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A self-photopolymerizable acrylated monomer from macaw vegetable oil

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Declarations

Conflicts of interest/ Competing interests: Not applicable.

Availability of data and material: Not applicable.

Code availability: Not applicable.

Abstract

The photopolymerization process has been widely studied due to its use in painting/coating, dentistry, creating photoresist materials and more recently in 3D printing. Therefore, new monomers have been synthesized to be used in this growing area. Here, a new Brazilian biomass derived, renewable monomer from macaw vegetable oil is presented. This monomer can self-polymerize without photoinitiation under UV light, reaching a monomer conversion of 75% and a conversion of 88% when ethyl 4-(dimethylamino)benzoate is present as a coinitiator. Furthermore, the final polymer has an orange color under visible light and exhibits fluorescence (a blue color) under UV radiation. Monomers and polymers formed from macaw vegetable oil are thermally stable up to 220 °C, as evidenced by thermogravimetry (TG). The polymers formed also exhibited a glass transition temperature of 2.6 °C, as observed in differential scanning calorimetry (DSC) curves and dynamic-mechanical analysis (DMA). This new monomer presents an alternative monomer to be used in 3D printing, in a similar manner to other vegetable oils such as soybean and linseed.

Keywords: *macaw oil, photopolymerization, renewable material, luminescent polymer, acrylated monomer, Brazilian biomass, 3D printing.*

Introduction

The photopolymerization process has been used since 1960 in fields such as odontology, paint/varnishes, coatings and adhesives [1]. Nowadays, photopolymerization is widely used in the 3D printing industry, which was estimated to be worth *c.a.* 11 billion US dollars in 2019 [2]. Acrylic and methacrylic monomers are normally used in this process, however the majority of these monomers are petrochemically derived. There is therefore a current interest to reduce the use of petroleum-derived monomers, and to replace them with new acrylic monomers obtained from renewable materials (for instance acrylated vegetable oil).

Acrylated vegetable oil can be synthesized from epoxidized vegetable oils and acrylic acid, often by the use of a catalyst at elevated temperature [3]. Usually, soybean and linseed oils are used in the acrylation process, due to their high content of unsaturated fatty acids [3,4]. In addition, soybean oil is used in the food industry and commercially as a frying oil. Based on the success of these vegetable oils as a sustainable alternatives to petrochemically derived monomers, and to reduce the current high demand for these vegetable oils, a new and alternative substitute obtained from Brazilian biomass is presented in this work.

Macaw palm (*Acrocomia aculeata*) produces fruits with a high content of vegetable oil and is widespread in the Brazilian Cerrado [5]. These fruits can provide a production of oil per hectare (4000 L), which is eight times higher than soybean production (500 L). Furthermore, the Brazilian government has been incentivizing the use of macaw oil in biodiesel and materials production [5,6]. The macaw vegetable oil (MWO) has an unsaturated fatty acid content of 81.7%, which means it has high potential to be used polymeric research [6].

Experimental

Materials

Macaw vegetable oil (leaking data: 03/2019; batch code: MAO073/18) was acquired from Mundo dos Óleos (Brasília, Brazil). Amberlite IR120, hydrogen peroxide (30% H_2O_2), glacial acetic acid (≥ 99%), tetraethylammonium bromide (TEAB; 99%), perchloric acid (70%), diethyl ether (≥ 99.9%), acrylic acid (anhydrous, 99%), hydroquinone (≥ 99%), imidazole (≥ 99.5%), camphorquinone (97%), curcumin (≥ 80%), abietic acid (75%), riboflavin (≥ 98%), and ethyl 4-(dimethylamino)benzoate (≥ 99%) were acquired from Sigma-Aldrich and utilized without further pre-treatment.

Syntheses of epoxidized and acrylated macaw vegetable oil

The epoxidation of macaw oil was performed according to the literature procedure [6], resulting in an epoxidized macaw oil (EMWO) with 0.339 mol of oxygen in an epoxide environment (as determined via the standard ASTM D1652-11 titration method) [7]. Thereafter, the EMWO (14.0142 g), acrylic acid (9.7112 g), imidazole catalyst (0.8100 g) and hydroquinone inhibitor (0.0420 g) were placed into a round-bottomed flask with a magnetic stirrer bar. The reaction mixture was heated under reflux conditions for 5 h at 80 °C. Then, the crude product was cooled and poured into a separating funnel along with 30 mL of diethyl ether. The organic layer was washed with distilled water until total ~~remotion~~ removal of residual acrylic acid. Thereafter, the organic layer was dried with magnesium sulfate and concentrated *in vacuo* to obtain the final product (12.4788 g) as an orange viscous liquid (Acrylated Macaw Oil -AMWO, Figure S1). The formed AMWO contained 0.1152 ± 0.0032 mol of oxygen in an epoxide environment, which means that there is 66.6% incorporation of acrylic groups into the triacylglycerol structure.

Photopolymerization reaction

Different photoinitiators (PI) were used in this study, including camphorquinone (CQ), abietic acid (ABA), curcumin (CUR) and riboflavin (RIB). Ethyl 4-(dimethylamino)benzoate (EDB) was used as co-initiator. Six quantities of AMWO (1.0000 g) were added to six different polypropylene containers. In four of them, 0.5 mass% of different PIs (CQ, ABA, CUR or RIB) along with 0.5 mass% of EDB, compared to AMWO, were added. In one container, EDB was added without a PI, and in another container, neither PI or EDB were added to the AMWO sample. Thereafter, AMWO photopolymerization occurred using a PR160 UV lamp (370 nm) from Kessil (purchased from Import Now, Brazil) or a blue LED lamp (430–490 nm, model D-2000, purchased from DMC, Brazil).

Sample characterization

Mid-infrared spectroscopy analysis (MIR) and monomer conversions (MCs)

MIR spectra for EMWO, AMWO and synthesized polymers were obtained using a Bruker Vertex 70 FT-IR spectrometer, with attenuated total reflectance (ATR) using a diamond crystal, in the region of 4000-500 cm^{-1} (with a resolution of 4 cm^{-1}). Monomer conversions (MC%) were calculated with Eq. 1, using the total area from the carbon

double bonds at 1618 cm^{-1} and 1637 cm^{-1}; where $A_{t=0}$ is the total area for the monomeric mixture and $A_{t=xs}$ is the area value obtained for each polymer spectrum obtained at different times. Each polymerization was run over 300 s with a spectrum collected at 10 s intervals [8]. The rate of polymerization was calculated following the literature procedure [9].

$$MC\ (\%) = \left[1 - \left(\frac{A_{t=x}(C=C)}{A_{t=0}(C=C)}\right)\right] \times (100) \quad (1)$$

^{1}H-NMR analysis

The ^{1}H-NMR spectrum of AMWO was obtained using an Ascend III 600 MHz NMR spectrometer (Bruker). Chloroform ($CDCl_3$, 99.8% D, Sigma-Aldrich) containing tetramethylsilane (TMS) was used as the NMR solvent.

UV-Vis analyses in liquid state and photolysis study

The UV-Vis spectra for each photoinitiator solution (0.5 mg mL^{-1} in ethyl acetate) and a AMWO solution (0.5 mg mL^{-1} in ethyl acetate) were collected using a Cary 8854 spectrophotometer (Agilent Technologies). Spectra were run at room temperature using a Quartz cuvette with an optical path of 1 cm.

Photolysis studies were performed using the aforementioned AMWO solution and the same Quartz cuvette at room temperature. UV-Vis spectra of this solution after UV exposure (from a Kessil PR160-370 nm UV lamp) were collected over time. A total of seven spectra were collected, with the first sample obtained at 0 s (i.e. the blank sample), and the following at 10 s, 20 s, 30 s, 60 s, 180 s and 300 s.

UV-Vis analysis in solid state

UV-Vis spectra for solid state analysis were obtained using a Lambda 1050 double beam spectrophotometer (Perkin Elmer) in the 600-280 nm range, using a polymeric film as a sample.

Thermal analysis: simultaneous thermogravimetry-differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA)

Simultaneous TG-DTA curves for AMWO and the two polymers that exhibited the best conversions under UV light (the AMWO EDB only and AMWO CQ/EDB systems) were obtained using a Netzsch STA 449 F3 simultaneous module. Samples (30 mg) were placed into an α-alumina open crucible (200 mL). A temperature range of 30

to 700 ºC was used, under a dry air atmosphere (with a flow rate of 70.0 mL min^{-1}) and a heating rate of 10.0 °C min^{-1}. These TG curves were also used to obtain thermal stability, mass loss steps, and mass difference (Δm) information about the analyzed samples.

DSC analyses were performed in a Mettler-Toledo DSC apparatus (model DSC 1 Star^e) using 10 mg of sample, which were analyzed in a 40-µL closed aluminum crucible with a perforated lid. At first, samples were cooled from 25 °C to -35 °C, and maintained at -35 °C for 10 min, before heating from -35 °C to 200 °C. Thereafter, the sample was cooled again to -35 °C (which was maintained for 10 minutes) and then heated to 200 °C, with a flow rate of 50.0 mL min^{-1} in a dry air atmosphere and setting a heating rate of 10.0 °C min^{-1}. Three samples were analyzed via this method: AMWO and the two polymers which reported the higher conversions under UV light.

DMA analyses were executed in a Q800 apparatus (TA instruments). The two polymers which exhibited higher conversions under UV light were analyzed. The polymer samples were cut into pieces of 20 mm length, 5 mm width and 1 mm thickness prior to analysis and analyzed from -50 °C to 30 °C under a nitrogen atmosphere, using a frequency of 1 Hz and a heating rate of 3 °C min^{-1}. The DMA provided curves which were used to obtain storage modulus (E') and tan-δ values.

Results and discussion

MIR and ^{1}H-NMR analyses

MIR spectra for EMWO and AMWO are shown in Figure 1. After the acrylation reaction, two new bands were observed at 1618 cm^{-1} and 1637 cm^{-1}, relating to C=C bond stretches present in α,β-unsaturated acrylic groups (as highlighted by the blue dashed box). The band at 2978 cm^{-1} (highlighted by the dashed red box) is associated with the stretching of a vinylic C-H (C=C-H) bond [10]. Two bands are also exhibited at 1116 cm^{-1} and 1182 cm^{-1} (green dashed line), which are related to the stretching of α,β-unsaturated esters [C=C-C(=O)-O-C)] [11].

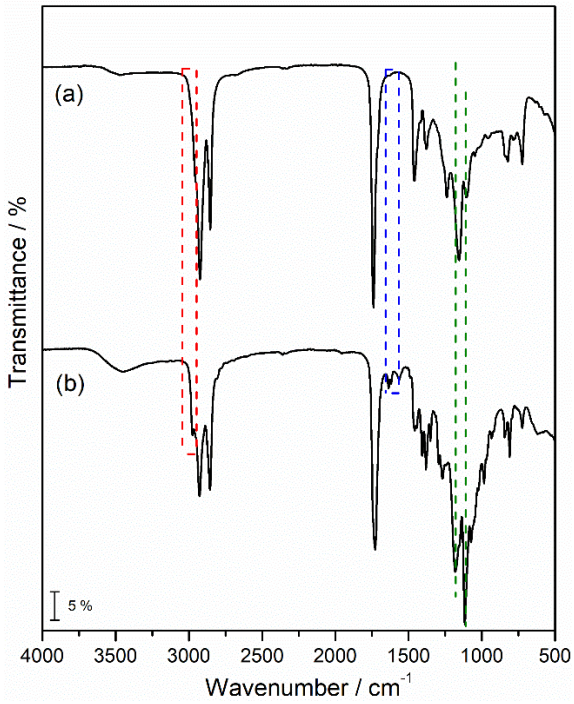

Figure 1. MIR spectra for EMWO (a) and AMWO (b).

Figure 2 shows the ^{1}H-NMR spectrum for AMWO, with signals at 2.70, 2.90 and 2.99 ppm relating to hydrogens attached to epoxide rings (highlighted in blue) [6]. These signals indicate the presence of residual unreacted epoxide. Using these signals, conversions could be calculated via ^{1}H-NMR analysis, indicating that 68.4% of acrylic acid was incorporated in AMWO, which is in agreement with the titration result (66.6%). The vinylic hydrogens of the acrylic group incorporated into the vegetable oil structure appear as three multiplet signals at 5.83, 6.13, and 6.40 ppm (highlighted in red) [12].

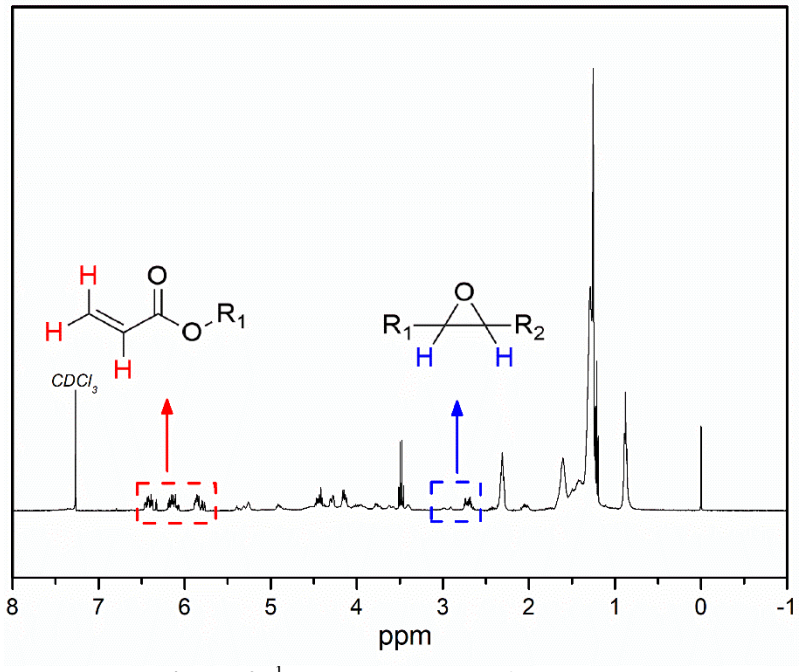

Figure 2. ^{1}H-NMR spectrum for AMWO.

UV-Vis liquid state analysis and AMWO Photolysis

The UV-Vis spectra for each photoinitiator (PI) and AMWO are exhibited in Figure 3, with the blue light region (430-490 nm) highlighted in blue and the UV region (370 nm) highlighted by a purple line. The CQ sample shows an intense band with λ_{max} at 471 nm, which starts in the blue region and continues to the UV region, thus indicating that CQ can absorb light in both regions. The CUR sample has an absorption band between 500 nm and 300 nm with a λ_{max} at 416 nm. indicating therefore that CUR can also be used in both light sources.

The RIB sample exhibits a low intensity band in the blue region, between 368 nm and 424 nm, and a band with high intensity at 395 nm, which indicates RIB exhibits better absorption in UV light compared to blue light. The ABA sample exhibits a lower absorption in the blue light region compared to the UV region, as it presents a band starting at 400 nm and ending at 250 nm with a λ_{max} at 258 nm. This therefore indicates that although ABA is not a great PI for blue light, it shows promising activity under UV light.

The AMWO sample does not show a significant absorption in the blue light region, showing an absorption within the UV region between 410 nm and 344 nm.

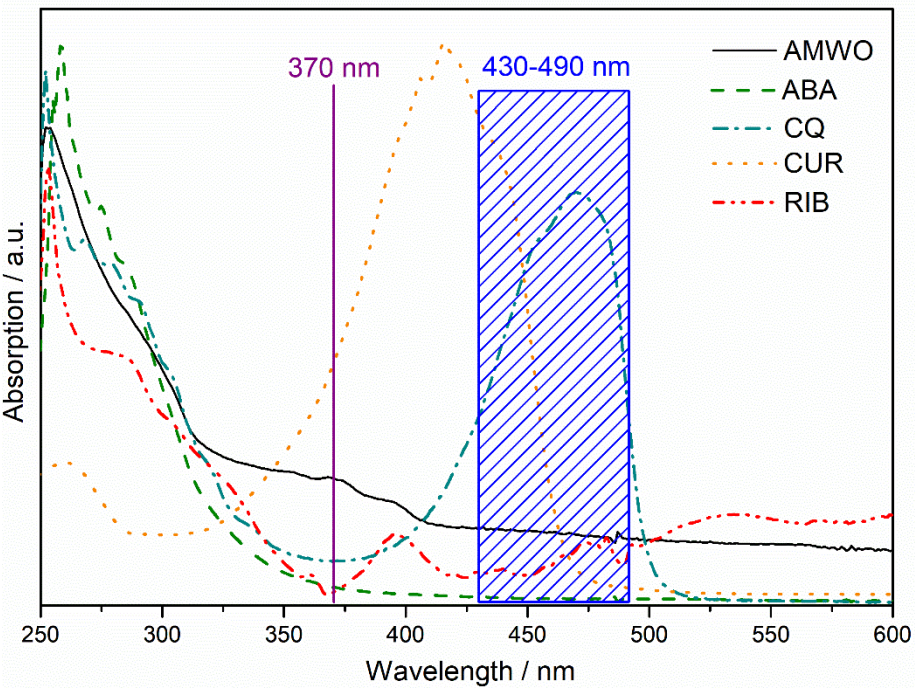

Figure 3. UV-Vis spectra for each photoinitiator and AMWO.

The photolysis study for AMWO was performed under UV light (370 nm) and spectra were obtained over time. A total of seven spectra were obtained, with the first sample obtained at 0 s (i.e. the blank sample), and at 10 s, 20 s, 30 s, 60 s, 180 s and 300 s). Reduction in the intensity of some bands over time (at 362 and 292 nm) indicates that a photolysis process occurred, in particular an auto-photopolymerization reaction [13]. A similar process was reported in 2009 by Huang *et al.* highlighting that a new polyacrylated monomer could undergo an auto-photopolymerization reaction. They also discovered that the photolysis process of this polymer occurred with a decrease in band intensity related to the π–π^* transition (which occurs in the acrylate group). In order to perform this process, Huang *et al.* needed to use a more energetic light source (253-366 nm) compared to our findings [13].

In our research, the photolysis study showed a decrease in band intensity in two regions, the band between 320 nm and 380 nm (Figure 4), including a small peak at 362 nm, and between 280 nm and 320 nm (with a λ_{max} of 292 nm). These bands are related to π–π^* excitation (i.e. reaching a triplet state) occurring in the vinyl group of the acrylate. Once in this triplet state, the excited electron can withdraw a hydrogen atom from the methylene (CH_2) group close to the oxygen, thus forming a new radical [13]. This radical can then attack another vinyl group, consequently causing a chain-growth polymerization process and reducing its absorption in the UV-Vis spectrum.

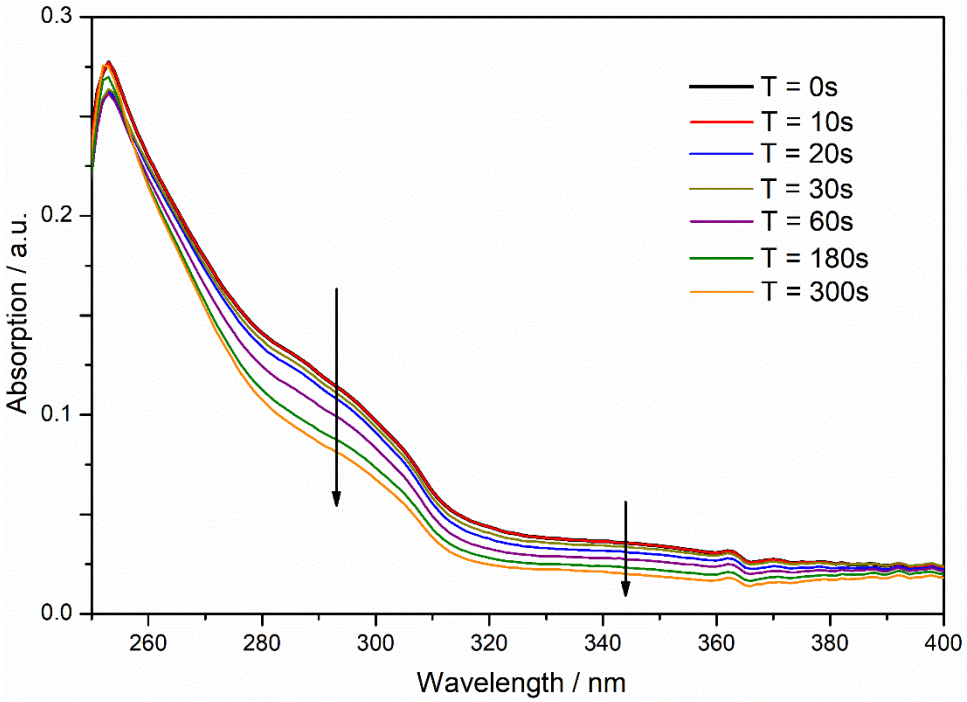

Figure 4. Absorption spectra for AMWO at different times during the photolysis process. The AMWO sample was analyzed at a concentration of 0.5 mg mL^{-1} in ethyl acetate.

AMWO photopolymerization study with different photoinitiators and UV-Vis solid state analysis for polymeric film.

Normally, the photopolymerization of acrylated vegetable oils occurs under UV light, using *Type I* photoinitiators such as diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), 1-hydroxycyclohexyl phenyl ketone (HCPK) or 2,2-dimethoxy-2-phenylacetophenone (DMPA) amongst others. In 2019, Kousaalya *et al.* performed a photopolymerization reaction under UV light using acrylated soybean oil (ASO), with DMPA and HCPK as PIs. Under these conditions, they reported MCs of 80% with DMPA (2 wt.%) and 85% with HCPK (4 wt.%), after 60 s of light exposure. The MC could be increased to 100% using DMPA (2 wt.%) at 75 °C [14]. Liu *et al.* also demonstrated that AESO conversions up to 90% could be achieved in 300 s under UV light using TPO (3 wt.%) [15].

In our study, a *Type II* photoinitiator was used and initially studied under blue light conditions (430-490 nm). To calculate the MCs obtained in Eq. 1, the area of C=C band between 1618 cm^{-1} and 1637 cm^{-1} was used. Figure S2 shows the spectra for AMWO and the polymer obtained after 300 s of UV irradiation. As expected, the polymer does not display an intensity band related to a C=C bond, thus proving a polymerization process has occurred. The CQ/EDB system reached a conversion of

86% in only 10 s and a total conversion of 98% after 300 s, which was the highest conversion obtained for all systems (Figure 5a). The CQ samples showed a high absorption in the blue region as previously discussed, which explains its excellent performance. As expected, the rate of polymerization (Figure 5b) reached a maximum value at 10 s, with no variation in the rate of polymerization observed at later time points, indicating the rate of conversion starts stabilizing after 10 s.

The AMWO system without PI and EDB showed the second highest conversion, reaching 46% after 300 s. Interestingly, only 6% of monomer was converted after the first 10 s (Figure 5a). This indicates a slow polymerization reaction occurred, due to poor excitation in the blue light region. When the AMWO system was analyzed in the presence of EDB (without a PI), it exhibited a conversion of only 9% in 50 s. The final conversion value obtained after 300 s was 28%, resulting in a polymer that was not rigid but contained gel-like features.

For the ABA/EDB system, a conversion of 2% was observed after 10 s and a maximum conversion of 41% (300 s) under blue light. This was expected as ABA exhibits a small absorption in the blue light region (Figure 3). The RIB/EDB system showed a poor conversion in the first 10 s (<1%), reaching only 21% conversion after 300 s, perhaps for two main reasons. Firstly, RIB does not exhibit a high absorption in the blue region, and secondly, RIB showed poor solubility in the AMWO sample.

Despite the high absorption of the CUR/EDB system in the blue region, this system showed a low conversion after 300 s (20%). In 2015, Zhao *et al.* reported a maximum conversion of 71% using a formulation containing TEGDMA/Bis-GMA (30:70) as monomers, and a CUR/iodonium salt/ triphenylphosphine mixture as a PI, under blue light [21]. The same authors reported that changing the PI system (CUR/EDB) and light source (from blue to UV) increased the conversion of this formulation to 48% [16]. In 2017, Oliveira *et al*. reported a conversion of 55% after 400 s using a CUR/EDB system and UDMA as monomer [17]. These high conversions can perhaps be explained in two ways. Firstly, although CUR has a high absorption, highly absorptive compounds when present in higher concentrations tend to be suppressed by an aggregation-based quenching effect, which hinders electron excitation and light emission [18]. Secondly, CUR exhibits a solvatochromic effect, which means it can change its region of absorption when solubilized in AMWO [19].

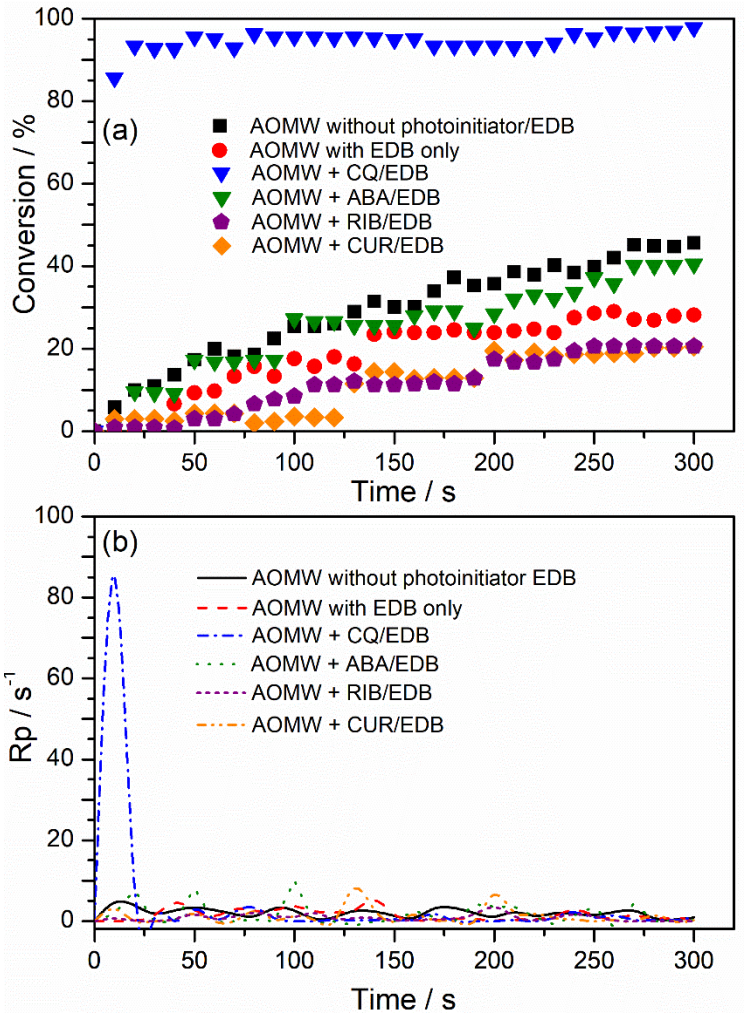

Figure 5. Monomer conversion (MC) curves obtained for synthesized polymers under blue light (a) and rates of polymerization (b).

Interestingly, the polymerization of AMWO using a CUR/EDB photosystem under UV light only achieved a conversion of 2% (Figure 6a). Although CUR has a high absorption under UV light, the low conversion reported can be attributed to a quenching effect, due to the high concentration of CUR. For the RIB/EDB system, the conversion reached 15% in the first 50 s, and a conversion of 43% in 200 s. The final polymer formed from this process had a solid form but was extremely fragile. This low conversion was expected because RIB exhibited a low solubility in AMWO. The ABA/EDB system provided a conversion of 6% after 10 s, reaching a conversion of 81% after 200 s and a total conversion of 85% after 300 s. The CQ/EDB system reached a high conversion in the first 10 s (28%) with excellent velocity as observed in Figure 2b. In just 50 s, the system achieved 92% conversion (which was the maximum conversion obtained overall).

The system without PI and EDB achieved a maximum conversion of 75% in 300 s, giving conversions of 9% and 45% after 10 s and 100 s, respectively. This result indicates that a self-polymerization process occurred as no photoinitiator was used and the reaction was dependent on AMWO excitation. Therefore, the AMWO can be polymerised without the presence of a PI, or can even be used as a PI for other systems containing other acrylated monomers. Whilst the addition of EDB to AMWO did not improve conversion velocity, achieving only 10% in the first 10 s, the addition of EDB did increase the maximum conversion reported after 300 s (88%), giving comparable results to the ABA/EDB and CQ/EDB systems. Therefore, AMWO self-polymerization can also be assisted by the addition of EDB. These results are better than those previously reported in literature for *Type I* PIs. Table 1 shows the conversions obtained for each system over time.

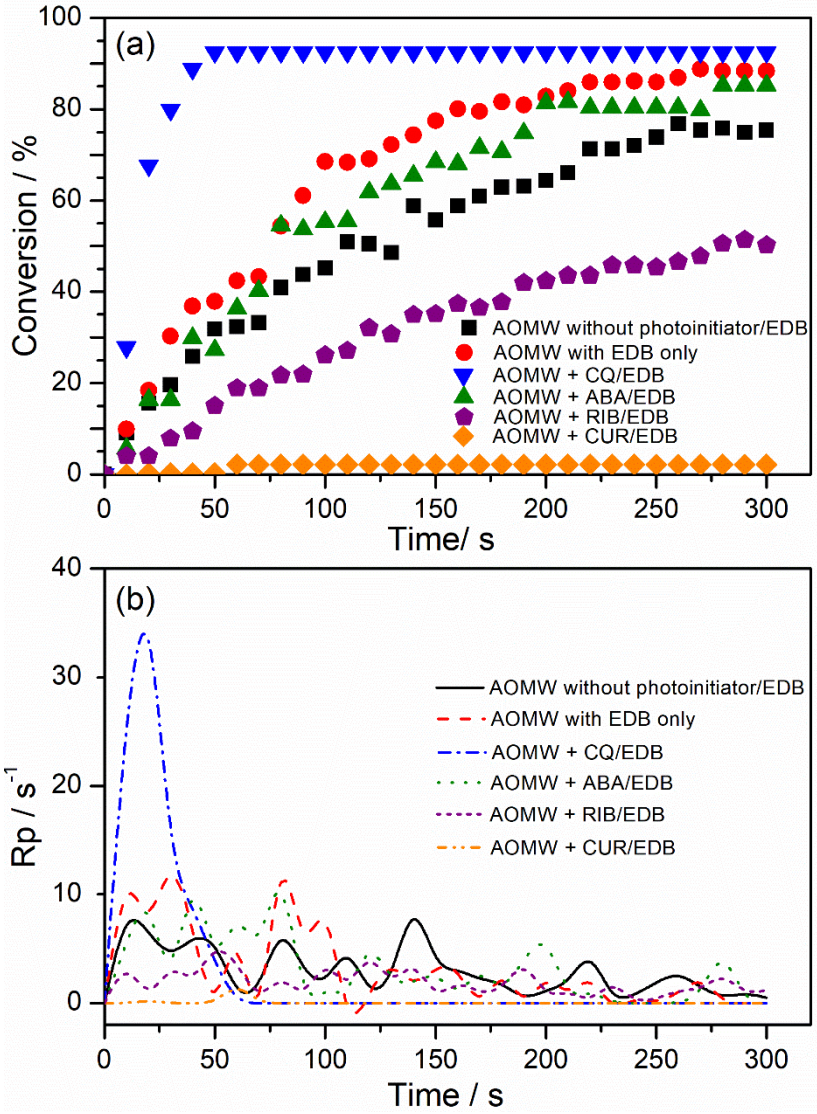

Figure 6. Monomer conversion (MC) curves under UV light for synthesized polymers (a) and rates of polymerization (b).

Table 1. Monomer Conversion (MC / %) values for each sample during the polymerization process under blue and UV light.

	Sample	MC / %				
		10 s	50 s	100 s	200 s	300 s
Blue light	AMWO w/o PI/EDB	6	17	25	36	46
	AMWO + EDB only	0	9	17	24	28
	AMWO + AA/EDB	2	17	27	28	41
	AMWO + CQ/EDB	86	96	96	96	98
	AMWO + RIB/EDB	1	3	8	17	21
	AMWO + CUR/EDB	3	4	4	19	20
UV light	AMWO w/o PI/EDB	9	32	45	64	75
	AMWO + EDB only	10	38	68	83	88
	AMWO + AA/EDB	6	27	55	81	85
	AMWO + CQ/EDB	28	92	92	92	92
	AMWO + RIB/EDB	4	15	26	43	50
	AMWO + CUR/EDB	0	2	2	2	2

As demonstrated in Figure 7, the AMWO polymer formed without using a PI or EDB has an orangish color under visible light and is fluorescent under UV light, emitting a blue color. This fluorescence property under UV light can be related to the aggregation induced emission (AIE) effect, due to electrons in a non-ligand orbital from an oxygen atom interacting with another orbital from a second oxygen atom (in the polymeric structure), which consequently reduces the electron excitation energy [18,20]. The UV-vis spectrum (Figure 7) displays a low intensity band at 378 nm and a maximum band at 313 nm, hence the observed color.

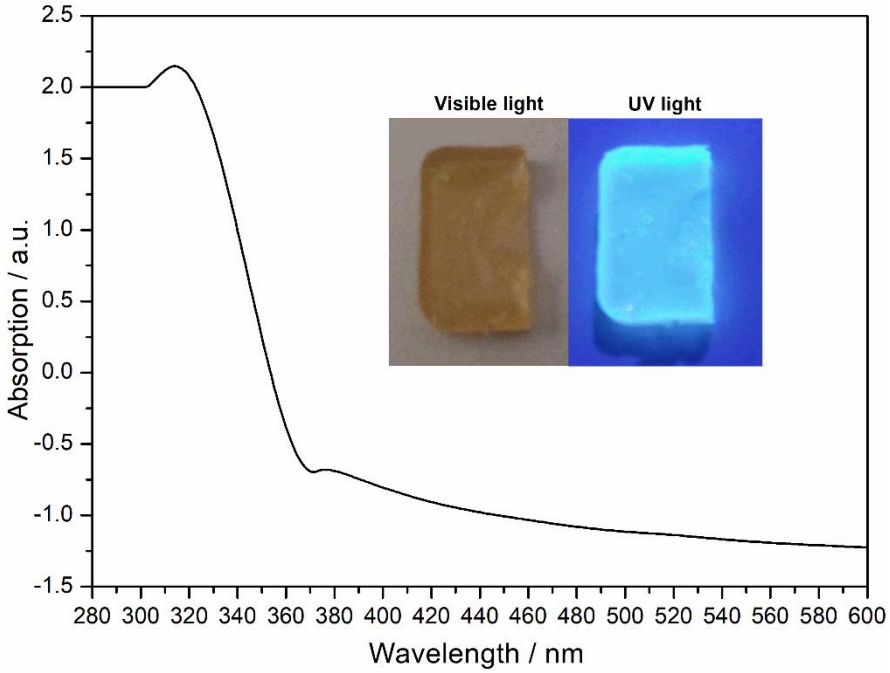

Figure 7. Solid state UV-Vis spectra for the AMWO polymer formed without PI or EDB, with its appearance under visible and UV light.

As a result of this conversion study, is possible to conclude that AMWO could be a promising monomer for 3D printing. The AMWO monomer could substitute acrylate soybean oil in other formulations containing acrylate/methacrylate monomers, such as UDMA, TEGDMA, Bis-GMA, and HEMA amongst others. Moreover, the fluorescent property of the AMWO polymer creates the possibility that it could be used in polymeric light-emitting diodes (PLEDs), to promote circularly polarized luminescence and in electrochromic devices [21-23].

TG-DTA, DSC and DMA analysis

Three representative samples were chosen for thermal analysis via TG/DTG-DTA and DSC analysis: an AMWO sample and the two polymers formed with the highest MCs under UV light. The TG and DTG curves for AMWO (Figure 8a) indicate that the sample is thermally stable up to 220.4 °C. The first step of mass loss occurs between 220.4 °C and 472.0 °C (Δm = 83.62%). Although the TG curve exhibits a simple step of mass loss in this range, the DTG curve displays five different mass loss processes that are consecutive and overlapped. These mass loss steps were attributed to acrylic and epoxide group degradation, followed by fatty chain degradation [24]. According to the DTG curve, the first step presents a maximum degradation rate (MDR) of 12.39 % min^{-1} at 383.2 °C, associated with the exothermic peaks observed in the DTA curve at 342.8 °C and 389.5 °C. Furthermore, the exothermic event at 149.7 °C without any

mass loss was associated with the thermal polymerization of AMWO. The second mass loss started at 472.0 °C and finished at 599.8 °C, with a Δm of 16.38%, which is associated with the degradation and oxidation of residual carbonaceous material. In the DTA curve for AMWO, this event appeared as an exothermic peak at 506.7 °C.

Figure 8b exhibits the TG/DTG-DTA curves obtained for the AMWO polymer formed with CQ/EDB under UV light. This polymer is thermally stable up to 220.2 °C, when the first step of mass loss begins and finishes at 473.0 °C (Δm = 81.35%), linked with the exothermic peak at 382.0 °C. As previously observed for the AMWO monomer, this first mass loss step is also complex, with a MDR of 10.56 % min^{-1} at 367.6 °C. As expected, this polymer had a lower MDR value due to the high MC result reported via MIR analysis. A higher MC will create a polymer with a higher crosslink density, which in turn affects thermal degradation and makes the bonds between the monomer chains stronger. In the DTA curve, a polymerization process was not observed. The second mass loss step was also related to carbonaceous material degradation, occurring from 473.0 °C to 600.1 °C (Δm = 18.65%) and was connected with the exothermic DSC peak at 526.2 °C.

The TG/DTG-DTA curve for the polymer formed using EDB alone under UV light is akin to the CQ/EDB polymer with no major differences (Figure S3).

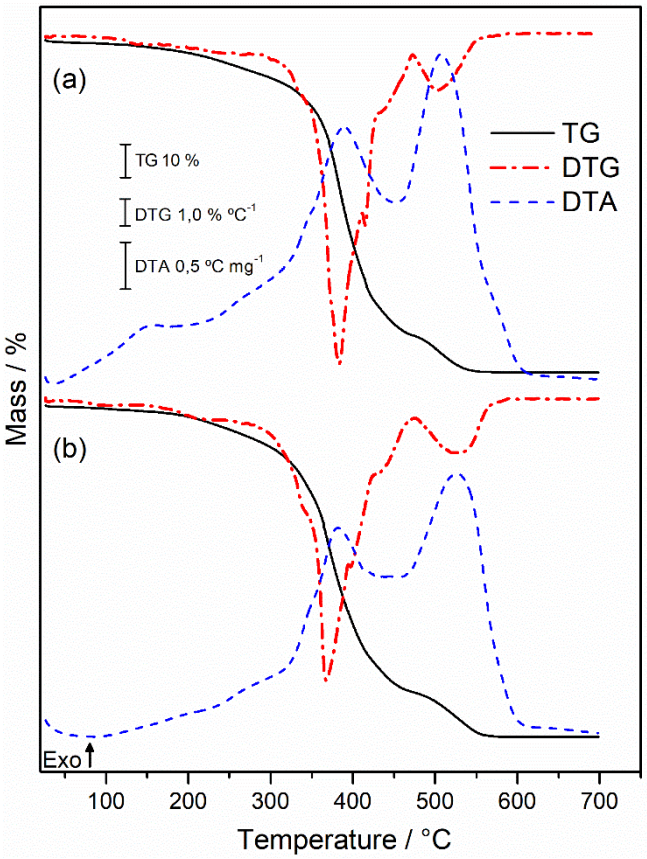

Figure 8. TG/DTG-DTA curves for AMWO (a) and the CQ/EDB polymer obtained using UV light (b).

The DSC curve for AMWO is displayed in Figure 9-a as two cooling and two heating cycles. As previously mentioned, the AMWO monomer is a viscous liquid at room temperature, and it was expected that AMWO would solidify during the cooling stage, considering it is a viscous liquid at room temperature. However, no exothermic event was observed in both cooling stages. A possible explanation could be that the material is too viscous and slowly solidifies during the cooling process, releasing low amounts of heat which were undetectable via DSC equipment [25]. This was further confirmed by the broad signals between 20 and -15 °C in the first cooling stage and between 15 and -20 °C in the second cooling stage.

Although the solidification process was not clearly observed during cooling, it appeared as an endothermic event in the heating cycle, with a peak at -0.4 °C (ΔH = 4.74 J g^{-1}), which is related to a melting process. Moreover, in the first heating stage an endothermic peak was observed at 83.3 °C (ΔH = 3.37 J g^{-1}) that could be related to a change in AMWO viscosity. Thereafter, an exothermic event is observed at 139.7 °C that is linked to a thermal polymerization process. In the second heating stage, only the endothermic event at -0.4 °C is observed. To elucidate these transition events, a visual

analysis was also performed using a DSC apparatus connected to a microscope (DSC-photovisual, Figure S4 and Video S1).

The CQ/EDB polymer system formed under UV light did not exhibit thermal events in both DSC cooling stages (Figure 8b). However, a baseline change was observed during the first heating cycle, which was related to a glass transition (T_g) event, with a midpoint temperature at 2.6 °C. Furthermore, an endothermic event at 86.1 °C was observed due to residual monomers changing viscosity (ΔH = 6.67 J g^{-1}). The monomers in this system also polymerized, as confirmed by the exothermic event at 176.5 °C (ΔH = 2.70 J g^{-1}). In the second heating stage, only a T_g event was observed (midpoint = 2.6 °C).

The DSC curve for the polymer formed using EDB alone under UV light exhibited similar behavior to the polymer formed using the CQ/EDB system under UV light (Figure S5).

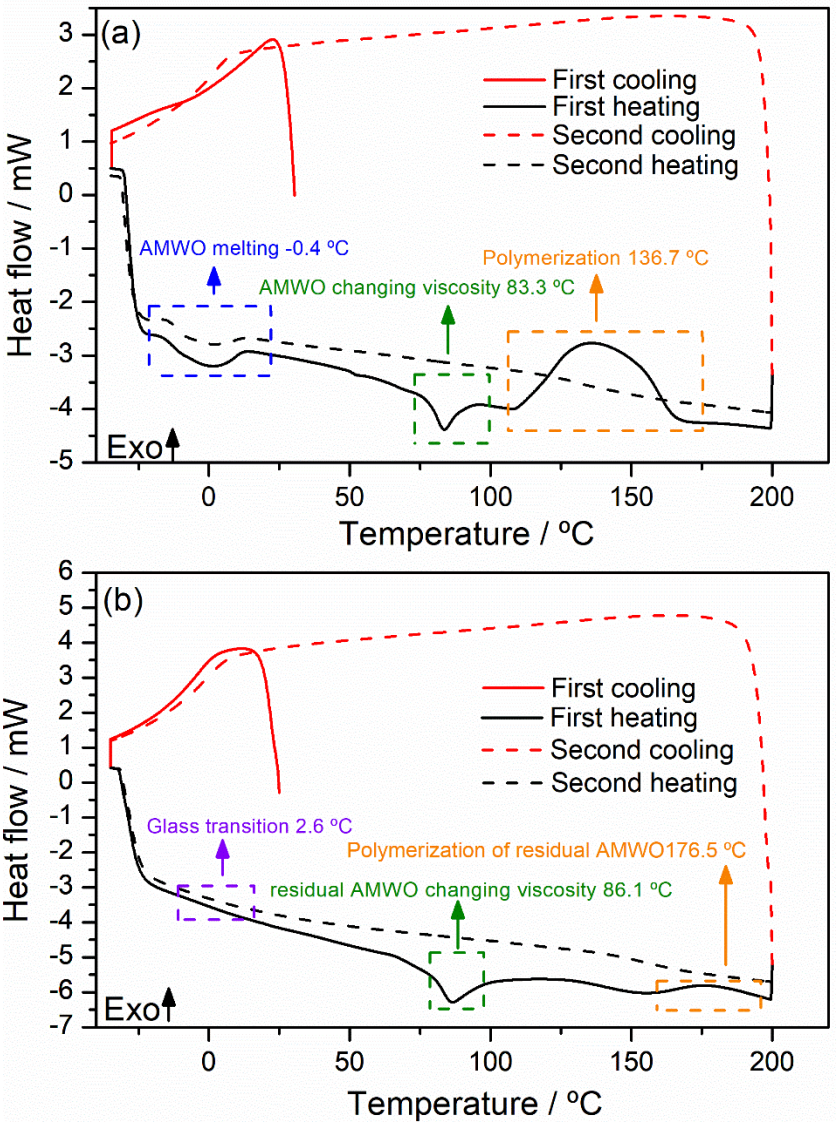

Figure 9. DSC curves for AMWO (a) and the CQ/EDB formed polymer using UV light (b).

To confirm the glass transition temperature observed via DSC analysis, both AMWO polymers formed under UV light using a CQ/EDB system and EDB only system were analyzed via DMA. The DMA curves for both polymers are displayed in Figure 10, illustrating the storage modulus (E') and the tan-δ values obtained. Both polymers have similar E' values, confirming the similarity in the crosslinking structure as measured earlier via MIR. The peak temperature of the tan-δ curve represents the glass transition temperature and are therefore in accordance with the DSC analysis. The CQ/EDB polymer system reports a T_g event at 2.77 °C and the polymer formed using EDB alone shows reports a T_g event at 2.56 °C.

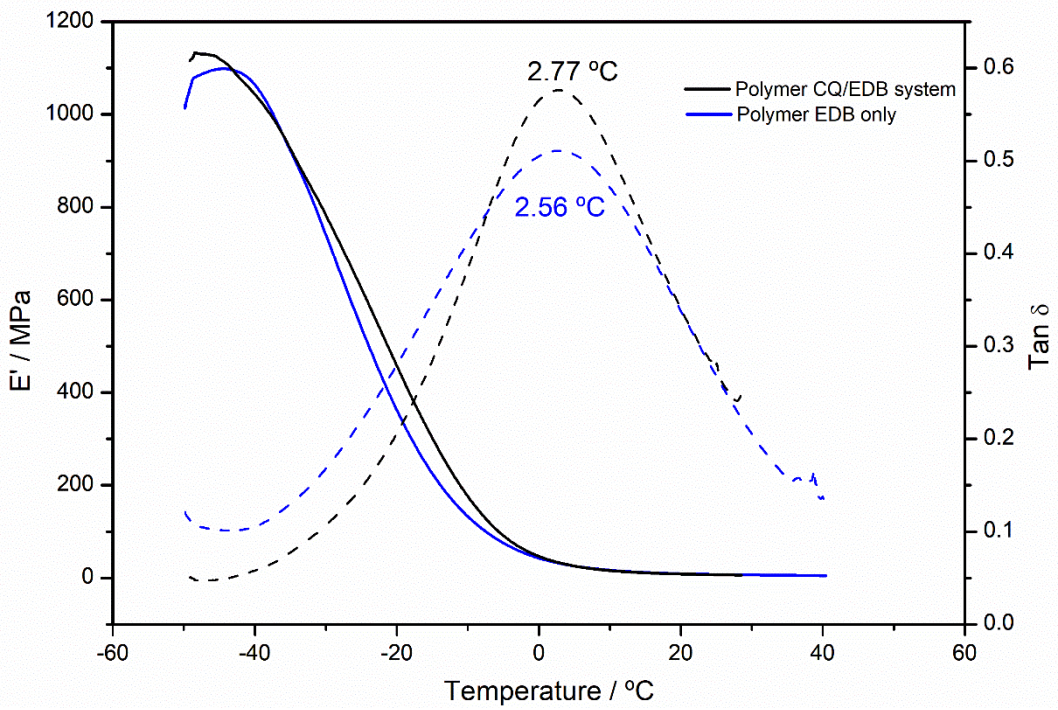

Figure 9. DMA analysis for the AMWO polymers formed under UV light using a CQ/EDB system and EDB only system, showing the storage modulus (E') and tan δ curves.

Conclusions

The acrylation reaction of the epoxidized macaw oil was satisfactory, giving 66.6% incorporation of acrylic groups into the vegetable oil structure, as confirmed by titration and MIR analysis. The AMWO monomer is an orange liquid that self-polymerizes under UV light (without a PI or EDB) achieving a monomer conversion of 75%. EDB can be used to improve this conversion (88%) and the CQ/EDB system also enhances the reaction rate and conversion (92%). All polymers formed exhibited an orange color under visible light and a blue color under UV light, therefore displaying fluorescent properties.

The AMWO monomer and polymer CQ/EDB formed under UV light are thermally stable up to 220.4 and 220.0 °C, respectively. The DSC curve exhibited glass transition temperatures, residual monomer fluidity (i.e. a change in viscosity) and residual monomer polymerization in the first heating stage. The DMA results corroborated the glass transition temperatures as determined by DSC.

The AMWO is a promising renewable monomer that could be used in 3D printers and other processes that depend on photopolymerization. Furthermore, it could be used an alternative and sustainable polymer with fluorescence properties, and thus used in

polymeric light-emitting diodes (PLEDs), electrochromic devices and to promote circularly polarized luminescence.

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