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Article

Microalgae as a Source for Stereolithography (SLA) 3D Printing Resin

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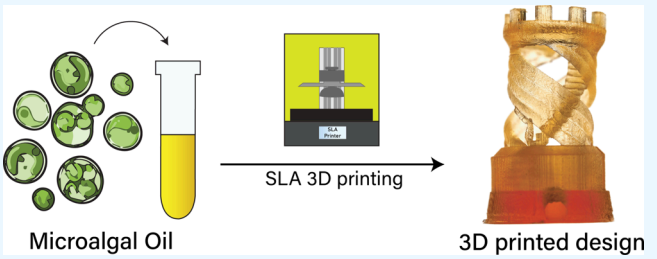
ABSTRACT: 3D printers are becoming common household and laboratory appliances thanks to the possibility of producing physical objects in a short time, at low cost, with low waste, and tailored to the needs of each user. One of the most widely used types of 3D printers is stereolithography (SLA) or masked stereolithography ((m)SLA), which uses light to photo cross-link a liquid resin to solid objects layer by layer. 3D printable resins consist of numerous components, with the biggest part consisting of usually methacrylates or acrylates. However, contrary to the trend of reducing plastic consumption, the methacrylates used for SLA resins are mainly petroleum derivatives. Biobased options made with soybean oil have become commercially available in the past few years. These oils are not very sustainable as soybeans have a high demand for land and water use, and there is competition for using soy as food or feed or for materials. In contrast to soybeans, microalgae have simple nutrient requirements and do not need arable land or freshwater, excluding them from competition with crops. They also have high CO_2 fixation and can produce and store a high oil content of up to 75% by biomass weight, which can be used for the production of the resin. Here, we show how to produce 3D printable resins based on microalgal oil. Starting from commercial microalgal oil, we perform epoxidation and methacrylation reactions on it to obtain reactive groups that can be used for polymerization. Subsequently, we formulated an SLA resin that we 3D printed and analyzed for mechanical performance.



KEYWORDS: *3D printing, stereolithography, microalgae, biobased materials, methacrylates*

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INTRODUCTION

3D printing has reached a maturity stage, and, thanks to the low costs and various printable materials, 3D printers are becoming common household and laboratory appliances.[1] Nowadays, it is possible to produce physical objects tailored to the needs of each user in a short time, at a low cost, and with low waste. Using 3D printers, in fact, it is possible to produce only the object needed directly on the spot where it is required without the need to mass produce several objects in a single place and then distribute them all over the globe. In this way, we reduce the amount of unused objects that will end up in waste, and the environmental cost of transporting them.[2,3]

The most common types of 3D printers are FDM (Fusion Deposition Modeling) and SLA (Stereolithography) or (m)SLA (masked Stereolithography). FDM printers melt a plastic filament and deposit it layer by layer, forming the final 3D structure. Stereolithography printers, instead, use a laser (SLA) or UV-LED ((m)SLA) to photo cross-link a liquid resin to solid objects layer by layer.[1] Arguably, in a time when the world is trying to reduce the use of plastic materials, 3D printing seems counterintuitive, in terms of "green" materials. More sustainable and biodegradable materials are available nowadays,[4] but mostly regarding FDM and filaments consisting of recycled PETG and biosourced PLA.[5] The same does not apply to SLA printers, for which the final cross-linked object cannot be recycled, and the main components of the resins still derive from petroleum-sourced products. It is, therefore, necessary for SLA 3D printing to go one step further, detach as much as possible from fossil sources, and shift to using biobased components.

Recently, more and more 3D printing resin brands have started offering biobased resin alternatives for SLA to creators. Various plant oil sources have been used commercially[6] and in research,[7,8] with most resin alternatives being based on soybean oil. This latter is chemically modified to acrylates[9] that are used in the resin formulation. However, cultivating soy

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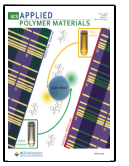

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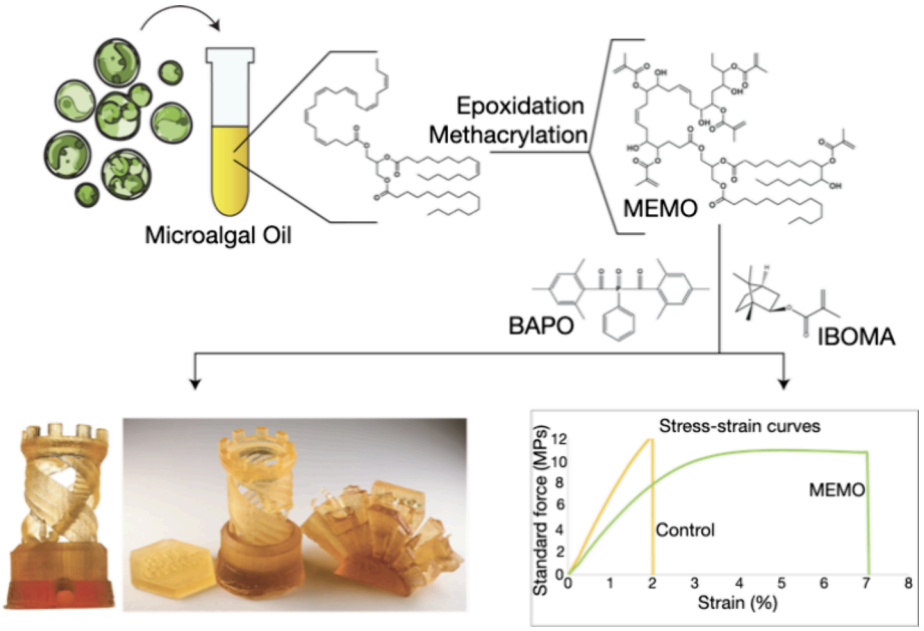
Scheme 1. Graphical Visualization of the Project[a]



[a]Starting from the microalgal oil, we performed epoxidation and methacrylation reactions to obtain the Methacrylated Epoxidated Microalgal oil (MEMO). The synthesized MEMO was then combined with a diluent (IBOMA) and a photoinitiator (BAPO) to develop a stereolithography (SLA) resin. This resin was subsequently processed using SLA printing techniques, and the mechanical properties of the resulting samples were compared with the properties of a commercial resin.

is associated with specific challenges. Its dual character of serving both as a crop and as an industry feedstock affects availability and prices. At the same time, it also raises sustainability issues since it requires considerable acreage, high water use, and high energy usage for its processing and transport.[10]

Microalgae, in contrast, can serve as a more sustainable feedstock material.[11] Their simple nutrient requirements and lack of requirements for arable land or fresh water exclude them from the competition with crops.[12,13] Their rapid growth leads to higher productivity than terrestrial crops, such as soy,[14] and by extension, leads to higher CO_2 fixation.[15] Microalgae cells, under optimum culture conditions, can produce and store a high oil content of up to 75% by biomass weight,[16] with 40% of it being polyunsaturated fatty acids like EPA (eicosapentaenoic acid) and DHA (docosahexaenoic acid).[17]

The carbon−carbon double bonds in fatty acids, thus, their degree of unsaturation, can be exploited through a series of chemical reactions to insert functional groups and transform them into a 3D printable resin compound. As previously reported for soybean oil, the raw material can be epoxidized, with epoxide rings introduced on the alkene bonds.[18] Using the high reactivity of the epoxide rings, methacrylate groups can then be inserted by a methacrylation reaction.[7] The final methacrylated compounds can be used to formulate a photocurable resin consisting mainly of sustainable biomaterials.

In this research, we used commercially available microalgal oil to formulate a highly biobased 3D printing resin. Following a similar protocol to soybean oil, the double bonds on the raw microalgal oil's fatty acids were first epoxidized. In a subsequent step, methacrylate groups were introduced at the locations of the epoxide rings. The products of every reaction were monitored by using 1H NMR spectroscopy. The resulting methacrylated microalgal oil was used as the main component in a photocurable resin. Aiming to increase the biobased material content of the resin, different resin formulations were produced, and the final materials were tested for their mechanical properties (Scheme 1).

In parallel with our efforts, Vazquez-Martel and co-workers demonstrated the use of microalgae as sustainable sources for the development of biocompatible material for 3D printing.[19] With their research, they produced microstructures with additive-free ink for two-photon 3D laser printing using chlorophyll derivatives already present in the microalgae extract. They also assessed the cytocompatibility of the obtained materials through cell viability assays. However, the findings for the microstructures printed can be difficult to apply on a larger scale and require some modification. In our work, great attention is given to the optimization of the synthesis and formulation of the resin to obtain printability and mechanical properties that are competitive with those of commercial resins.

MATERIALS AND METHODS

Materials. Microalgal oil was purchased from De Wit Specialty Oils BV (The Netherlands, www.dewitoils.nl) (Figure S4). The oil was produced from microalgae of *Schizochytrium* sp., and it contained 42.3% DHA (Docosahexaenoic acid). H_2O_2 30% (7722-84-1), H_2SO_4 98% (7664-93-9), triphenylphosphine (TPP) (603-35-0), and hydroquinone (HQ) (123-31-9) were purchased from Sigma-Aldrich. Formic acid 99% (64-18-6), NaCl (7647-14-5), Na_2SO_4 (7757-82-6), and isopropanol (67-63-0) were purchased from VWR International. Ethyl acetate (EtOAc) (141-78-6) was purchased from BIOSOLVE, $NaHCO_3$ (144-55-8), and methacrylic acid 99% (79-41-4) were from Fisher Scientific. Isobornyl methacrylate (IBOMA) (7534-94-3), and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) (162881-26-7) from TCI Europe. $CDCl_3$ (865-49-6) was purchased from Eurisotop. All reagents were used as supplied without further purification.

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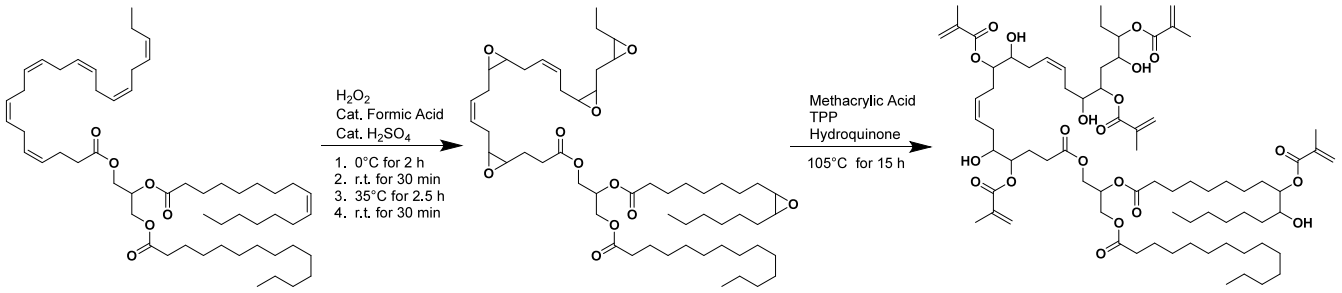

Figure 1. Epoxidation and methacrylation reactions of triglycerides. Due to the variability of the fatty acids connected to the glycerol, a representative triglyceride has been designed with (from the top to bottom) docosahexaenoic acid, palmitoleic acid, and palmitic acid, respectively, which are the most abundant in the percentage of the microalgal oil, according to the fatty acid profile (Figure S4).

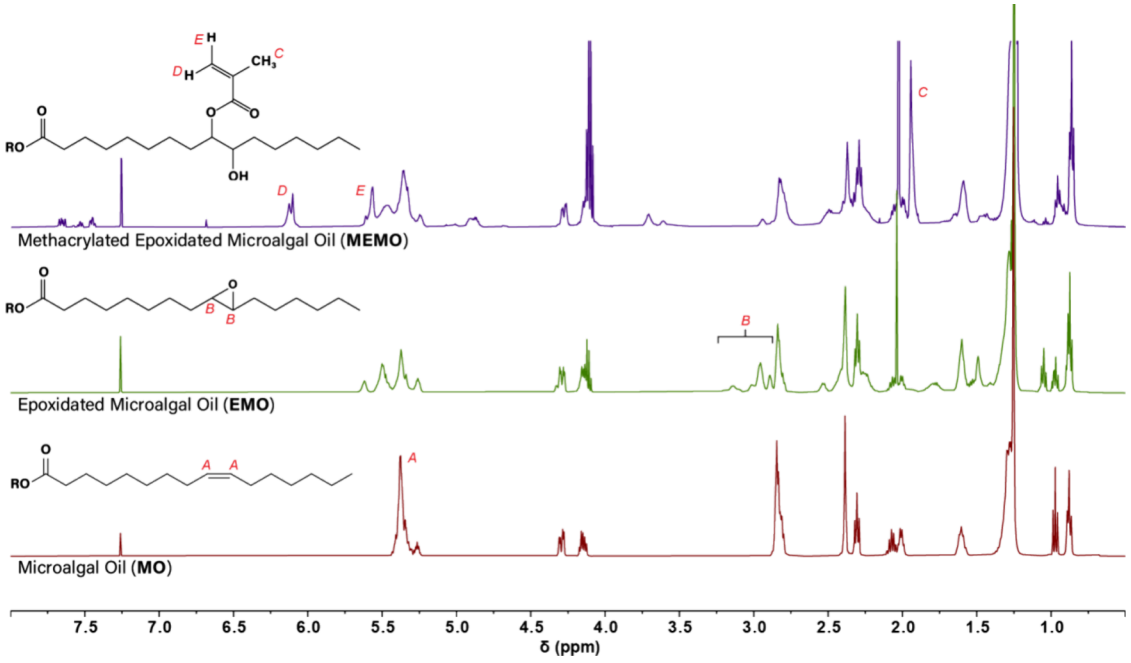

Figure 2. 1H NMR spectra in $CDCl_3$, from the bottom to top, respectively, raw microalgal oil and the products of successive reactions, first epoxidation and then methacrylation after purification, with peaks corresponding to epoxide groups appearing after the epoxidation reaction, disappearing after methacrylation, and new peaks denoting the presence of methacrylate groups. The molecules depicted in the figure show only the epoxidation and methacrylation reactions on the alkene moiety.

Prusament Resin Tough Anthracite Gray (www.prusa3d.com), Anycubic Eco Clear (www.anycubic.com), PLA filament 1.75 mm (www.real-filament.com), and EVA (Ethylene-vinyl acetate) sheets (www.mayku.me) were purchased online.

Epoxidation. In a 500 mL round-bottom flask placed on ice, 100 g of microalgal oil, 14 g of formic acid, and 0.5 mL of sulfuric acid were added while stirring at 200 rpm.[20] 112 g of hydrogen peroxide was added dropwise over 1 h and the mixture was left stirring on ice for one additional hour, followed by a 30 min rest at room temperature. Afterward, the reaction was placed in a water bath for 2.5 h at 35 °C. Subsequently, the mixture was placed at room temperature for 30 min, and it separated into two phases. Using a separatory funnel, the mixture was diluted with ethyl acetate and then washed with a sodium bicarbonate solution (5% w/v) until it reached pH 7. The organic phase was washed with brine and dried with anhydrous sodium sulfate at room temperature. The solvent was removed by vacuum to obtain the epoxidized microalgal oil (EMO).

Methacrylation. 10 g of EMO was placed in a round-bottom flask wrapped in aluminum foil. Hydroquinone (HQ) (0.25% w/w) and triphenylphosphine (1 or 2% w/w) were added with stirring at 200 rpm. After both the solids were solubilized, 2,8 mL of methacrylic acid was added dropwise using a syringe, and the reaction was heated at 105 °C. The reaction was stopped after 15 h, and the methacrylated epoxidized microalgal oil (MEMO) was diluted with ethyl acetate and washed with Milli-Q water and $NaHCO_3$ to eliminate the methacrylic acid in excess (Figure S3). The organic phase was washed with brine and dried with anhydrous sodium sulfate at room temperature. The solvent was removed by vacuum to obtain the methacrylated epoxidized microalgal oil (MEMO).

Characterization of EMO and MEMO. 1H NMR spectra were obtained using a Bruker 11.7 T Avance III spectrometer operating at 500 MHz for 1H, equipped with a TXI gradient probe. Deuterated chloroform ($CDCl_3$) was used as the solvent for all of the samples. The Degree of Modification (DoM) was calculated with respect to the CH proton from the glycerol, whose integral was set arbitrarily to 1. Based on that, the epoxides and the methacrylate peaks were integrated to evaluate the average number of functional groups compared to the glycerol in the raw oil. A DoM of 1 would mean that there is 1 epoxide group per glycerol molecule.

Microalgal Oil Resin (MiRe) Formulation. For the 3D printing resin, MEMO_1 (obtained with 1% of TPP) and MEMO_2 (with 2% of TPP) were mixed at different ratios with the diluent isobornyl methacrylate (IBOMA) and 2% w/w phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO). The mixtures were heated at 50 °C and stirred with a magnetic bar for 1 h. Rheological

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and viscosity analyses at variable temperatures were done on an AresG2.

3D Printing of MiRe. The resin was preheated to 40 °C and poured into the resin tank of the Lite 3DP Gen 2 printer. The design was sliced, and the printing parameters were set on Chitubox (CHITUBOX, China). Testing for the ideal printing settings, we applied varying bottom exposure times and exposure times per layer to assess the best printing conditions. After printing, the 3D-printed objects were all washed in isopropanol, dried, and postcured for 10 min using the CW1S (Original Prusa Curing and Washing Machine, Prusa Research, Czech Republic). After printing, the structures were placed in Methanol for a week. The 3D printed parts lost between 6 and 8% of their initial weight, showing that less than 10% of the resin is still mobile and can leach out of the material. Both controls (Prusament and Anycubic Eco) lost between 2 and 4% of their weight.

Mechanical Test. The mechanical properties of the different resin formulations were measured according to ISO 527-2 (*"A minimum of five test specimens shall be tested for each of the required directions of testing. The number of measurements may be more than five if greater precision of the mean value is required. It is possible to evaluate this by means of the confidence interval (95 % probability)"*) using a Zwick Z010. Testing dogbones were designed in Tinkercad () according to the ISO 527-2 standard and sliced in PrusaSlicer 2.8.0 (Prusa Research a.s., Czech Republic). Using an Original Prusa MK4S 3D Printer (Prusa Research a.s., Czech Republic), positive testing dogbone templates were 3D printed using PLA. The templates were then used for thermoforming molds from EVA (ethylene-vinyl acetate) sheets of 1.5 mm thickness, using the Mayku Multiplier (Mayku Limited, UK) thermoforming machine. The testing bars were created by casting the different resin formulations into the EVA mold and curing for 10 min in the CW1S. The dogbones were stored in a climate chamber at 23 °C and 50% RH for 1 week for conditioning before being tested. Mechanical tests were also performed on control material obtained from Prusament Resin Tough Anthracite Gray and Anycubic Eco Clear following the same procedure.

RESULTS AND DISCUSSION

Synthesis and Characterization. To obtain the main component of the photocurable resin, the first step was the addition of methacrylic groups to the fatty acids in the starting microalgal oil through epoxidation and methacrylation reactions. The double bonds of the fatty acid from the commercial microalgal oil were epoxidated using H_2O_2 and formic acid[20,21] (Figure 1). The reaction was exothermic, and it was placed for the first two h on ice and then at 35 °C to avoid overheating and, consequently, side products and safety hazards. Due to the potential thermal instability, the reaction was conducted five times to assess the reproducibility of the procedure without observing relevant variations between different batches. At the end of the reaction, the product obtained was a bright orange oil, which was neutralized with a solution of $NaHCO_3$. The epoxidized microalgal oil (EMO) was stored at 4 °C until it was used. Samples of EMO and the oil used as starting material were used for 1H NMR spectroscopy (Figure 2). Comparing the raw microalgae spectrum to those of the epoxidation products, peaks at 5−5.5 ppm indicate the decrease of double bonds, and new peaks around 3 ppm appear, corresponding to the formation of epoxide groups during the epoxidation process.[7,22] The degree of modification (DoM) obtained with the different batches of EMO is 2.3 ± 0.1. A detailed NMR characterization of the EMO can be found in Figure S1. Trying to increase the number of epoxide groups in the oil resulted in self-polymerization.

The EMO obtained was then methacrylated using methacrylic acid, triphenylphosphine (TPP) as a catalyst, and hydroquinone (HQ) as a radical scavenger[23] (Figure 1). Different procedures were tested for methacrylation because of the self-polymerization of the reaction mixture under various conditions. From the observations made and the evidence from literature,[24] the temperature has a vital role in this side reaction. It was also observed that slowing the addition of methacrylic acid at a lower temperature helped to prevent this effect. The methacrylic acid was, therefore, added dropwise at room temperature to avoid polymerization. The reaction was also performed with different concentrations of the reagents, and interesting behavior was observed when different amounts of TPP were used. By variation of the concentration of TPP from 1 to 2%, a relevant increase in methacrylic groups bound to triglyceride molecules was observed, allowing materials with different degrees of modification to be obtained reproducibly. Although the mechanism of methacrylation in the presence of TPP is not yet clearly understood, we also observed that increasing TPP reduces the incidence of self-polymerization of methacrylic groups during the reaction. Reactions conducted with 2% TPP were found to be easier to handle and to scale up. At the end of the reaction, the obtained methacrylated epoxidated microalgal oil (MEMO) was purified from the methacrylic acid residue to remove possible reactive double bonds that can interfere during the successive curing step (Figures S2 and S3). For the purification step, the oil was diluted with EtOAc and washed with a water solution of $NaHCO_3$ (2.5% w/v). After all of the washing steps, the organic phase was dried over sodium sulfate, and the solvent was evaporated under reduced pressure. The purification of MEMO to remove the residues of methacrylic acid was also confirmed by diffusion ordered spectroscopy (DOSY). The purified MEMO, a dark orange oil, was stored at 4 °C until used, and a sample was taken to analyze the product with 1H NMR (Figure 2). Comparing the methacrylation product spectrum is compared to that of the epoxidation mixture, the peaks of the epoxide groups (3.00 ppm) decrease, and new ones corresponding to the methacrylic acid (5.5−6.5 ppm) appear. Peaks from the residual methacrylic acid were observed at 5.66 and 6.2 ppm. Through the processes of epoxidation and methacrylation, the triglyceride structure remained intact, as shown by the peak at 4−4.5 ppm. From the NMR, the MEMO obtained with 1% of TPP had a Degree of Modification (DoM) of 1.2 ± 0.1. Instead, using 2% TPP, the obtained DoM was 2.2 ± 0.2, where most of the epoxide groups were converted into methacrylates.

Resin Formulation. The MEMO obtained with 1 and 2% of TPP from the reactions described above was used to formulate a library of biobased methacrylate photoresins by mixing it with a diluent and a photoinitiator to obtain curable resins. As a diluent, we used isobornyl methacrylate (IBOMA), a molecule that has 70% of C from biobased resources,[7] and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) as the photoinitiator. Both components are widely used in the literature to formulate photocurable resins.[7,25−27] We used different percentages of MEMO and the diluent to analyze the influence of the diluent on the curing efficiency and the mechanical properties of the final product (Table 1). The resins were formulated using the MEMO with higher DoM (2% of TPP) and lower DoM (1% TPP) to evaluate the effects of the number of functional groups on the cured product. Five different resin compositions were prepared for both the

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Table 1. Microalgae Resin Formulation: MEMO was Mixed with Different Ratios of IBOMA, Producing Different Resins[a]

resin	TPP content (%)	MEMO % (w:w)	diluent (IBOMA) % (w:w)
MEMO_1_100	1	100	0
MEMO_1_80	1	80	20
MEMO_1_60	1	60	40
MEMO_1_50	1	50	50
MEMO_1_40	1	40	60
MEMO_2_100	2	100	0
MEMO_2_80	2	80	20
MEMO_2_60	2	60	40
MEMO_2_50	2	50	50
MEMO_2_40	2	40	60

[a]2% (w/w) BAPO was added to all of the compositions.

MEMO with 1% of TPP (MEMO_1) and 2% of TPP (MEMO_2), starting from 100% of the oil in the absence of diluent, and gradually increasing the amount of IBOMA until 60%. For all the formulations, 2% of photoinitiator was added to the mixture. The resulting resins were used immediately for mechanical and 3D printing tests. However, to evaluate the stability of the resin over an extended period of time, a sample of the MEMO_2_60 resin was stored at 4 °C in the fridge for one month, covered by aluminum foil. We observe the formation of a precipitate that disappeared when warming up the resin at 40 °C under agitation. Due to this behavior, we speculate that the precipitate is probably unsaturated fatty acids that solidified or the photoinitiator that precipitated due to the low temperature. Because of the reversibility of the process, the resin does not require to be prepared strictly before each print but it can be stored in the fridge and warmed before its use. We have also compared the viscosity of the MEMO_2_60 at different temperatures to two commercially available resins and show that it has a lower viscosity in a broad range of temperatures (Figure S5). The viscosity of the MEMO_2_60 resin was also tested after storing it at room temperature for 3 months (Figure S6). The rheology tests indicate minimal changes between freshly prepared resin and resin that is 3 months old.

Mechanical Tests. All of the formulated resins and the commercial resins (Table 1) were cured in molds and tested with a stress−strain analysis to evaluate the E-Modulus before selecting the most suitable formulations for 3D printing. The formulations chosen for MEMO with 1 and 2% of TPP were obtained with different percentages of IBOMA, to analyze the effect of the diluent on the mechanical properties. The diluent indeed represents a key component to optimizing the viscosity of the resin, however, it also influences the mechanical properties of the solid, cured, product. The objective of these tests is to determine which formulation allows, at the same time, to decrease the viscosity of the MEMO and obtain optimal mechanical properties. For each formulation, five samples were tested, and the results obtained are shown below (Table 2 and Figure 3). Besides the different MiRe formulations tested, we performed mechanical tests on the commercial resin Prusament Resin Tough Anthracite Gray, and the Anycubic Eco clear, a soybean oil resin, for comparison.

The mechanical tests were performed on UV overcured dogbones for two main reasons: (a) to remove the layer-by-layer structural strength and compare the different resins cured in the same mold and (b) to ensure that most, if not all, of the methacrylates reacted, and that the modulus primarily comes from the structure. From the measurement, we calculated the E-Modulus, the stress-max, and the elongation at break for all of the formulations. The E-Modulus is a measure of the stiffness of a material, the stress-max is a measure of how strong a material is, the elongation at break represents the elongation of the sample before the rupture, and it is a measure of the elasticity of the material. All of the samples tested showed good elastic behavior, higher in the samples obtained with MEMO_1 due to the lower degree of modification. On the other hand, the samples from MEMO_2 were stiffer and more robust. The formulations tested showed higher values of the E-Modulus, the stress-max, and the elongation at break when the IBOMA increased up to 40%. The presence of a certain percentage of the diluent helped to stabilize the structure of the cured products. However, with increasing IBOMA up to 50 and 60%, MEMO_1 samples were too brittle to be tested, and the samples from MEMO_2 showed a decrease in stress-max and elongation at break and an increase of the E-Modulus. This behavior can be explained by considering the influence of the IBOMA properties on the samples. With higher concentrations of diluent, the small dimensions of the monofunctional IBOMA monomer can cause homopolymerization without creating a 3D network. This results in longer polymers (higher E-Modulus) but lower cross-link density, making the material more fragile and brittle. Among the formulations analyzed, MEMO_2_60 (60% MEMO obtained with 2% TPP, 40% IBOMA, and 2% BAPO) showed promising properties, with an E-Modulus and stress-max lower than the Prusa resin, but with the elongation at break value between 2 and 3 times higher. The opportunity to have a more elastic 3D printed material can help in working with objects that need to be stretched without breaking. Considering the results obtained, MEMO_2_60 was selected for application in stereolithographic 3D printing.

Table 2. E-Modulus, Stress-Max, and Elongation at Break Results and Standard Deviation for Different Resin Formulations of MEMO_1 and MEMO_2

	E-modulus (MPa)		stress-max (MPa)		elongation at break (%)	
sample	avg.	stdev.	avg.	stdev.	avg.	stdev.
control (Prusament)	665.3	39.9	17.7	3.1	3.3	0.7
Anycubic Eco	1499	172	26.5	5.6	1.7	0.5
Memo_2_100	2.4	0.5	0.2	0.0	4.2	2.2
Memo_2_80	33.0	2.0	2.7	0.2	17.6	2.5
Memo_2_60	412.5	30.0	11.3	0.4	8.3	2.0
Memo_2_50	733.0	85.0	5.3	3.5	0.5	0.3
Memo_2_40	983.0	148.0	4.0	2.2	0.4	0.3
Memo_1_100	0.9	0.3	0.2	0.0	11.8	1.3
Memo_1_80	1.2	0.1	0.3	0.1	26.3	4.6
Memo_1_60	8.5	4.3	1.3	0.5	41.3	7.0
Memo_1_50	too brittle					
Memo_1_40	too brittle					

mSLA 3D Printing. To find the ideal printing settings, we tested varying the bottom exposure time and exposure time per layer. We started observing the printability of our resins from 50 s of exposure time per layer for design without complex architecture, where the printed object before the postcuring step showed a gel-like behavior due to the incomplete

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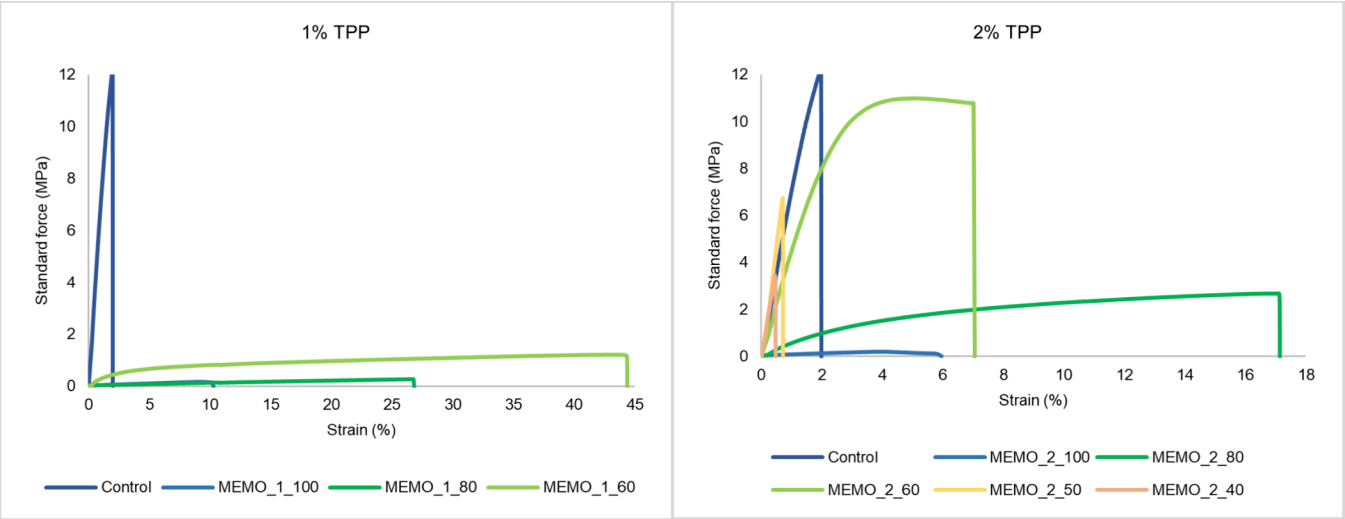

Figure 3. Representative stress−strain curves for products obtained with different resin formulations, with 1 and 2% of TPP MEMO. All the samples were cured in bulk for 10 min.

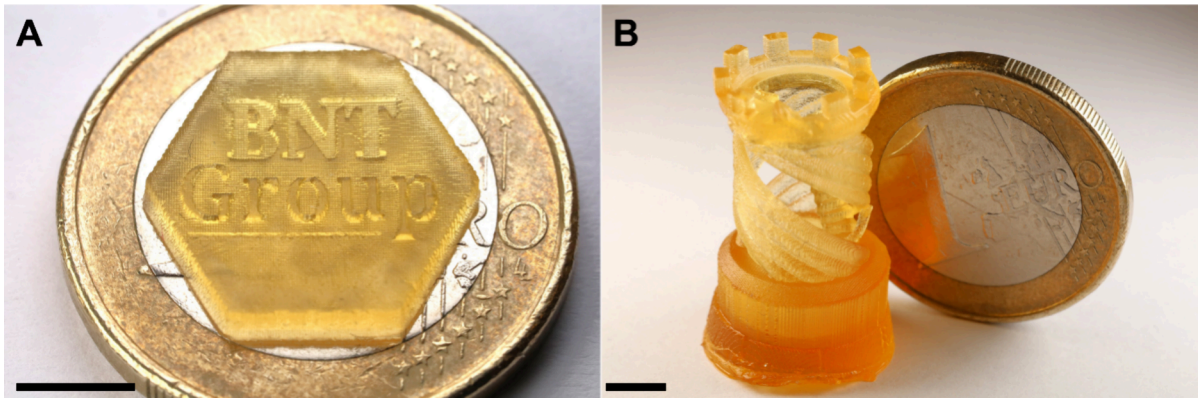

Figure 4. 3D printed objects obtained with the Microalgae resin (scale bars = 5 mm). (A) BNT logo obtained with 50 s of exposure. (B) Rook tower prototype obtained with 90 s of exposure.

polymerization of the sample (Figure 4A). Despite this, we were able to achieve both negative and positive features with high levels of detail, with a negative line thickness of 200 μm (almost 2 pixels in the mSLA printer used). We decided to test our resin also with more complex 3D designs by printing a rook and an SLA printing test. To obtain good stability of the printed object we had to increase the exposure time from 50 s up to 90 s, achieving a more complete polymerization (Figure 4B). Also with these settings, the printed designs showed good stability and a high level of detail. All of the printing tests have been conducted on the Lite3DP Gen 2 printer, which has smaller dimensions but also a less powerful LED source than most of the printers available on the market. So, to analyze the differences between the MiRe and a commercial resin, we compared the settings and the results obtained with the Prusament Resin Tough Anthracite Gray. Differently from the MiRe, where we used 110 s of initial exposure and an exposure time between 50 and 90 s, for the commercial resin, we chose an initial exposure of 40 s and an exposure time of 8.2. Similar settings were also able to cure Anycubic Eco Clear. The shorter exposure time of the commercial resin is due to extensive optimization of the resin composition. We believe that with similar experimentation it is possible to reduce the exposure time also of our MiRe.

CONCLUSIONS

In conclusion, with this work we have successfully developed a microalgae-based photocurable resin for SLA printers. The microalgal oil was epoxidated and methacrylated to obtain the MEMO, with a DoM between 1.2 and 2.2 based on the reaction protocol performed. By mixing MEMO with IBOMA as a diluent and BAPO as a photoinitiator, we created a library of biobased methacrylate photoresins. Performing mechanical tests on samples obtained with different compositions, we selected the resin formulation used to print 3D designs. The fabricated prototypes showed not only interesting mechanical properties, with an elongation at break significantly higher than a commercial resin, but also compatibility with the mSLA technology, with printed details of 200 μm. Although the resin cures ten times slower than the Anycubic Bio Clear, the formulation can still be improved both in terms of mechanical properties and in terms of printability, by, for example, changing the diluent or increasing the percentage of the photoinitiator. This biobased resin provides a more sustainable alternative to the more common soybean oil-based resins, to increase the use of green materials in additive manufacturing.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.5c00568.

1H-NMR of the EMO and MEMO; fatty acid profiles of the raw oil; and rheological data of the resins (PDF)

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Notes

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