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Selection of conventional photoinitiators to produce biocompatible UV epoxidized soybean oil resin mixtures for 3D printing technology

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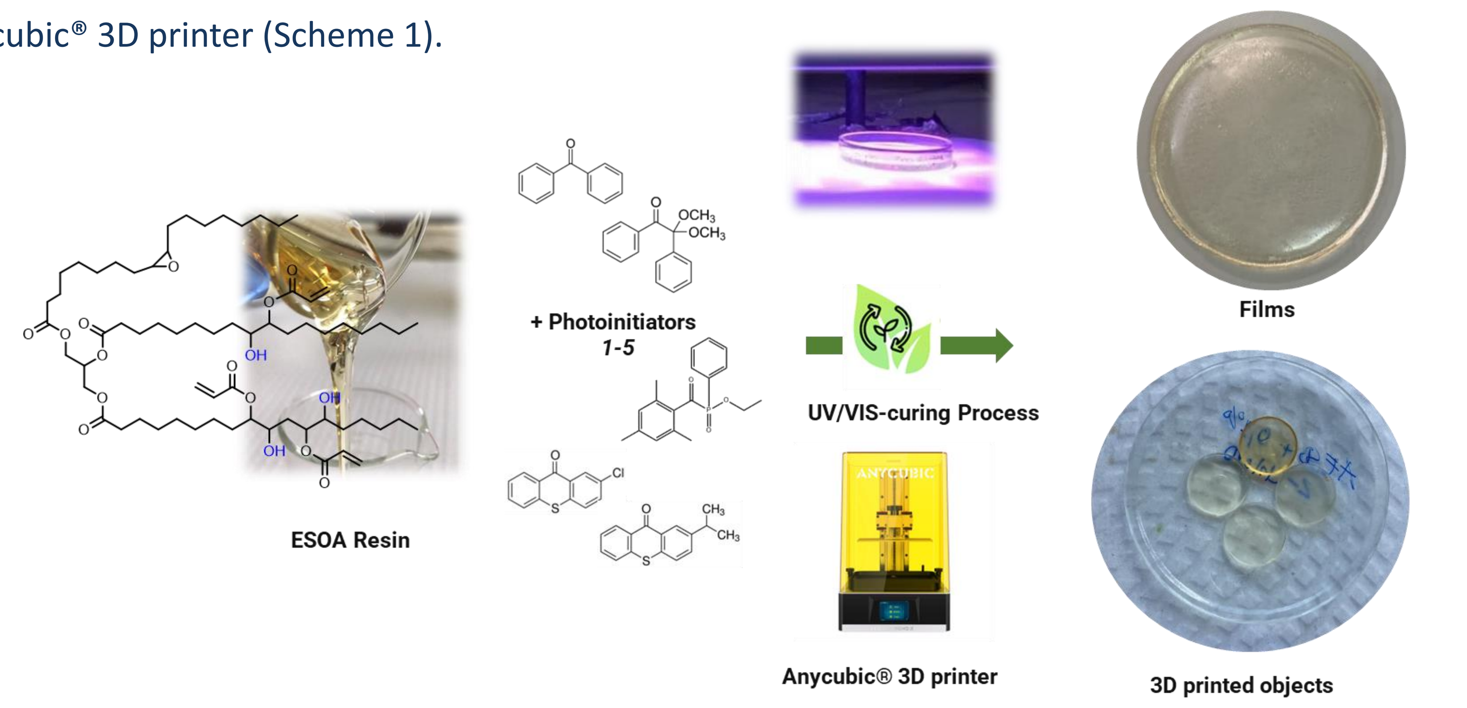
Introduction

The use of natural-based resins as matrices for 3D printing is currently an expanding area with a considerable potential to explore. These materials, in addition to presenting high biocompatibility, come from renewable natural resources, making them very attractive in terms of cost and environmental needs. In the production of objects by photopolymerization, natural-based resins can be used with photoinitiators, making them amenable to UV-Vis curing. Thus, the choice of natural resins, photoinitiators and light sources, will allow to propose new formulations, with the biocompatibility properties of the natural material, and which can compete with those available on the market, justifying the research in this area.

Materials and Methods

Different mixtures of ESOA were prepared, with 1-0.01% of photoinitiators (w/w, initial resin basis) and operational parameters such as curing time and UV-Vis wavelength source, were tested. Initial studies were focused on the preparation of films, in Ø 5 cm Petri dishes, and optimal conditions were selected to produce the pieces. A computer-aided design software was used to project the desirable models and pieces were produced in an Anycubic® 3D printer (Scheme 1).



Scheme 1. Overview of preparation of films and 3D pieces

Production and Characterization of Films

As mentioned, different mixtures were prepared, and films were produced. As an example, Figure 1 shows the visual results obtained for different mixtures of ESOA with 2-isopropylthioxanthone (ITX) and Figure 2 exhibits the visual results obtained for different mixtures of ESOA with ethylphenyl (2,4,6-trimetylbenzoyl) phosphinate (TPO-L).

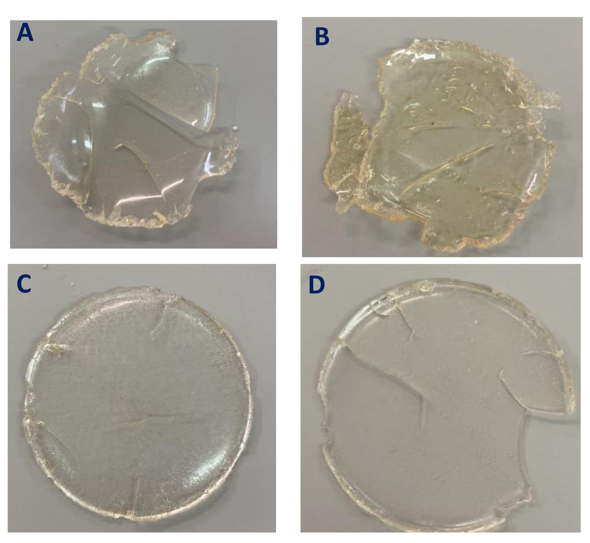


Figure 1. ESOA + ITX films cured with **a** 405 nm lamp. ***A***) 0.5% ITX; ***B***) 1% ITX; **C**) 0.1% ITX and **D**) 0.05% ITX.

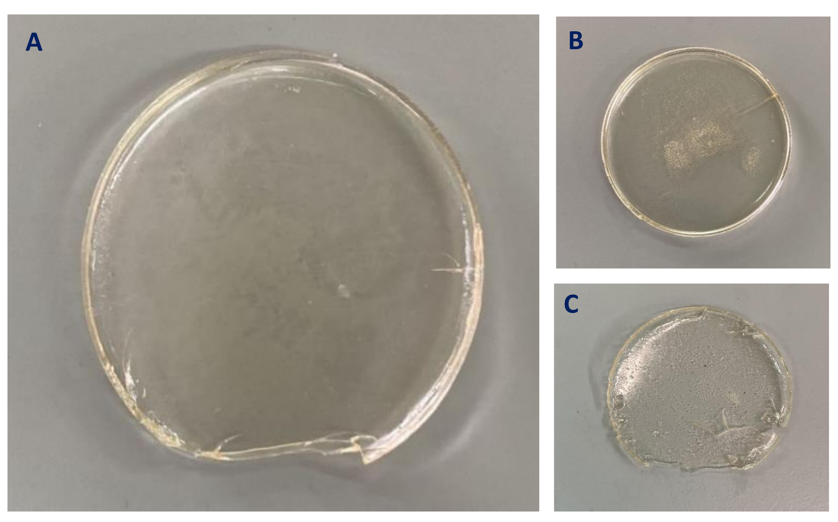


Figure 2. ESOA + TPO-L films cured with **a** 405 nm lamp. ***A***) 0.01% TPO-L; ***B***) 0.1% TPOL-L and **C**) 0.5% TPO-L.

As can be seen, type and amount of photoinitiators were decisive to achieve viable mixtures to be cured by UV-Vis radiation. Different results were obtained for the five photoinitiators tested (***1-5***) and results allowed to select the optimal conditions for each mixture.

Microbiological tests

As a first approach to test bioactivity of the produced materials, antimicrobial tests were performed. Samples of Ø 10 mm of the different ESOA films produced (Table 1) were tested against two bacteria, namely, *Escherichia coli* ATCC 25922 and *Staphylococcus aureus* ATCC 25923, using the soft-agar overlay technique. After 24 h incubation at 37ºC, the diameter of the zone of inhibition around each film sample was measured (Figure 3).

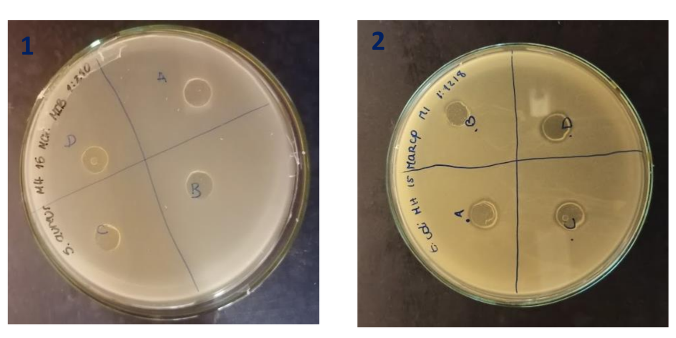


Figure 3. ESOA films against **1**) *S. aureus* A) 0.05% CTX, B) 0.1% CTX, C) 0.3% CTX, D) 0.5% CTX; ***2***) *E. coli* A) 0.05% CTX, B) 0.1% CTX, C) 0.3% CTX, D) 0.5% CTX.

Results presented in Table 1 reveal that most of the produced films do not show inhibition against the studied species. When inhibition was detected, it proved to be quite weak and was mainly observed against *Escherichia coli*.

Table 1 – Inhibition of ESOA films against *Staphylococcus aureus* and *Escherichia coli*.

	Inhibition	
Film samples	***Staphylococcus aureus***	***Escherichia coli***
ESOA + 0.05% CTX	No	Weak
ESOA + 0.1% CTX	No	No
ESOA + 0.3% CTX	No	Weak
ESOA + 0.5% CTX	No	Weak
ESOA + 0.05% ITX	No	Weak
ESOA + 0.1% ITX	Weak	Weak
ESOA + 0.5% ITX	Weak	Weak
ESOA + 1% ITX	Weak	Weak
ESOA + 0.1% BDX	No	Weak
ESOA + 0.3% BDX	No	No
ESOA + 0.5% BDX	Weak	No
ESOA + 1% BDX	No	Weak
ESOA + 0.1% BZF	No	Weak
ESOA + 0.3% BZF	No	Weak
ESOA + 0.5% BZF	No	Weak
ESOA + 1% BZF	No	No
ESOA + 0.01% TPO-L	No	Weak
ESOA + 0.05% TPO-L	No	Weak
ESOA + 0.1% TPO-L	No	No
ESOA + 0.5% TPO-L	No	No

Goals

In this study Epoxidized Soybean Oil Acrylate (ESOA) resin, an environmentally friendly cross-linking agent derived from soybean oil, was used and tested with different amounts of five conventional photoinitiators namely, benzophenone, 2,2-dimethoxy-2-phenylacetophenone, ethylphenyl (2,4,6-trimetylbenzoyl) phosphinate, 2-chlorothioxannthen-9-one and 2-isopropylthioxanthone, in order to obtain sustainable mixtures able to be cured by UV-Vis radiation and suitable to obtain 3D printed objects by stereolithography technique.

Production and Characterization of 3D Pieces

Two models of pieces (Figure 4) were projected using a computer-aided design software.

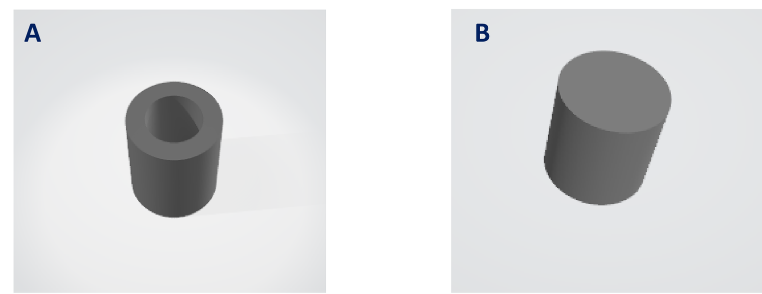


Figure 4. Models of pieces projected with SolidWorks ***A***) Hollow cylinder; ***B***) Full cylinder.

The most promising combinations of ESOA+photoinitiators were selected, from the results obtained in films productions, and were tested to obtain the projected 3D pieces in the Anycubic® printer. In all circumstances the printer parameters had to be adjusted and the results did not always reflect what was intended. As an example, Figure 5 shows some pieces produced with ESOA + 0,1% of CTX and ESOA + 0,5% of TPO-L, the most encouraging results.

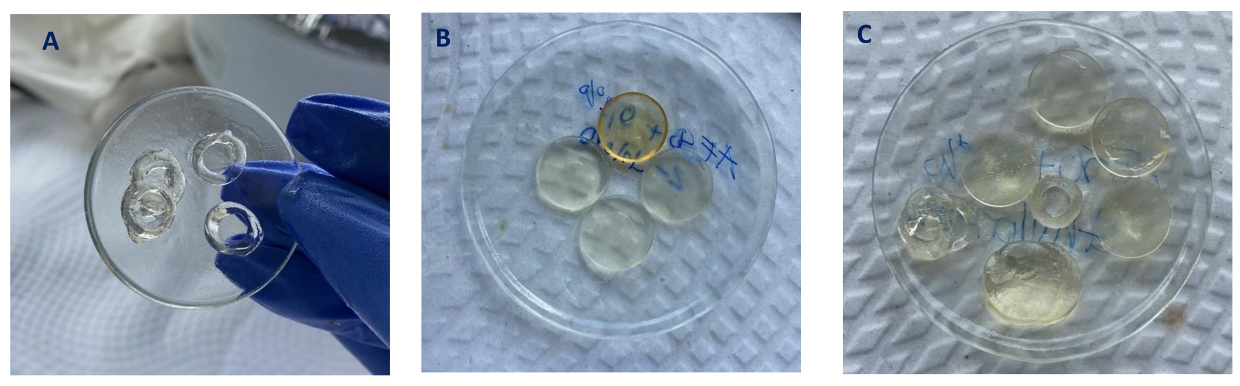


Figure 5. Visual aspect of pieces printed in the Anycubic® 3D printer ***A*** and ***B***) ESOA + 0,1% of CTX and ***C***) ESOA + 0.5% of TPO-L.

As reference 3D pieces of commercial Anycubic® resin were produced and hardness were assessed for all pieces (Table 2).

Table 2. Hardness (Shore A) of produced pieces

3D Piece	Thickness (cm)	Hardness (Shore A)	
ESOA + 0.1% CTX	0.10	85.1	85.1
		85.1	
		85.0	
	0.25	88.1	87.7
		87.0	
		87.9	
ESOA + 0.5% TPO-L	0.20	89.1	89.0
		89.0	
		88.9	
	0.25	92.5	93.2
		93.5	
		93.5	
Anycubic resin	0.25	97.0	97.0
		97.0	
		97.0	

As expected, for both pieces of ESOA resin mixtures, results show that with the increasing of thickness, the hardness slightly increases. When comparing pieces with the same thickness (0.25 cm) ESOA+0.5% TPO-L have a slightly higher hardness (93.2 Shore A) than those produced with AESO+0.1% CTX (87.7 Shore A). Although both proposed mixtures produced pieces with smaller hardness than the obtained for the reference Anycubic®, resin piece (97.0 Shore A) results are considered promising.

Conclusions

Here we demonstrated that using the appropriate photoinitiators ESOA resin can be cured by UV-Vis light. Results showed that of the five studied photoinitiators the most suitable to produce epoxidized soybean oil resin mixtures for 3D printing was ethylphenyl (2,4,6-trimetylbenzoyl) phosphinate. In general, no antibacterial activity was evidenced against *Escherichia coli* and *Staphylococcus aureus* by the studied new materials, therefore further assays against other bacteria are planned. Results of mechanical properties were also encouraging.

References

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Acknowledgments

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