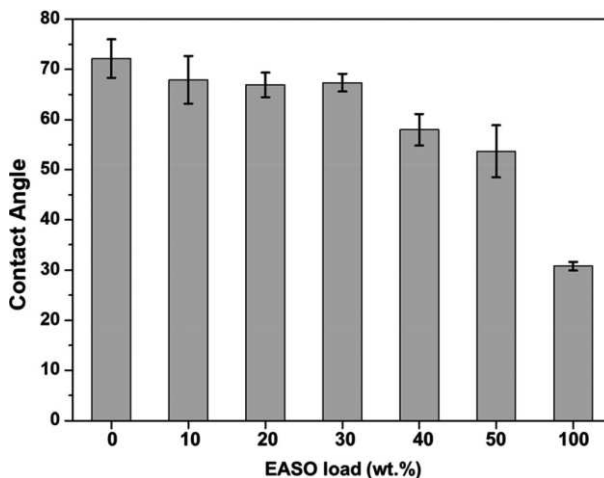


Figure 5: Water contact angles of 3D printed samples as a function of the EASO monomer loading

Conclusions

In the present work, we clearly demonstrated the feasibility of partially replacing crude oil-based photosensitive resin systems with epoxy-acrylate soybean oil, a biobased monomer, obtaining formulations that are suitable for 3D printing (SLA) processes.

The effects of increasing amounts of EASO monomer on the rheological behavior of the curable mixtures, as well as on the thermal, mechanical and surface properties of the 3D printed parts was thoroughly investigated. The formulations containing up to 30 wt.% of EASO showed mechanical properties similar to other commercial resins (with significant enhancements in flexibility and wettability).

Besides, visual assessment of all the prepared samples confirmed that the designed PY-EASO formulations are suitable for 3D printing processes.

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