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Biobased polyester from soybean oil: Synthesis, characterization and degradation studies

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ABSTRACT

Industrially used polymers derived from fossil fuels have a negative environmental impact when being disposed of. They could be efficiently replaced by natural polymers, which are potentially degradable and which can match or even surpass them in mechanical performance. In this work, a rigid thermosetting polymer is obtained by copolymerization of maleinated acrylated epoxidized soybean oil (MAESO) with styrene (St). MAESO is synthetized by epoxidation, acrylation and maleinization from industrial soybean oil (SO). Resin characterization is performed using FT-IR, ^{1}H NMR and SEC, while copolymer characterization includes a mechanical test, degradation test and SEM. The aim of this work is the replacement of unsaturated polyester (UP) and the optimization of the SO modification reaction in MAESO. The replacement of UP by 25, 50 and 100% of MAESO enables improvements in the mechanical properties. Additionally, it is assessed whether the replacement of UP by MAESO is enough to improve the degradation properties, and the effect of degradation on the mechanical properties is analyzed. MAESO-St copolymers improve the degradation process in relation to UP, and 240 days of *in vitro* degradation in the presence of *Aspergillus niger* and *Alternaria alternata* fungi causes cracks, surface damage and changes in the mechanical properties of the degraded copolymer. **Polyolefins J (2022) 9: 45-60**

Keywords: Biobased polymers; soybean oil; degradation; unsaturated polyester resins; maleinization.

INTRODUCTION

Thermosetting polymers are widely used in different industrial applications. Most of them are synthesized from non-renewable natural resources [1]. Within this family of materials, unsaturated polyester resins (UP) are polymers most commonly used in component reinforcement parts for marine, transport or construction applications, as well as for electrical materials and everyday consumer products [1,2]. However, the use of fossil fuels to develop these products implies an environmentally unfriendly process [3,4]. This limitation led to the study of various substances as their potential replacements. Thus, researchers have been studying the potential of biodegradable natural products, such as vegetable oils,

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as possible replacements for commercial synthetic polymers. To this effect, soybean oil (SO) is one of the most extensively considered products due to its versatility, since functional groups can be modified to form potentially reactive molecules.

The obtention of SO in Argentina is widespread and results in an attractive option for the development of industrial by-products. The average unsaturation degree for SO is 4.6 double bonds per triglyceride (TG) molecule. These unsaturations are not reactive enough to be directly copolymerized by free radicals; therefore, TG molecules contained in SO must be derivatized. The introduction of functional groups to the TG molecule involves several types of reactions [5], epoxidation and hydroxylation being the most common. Polyols obtained by epoxidation of SO can also be acrylated, thus creating a material suitable for glossy coatings and adhesives. These acrylate esters are easily polymerized through the remains of vinyl acrylate, yet the resulting polymers are amorphous and flexible due to their low crosslink density and degree of cohesiveness [6]. Accordingly, it is necessary to modify the molecule structure, esterifying the alcoholic residues with maleic anhydride (MA), which enables an increase in the number of reactive groups available for copolymerization with styrene (St).

The structures obtained by modifying and crosslinking SO result in rigid products. Research in this field reported the optimization reactions of epoxidized SO (ESO) and acrylated ESO (AESO) to be used in different applications [5,7,8,9]. In this regard, ESO copolymers maleinated with St as a substitute for epoxy resins have been evaluated, obtaining thermosets with good mechanical properties when cured at over 190°C [5, 10]. Partial substitutions of UP with ESO and commercial AESO were also evaluated to develop materials reinforced with cane fiber and nanoclay [11,12]. MAESO-St copolymers were synthesized from commercial AESO and evaluated as UP replacements for the production of sheet-molding compounds, studying the effect of the comonomer, viscosity and MgO interaction in the structure-property ratio [13]. The mechanical behavior of MgO-filled MAESO-St copolymers was comparable to that of orthophthalic unsaturated polyester resins [14]. Many authors have proposed AESO as a replacement

for St in UP resins in fiberglass-reinforced composites, improving flexibility and stress resistance [15,16]. The degradation capacity of methacrylated AESO resins copolymerized with methacrylated vanillyl alcohol was measured in a microbial degradation test in soil, and then compared to that of pure AESO [17].

The use of MAESO can be considered as an ecologically sustainable improvement in the substitution of resins derived from fossil fuels. However, there are contradictions in this assumption since, in order to obtain a product with good mechanical properties, it is necessary to use acrylic acid (AA), MA and St, which are all derived from fossil fuels. This fact raises doubts as to whether the replacement of MAESO is enough to provide environmental benefits by the time of disposal compared with the UP it is intended to replace. For this reason, it is of interest to evaluate the comparative degradation of MAESO and UP in controlled environments, as well as to examine the impact of this on their mechanical properties. This will allow for an estimation on how the degraded material structure is modified, which would be an improvement in the possibility of replacing those components that still depend on fossil fuels.

Most of the studies reviewed only focused on the synthesis of a single reaction or on the maleinization of commercial products. However, no studies were found to investigate the complete optimization of the reaction from SO to MAESO. On the other hand, researchers do not seem to have focused on the use of spectroscopy in conjunction with other techniques as a means to evaluate the product structure regarding the improved yields and mechanical properties achieved.

An interesting structure-property study was performed by monitoring the viscosity of a sample during the catalyzed reaction [14]; however, the developed polymer structure was not analyzed regarding the influence of functional groups present in the course of the reaction. Thus, it seems necessary to further analyze the structure achieved during the complete course of the reaction and its influence on mechanical properties.

Based on this, one of the objectives of this work was the preparation of a degradable biobased polyester using SO. To that effect, an optimization of the reaction process using industrial SO was studied.

Spectroscopic techniques were used to monitor the products obtained, based on the different reaction variables studied. Once the product was obtained with good yields, it was copolymerized with St and its mechanical tests were then statistical compared with those for commercial isophthalic UP in different proportions.

Another complementary objective was to study the degradation process of the MAESO-St copolymer in specific disposal conditions and to compare it with the degradation for UP commercial resins. An in vitro degradation process was carried out by chemical hydrolysis and the action of microbial biomass comprising Aspergillus niger and Alternaria alternata fungi. According to our bibliographic search, there are very few previous records on this topic applied to UP.

EXPERIMENTAL

Materials

Soybean Oil (SO) was obtained from ERI Cotagaita (Argentina). The reagents used were formic acid (AF) 98%, hydrogen peroxide 30%, hydroquinone 99.5% (HQ) (Cicarelli); maleic anhydride (MA) 99%, acrylic acid (AA) 99% (Merck); sulfuric acid 98% (H_2SO_4) (Cicarelli); styrene 99.85% (St) (Pemex); methyl ethyl ketone peroxide (MEK); cobalt octoate 2.5% (OCo), and unsaturated polyester resin (Poliresinas San Luis, Argentina). The reagents used in auxiliary techniques were 99.5% absolute ethanol (Biopack); potassium hydroxide 98%, alcoholic phenolphthalein solution 1%, toluene, 99.5% potassium biphthalate, petroleum ether 30-65°, sodium bicarbonate and sodium chloride 99.5% (Cicarelli); meat peptone and malt extract (Laboratorios Britania); anhydrous glucose 99.5%, glycerol 99.9%; potassium phosphate, potassium dihydrogen phosphate, ammonium nitrate, magnesium sulfate heptahydrate, zinc sulfate heptahydrate, copper sulfate pentahydrate, iron sulfate heptahydrate and manganese sulfate monohydrate (Cicarelli); ethanol 96% (Biopack); and deuterated chloroform (Sigma Aldrich).

Methodology

Epoxidized Soybean Oil (ESO)
SO and AF were placed in a 3-necked round bottom flask under mechanical stirring at 300 rpm. Cold peroxide (5-8°C) was added dropwise (for 1 h), to avoid SO degradation. Three different molar ratios of C=C:AF:H_2O_2 were evaluated: 1:0.56:1.9, 1:1:1.9 and 1:1.27:1.9. The selected temperature, 55°C, was kept constant by an automatic thermostatic bath for 7 h [18, 19]. The synthesized ESO was extracted by dissolution in petroleum ether. It was also washed and neutralized using distilled H_2O, dilute sodium bicarbonate solution (3%), and then a saturated NaCl solution. The remaining solvent was evaporated in a rotary evaporator. All reactions were evaluated by FT-IR. The ESO obtained in each case was also analyzed by ^{1}H NMR.

Acrylated Epoxidized Soybean Oil (AESO)
Conditions for this reaction were adapted from Saithai [8], with changes in reaction temperatures chosen by averaging values from different authors [8,9]. The ESO was heated to 60°C in a jacketed reactor with mechanical agitation at 300 rpm, and AA was added in a molar ratio of 1:10 or 1:20 ESO/AA. An addition of 0.05% of hydroquinone was made, the whole system was heated to 95°C and then maintained to constant acidity. The AESO obtained was washed as in the case of ESO. The reaction was monitored using the acidity index (AI) of the product until a constant value was reached. The AESO product was evaluated by FI-TR and ^{1}H NMR. Four reactions were carried out, starting from the products obtained during epoxidation, and modifying the incorporated ESO:$C_3H_4O_2$ molar ratio. In Table 1, the reaction conditions used are shown for each of the products.

Maleinated Acrylated Epoxidized Soybean Oil (MAESO)
The synthesis of MAESO was done according to Lu [13]. The best AESO obtained in the previous synthesis stage was maleinated. The reaction was monitored by the AI. The MAESO obtained was evaluated by means of FI-TR and ^{1}H NMR.

Copolymerization and curing
Specimens of optimized MAESO were prepared as indicated in Table S1. The polymer obtained from MAESO copolymerized with St will be referred to as MAESO-St. Replacements of 25, 50 and 100%

Table 1. Experimental conditions for epoxidation/acrylation/maleinization reactions.

	C=C:AF:H$_2$O$_2$	ESO:AA	AESO:MA	T (°C)	Time (h)	Inhibitor (%)	Product
Epoxidation	1:1.27:1.90 1:1:1.90 1:0.56:1.90			55	7		ESO 1 ESO 2 ESO 3
Epoxidations- Acrylation	1:1.27:1.90 1:1:1.90 1:0.56:1.90 1:1.27:1.90	1:10 1:20		95	7	HQ 0.05%	AESO 1 AESO 2 AESO 3 AESO 4
Epoxidation- Acrylation- Maleinization	1:1.27:1.90	1:10	1:3	85	6	HQ 0.05%	MAESO

(pressure=1 atm; mechanical agitation; epoxidation and acrylation atmosphere: air; maleinization atmosphere: N$_2$)

MAESO-St on UP were produced in order to study their mechanical and degradation properties.

The MAESO resins were mixed with 33% of St, 0.8% w/w of a 2.5% OCo solution and 1.5% w/w of MEK. The resulting mixture was transferred to standardized silicon molds to obtain specimens for Shore-D hardness, flexural properties, Charpy impact and biodegradation tests. Molds were placed in a drying oven with a temperature ramp of 1°C/min up to 100°C and kept there for 2 h. Specimens were then post-cured at 130°C for 2 h and polished with orbital sandpaper # 400.

Characterization techniques
• Characterization of resins
Reactions were followed by FT-IR and ¹H NMR studies. The IR characterization of compounds was performed using ThermoScientific Nicolet IN 10 with a wavenumber range of 4000 to 500 cm⁻¹. The ¹H NMR spectra for ESO, AESO and MAESO were recorded with a Bruker UltraShieldTM 400 spectrometer at 400 MHz. Samples were prepared by dissolution of 50 mg of the compound in 0.5 ml of CDCl$_3$. All spectra were evaluated using the Mestre-C© software.
AI was determined following ASTM D3644-15 [20]. In order to characterize the molar mass distribution in MAESO resins, size exclusion chromatography (SEC) was used. A Waters Breeze 1525 chromatograph with a W2414-410 refractive index detector was employed at 30°C. A Waters Styragel HR4E column (7.8 x 300 mm²) was used. The columns were run at 45°C and samples were eluted with THF at a flow rate of 1 ml/min. For MAESO molecular weight determination, samples of 0.1% w/w were prepared in HPLC grade

THF. The injection volume was 50 µl. Polystyrene standards were used for calibration.

• Characterization of materials
The 3-point flexural tests were carried out on a Shimadzu AGS- X universal testing equipment with a 20 kN load cell. The specimens and test methodology were according to ASTM D790 [21]. Charpy impact tests were made under the specifications of ASTM D 6110 [22] on a Tinius Olsen IT-504 tester. Hardness was measured according to the ASTM D 2240 standard [23] using a Rholl Shore D mechanical durometer with a reading accuracy of 0.5 hardness units.
Morphological analyses on degraded and non-degraded copolymer samples were performed using a ThermoFisher Phenom pure desktop SEM with a magnification range of 20 to 20000X. The accelerating voltage was 5 kV and a resolution ≤ to 30 nm.

• Statistical analysis
The statistical analysis was performed using the Infostat© software [24]. The data were examined by means of ANOVA, and the results were compared with a DGC posteriori test at a 0.05 significance level. The differences among mechanical characteristics of specimens were analyzed and the results were expressed as the mean of three repetitions.

Degradation test
From cured materials, 3-mm-thick specimens of 100 mm² were obtained. All materials were then washed with an ethanol:water (1:1) solution and dried to constant weight in a vacuum oven at 60°C. The weight for each specimen was recorded (A). Before that and

after degradation, specimens were dry-sterilized for 6 h at 120°C.

a) Degradation by microbial hydrolysis (Broth culture technique): for enzymatic degradation, Aspergillus niger (ATCC 16404) and Alternaria alternata (LMFIQ058) strains, provided by CEPROCOR and FIQ-UNL respectively, were used. Microorganisms were used for inoculum preparation in liquid malt extract. Inoculum preparation is described in S2.

Seed inoculation was made at 5% v/v with a micropipette in flasks containing sterile specimens with 20 ml of basal salt medium. For each material and microorganism type, 7 flasks with inoculated specimens and 7 control tubes were prepared. Additionally, 9 test tubes with 25 ml of basal salt medium inoculated for each fungus were seeded in order to degrade specimens for the flexural tests. The basal salt medium composition was taken from Spontón et al [25]. Flasks and test tubes were cultivated at 30°C for 240 days in a growing stove. Samples were taken at 5, 10, 30, 60, 90, 180 and 240 days. Material monitoring was carried out through the determination of weight loss and dry biomass growth.

b) Degradation by chemical hydrolysis: chemical hydrolysis determination was conducted in culture flasks with sterile distilled water; 3 flasks with 7 specimens each were cultivated at 30°C for 240 days in a growing stove. Samples were taken at 5, 10, 30, 60, 90, 180 and 240 days. Extracted samples were washed with an ethanol:water solution (1:1), and dried at 105°C to constant weight. Material monitoring was carried out through a weight loss determination technique.

Biomass growth determination

For biomass growth determination, flask contents were filtered twice, in a silk cloth filter and a cellulose nitrate membrane (0.45 μm). The membranes and silk cloth were weighed before and after filtration to record the growth in the wet biomass. They were then dried in an oven at 105°C for 24 h and the dry biomass weight was recorded.

Weight loss determination

To determine weight loss, materials were washed with an ethanol:water solution (1:1) and dried in an oven at 105°C to constant weight (B). Weight loss was obtained from equation (1):

$$Weight\ loss(\%) = [(A-B)/A] \times 100 \qquad (1)$$

RESULTS AND DISCUSSION

Synthetic process

The complete synthetic process is shown in Figure 1. Three steps can be distinguished there: a) epoxidation, b) acrylation, and c) maleinization. In a), the SO modification reaction starts with the formation of a peracid in situ through the Prileschajew reaction. The product obtained is called ESO (Figure 1, reaction a). Reaction b) involves the introduction of acrylate groups into the ESO through AA, hence this acid attacks the oxirane ring to produce a hydroxyl ester: AESO (Figure 1, reaction b). Finally, in c), in the presence of alcohols, MA participates in esterification reactions whose mechanism can easily proceed at moderate temperatures to generate mono-alkyl esters. The alcohols present in the modified TG come from the oxirane opening reaction generated during acrylation, and are suitable for the MA esterification reaction, which requires a minimum stoichiometric equimolar ratio of MA to the -OH group content. The product obtained in this step is MAESO (Figure 1, reaction c).

Product characterization studies

FT-IR Spectroscopy

In this study, FT-IR was used as the main technique to evaluate the variation of the molecule functional groups throughout the course of the reactions, which contributes to predicting the relationship between the different variables and structures obtained.

FT-IR spectra of SO and ESO synthetized under different conditions (Table 1) are shown in Figure 2a. All spectra were standardized based on the 2927 cm^{-1} band, corresponding to the stretching of the C-H bond of the alkanes (1). The 820 cm^{-1} band (2) was attributed to the vibrations of the cis-epoxides in the epoxy ring [26]. The signal between 3010 and 3050 cm^{-1} corresponds to the stretching of the double bond of the alkenes. At 1745-1750 cm^{-1}, a stretching of the ester bonds (C=O) is observed, while the signals

between 1110-1170 cm^{-1} are attributed to the stretching of the C-O bond of the ethers and esters. The wide signal around 3500 cm^{-1} corresponds to the stretching of the -OH groups.

ESO 1 shows a relatively stronger signal at 820 cm^{-1} as well as a significant decrease in the 3010-3050
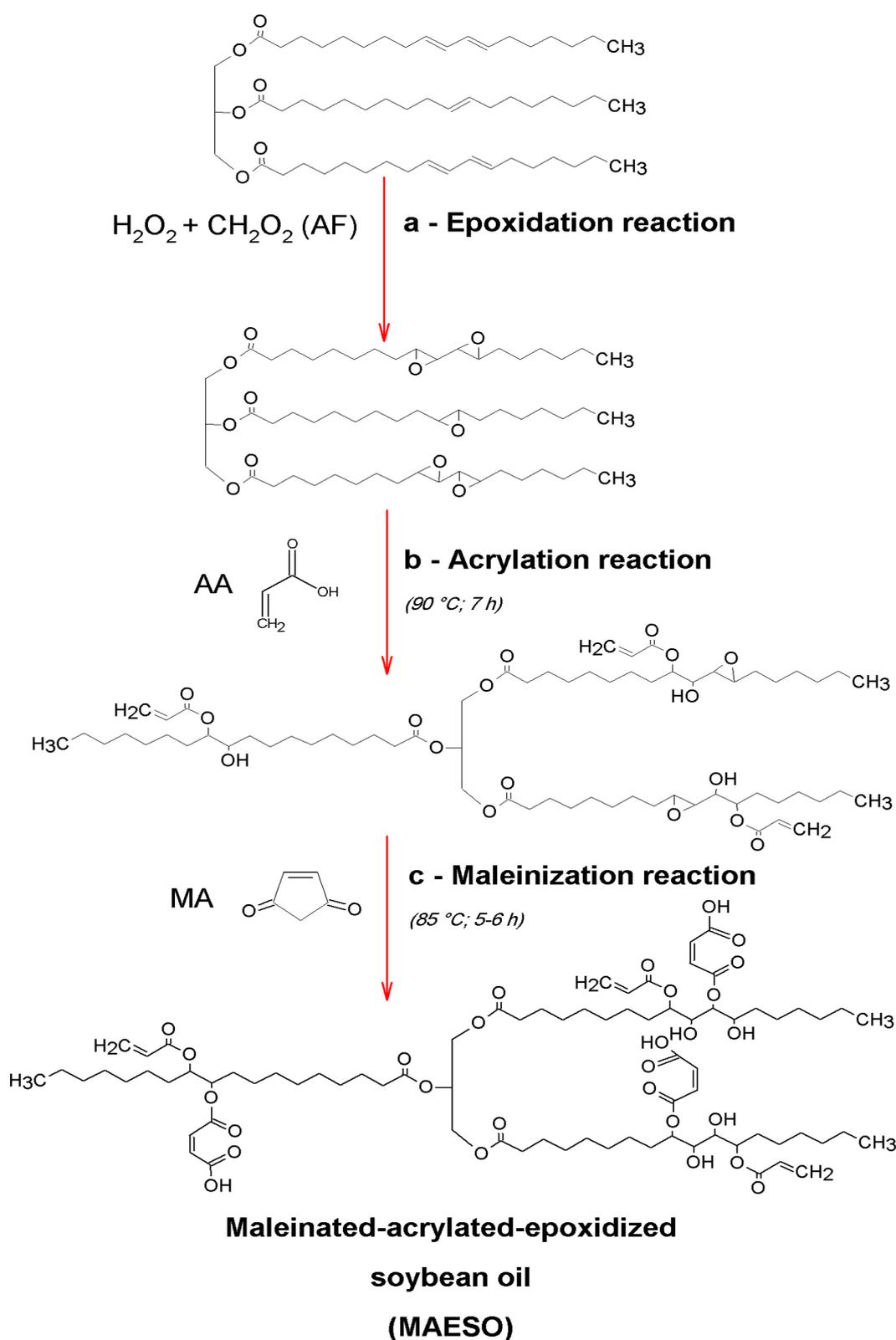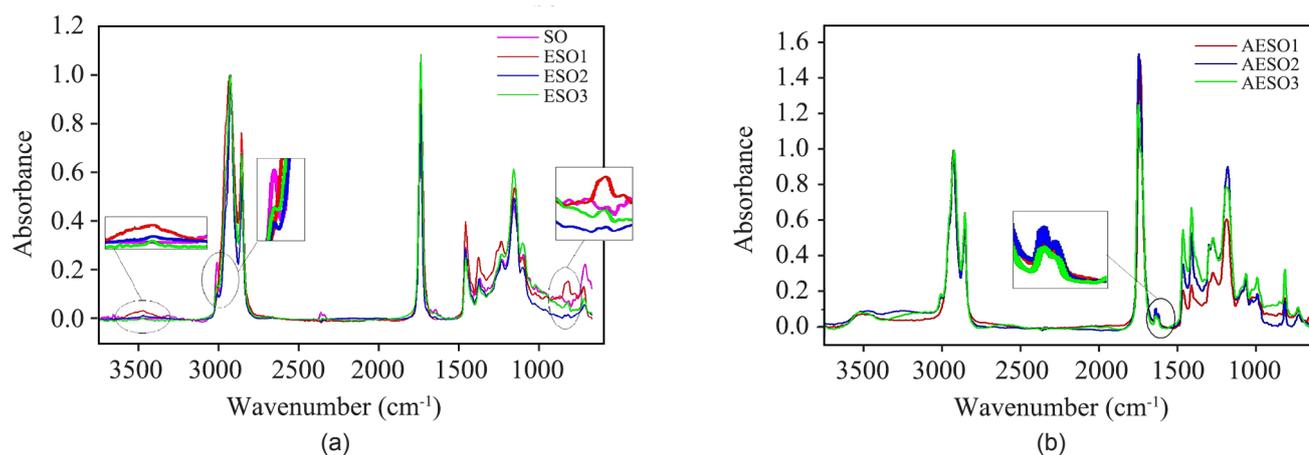

Figure 1. MAESO synthesis scheme.

Figure 2. a) FT-IR spectra for SO and ESO 1, 2 and 3, b) FT-IR spectra for AESO 1, 2 and 3.

band, demonstrating higher consumption of double bonds in the carbon chains. Likewise, an increase in the 3500 cm^{-1} region shows the presence of -OH groups corresponding to the incipient opening of oxirane rings. This can be supported by a signal ratio calculation (Table S3), where the band corresponding to the unreacted double bonds falls in the order ESO 3 > ESO 2 > ESO 1. In ESO 1, residual C=C bands are not observed. In correlation with this, the band of oxirane groups decreases in reverse order. These values show that the ESO 1 reaction has the best double bond conversion on epoxy rings, these conditions (6 h, 55°C, C=C:AF:H$_2$O$_2$ 1:1.27:1.9) being optimal for the next acrylation step.

The overlapped graphs with the AESO 1, 2 and 3 (reaction b on Figure 1) FT-IR spectrum results can be seen in Figure 2b. For AESO FT-IR, the bands at 1636 cm^{-1} were assigned to the vibration absorption of C=C, representing the incorporation of acrylate into the ESO structures. Other characteristic bands were visible, like acrylate -C-H stretching at 810 cm^{-1}, HC=C- stretching in the acrylate group at 985 cm^{-1} and vibration of -C-H from acrylate at 1400 cm^{-1}. An analysis of the absorbance ratio of the FT-IR signals is provided in Table S3, which complements the analysis of the spectra.

The absorbance ratios show a greater incorporation of double bonds in the 1636 cm^{-1} signal for AESO 1 and AESO 2, identified by the vinyl group vibrations. However, for AESO 2, and particularly for AESO 3, there is a higher ratio of signals between COC and C=O, which could be interpreted as the undesired

development of intramolecular polymerization reactions between hydroxyl of neighboring chains or two epoxy groups between etherification reactions [27]. This generates products with high molecular weight but little availability for copolymerization under adequate conditions with crosslinker monomers. The increase in absorbance signals ratio (COC:C=O) in acrylation reactions is inversely proportional to the conversion of double bonds into epoxides, which seems to indicate that residual double bonds not previously epoxidized are attacked by other mechanisms that lead to the development of intra- or inter-molecular ether bonds, thus decreasing the incorporation of acrylate groups to the oxirane ring [27].

In AESO 1, 2 and 3, the ESO:AA molar ratio used was 1:10. It is now being evaluated whether a higher excess of AA could increase the performance of the incorporation of acrylic groups into the ESO molecule. To this effect, the evaluation of a molar ESO 1:AA ratio equal to 1:20 is being considered. AESO 1 was compared with AESO 4, according to the conditions in Table 1.

Double bonds incorporated in the ESO molecule were similar for reactions 1 and 4; yet, when excess of AA predominates (reaction 4), the COC:C=O ratio increases about 24%, Table S3 backs up these statements. FT-IR results strongly agree with those reported by Rengasamy et al., which reference that the excess of AA acts as a catalyst and triggers the development of oligomerization reactions [27]. This fact suggests that the AESO 1 reaction presents the best conditions for incorporating the maximum number of
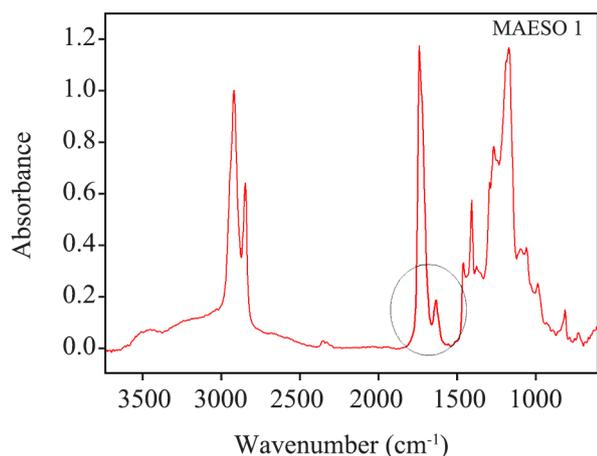
Figure 3. FT-IR for MAESO.

acrylates into the structure with minimum development of intramolecular polymerization evidence. AESO 1 is then maleinated to obtain MAESO (reaction c in Figure 1). Figure 3 shows the FT-IR spectrum for this product.

The FT-IR graph of MAESO 1 shows a good incorporation of double bonds at 1636 cm^{-1}, with a pronounced signal around 3100-3500 cm^{-1}, in agreement with the incorporation of terminal -COOH groups into the molecule. In Figure 3, a high ratio of COC:C=O absorbance signals is observed. This is because signals representing ethers and carbonyls increase during the maleinization reaction, and this increase should be proportional in both signals. However, it is known that there is a parallel reaction which is difficult to avoid, where some half-ester maleate groups can react through ether linkages with epoxide residues or hydroxyl groups of triglyceride chains, then forming an oligomerized structure [11].
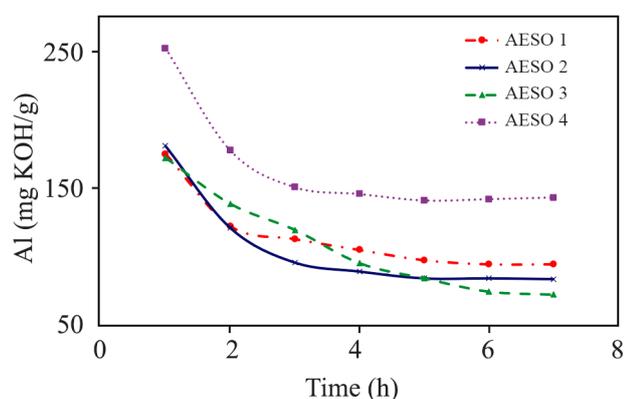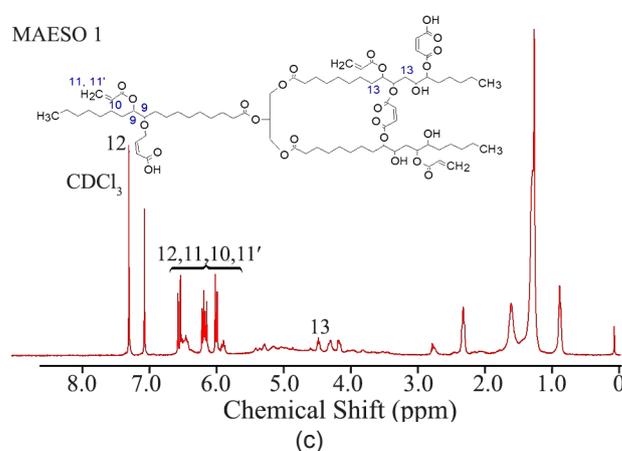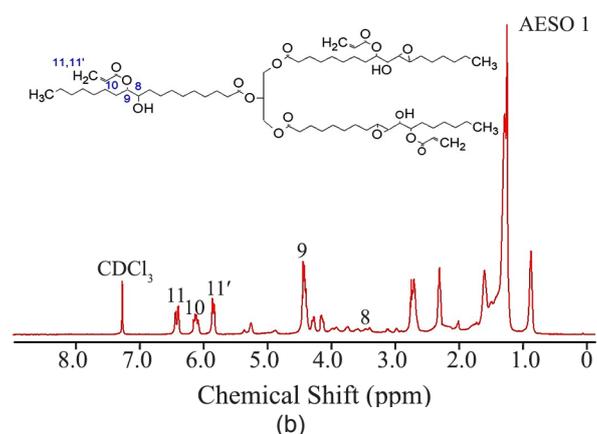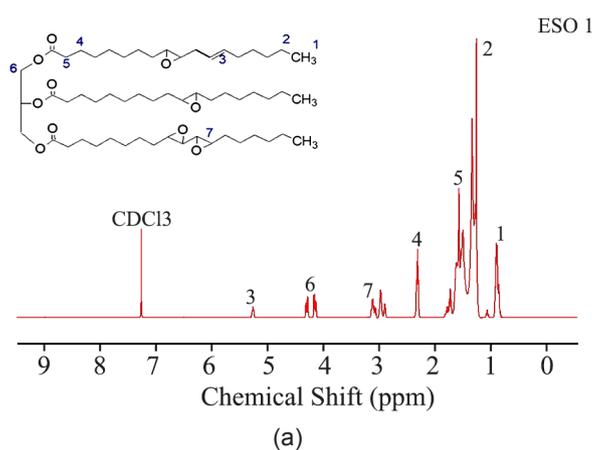

Figure 4. AI curves for AESO 1, 2, 3 and 4.

The most exacerbated increase in the COC signal in relation to the carbonyls shown in Figure 3 could then be attributed to the oligomerization of the structure.

Acidity Index (AI)
Figure 4 shows the AI curves obtained during the acrylation reaction in relation to reaction time. Reactions AESO 1 and AESO 2 reach AI value

(a)

(b)

(c)

Figure 5. ¹H NMR spectra for a) ESO 1, b) AESO 1 and c) MAESO 1.

stability after around 5 h, while reaction AESO 3 continues to decrease.

The reduction of AI in AESO 1, 2 and 3 reactions is similar. AESO 4 retains higher molar excess of free AA. Yet, the acidity reached at the end of the reactions remains high, which confirms the results found in the FT-IR analysis. As described above, this phenomenon could lead to adverse reactions for the continuity of the maleinization reaction. The best molar ratio ESO:AA for acrylation seems to be 1:10, according to spectroscopy and AI results. It is then defined as an optimized acrylation reaction to AESO 1 in this research study.

^{1}H NMR spectroscopy
Figure 5 shows the ^{1}H NMR spectra obtained for ESO 1/AESO 1/MAESO 1. Figure 5a shows the characteristic signal for ESO. Protons of the terminal methyl of the aliphatic chains on the esterified fatty acids (1) can be seen as a multiple signal with a chemical shift of 0.88 ppm. This signal was chosen as an internal reference for the integration of the signs. Saturated methylated groups found along the carbonated chain (2) are observed between 1.10 and 1.40 ppm, also as a multiple signal. Unsaturation can be identified by external allylic H and internal allylic H signals, with δ = 2.00-2.30 ppm and δ = 2.76 ppm, respectively, which are not visible in this spectrum. However, unreacted olefinic protons (3) can be seen with a chemical shift of 5.20-5.50 ppm [8, 28]. α and β carboxylic protons (5 and 4) can be found as a triplet at 2.32 ppm and as a single signal at 1.6 ppm, respectively. The presence of oxirane groups is visible through the adjacent methylenes, with a signal at 3.40-4.00 ppm (7). Methylene glycerol protons (6) are observed between 4.00 and 4.50 ppm. This latter signal was taken as a reference to calculate the molar ratio of the different groups present in the structure from the integration of areas of the signals obtained.

In Figure 5b, a very slight signal can be seen with a chemical shift of 3.75 ppm, assigned to the methine protons of the carbons adjacent to the -OH groups (8). On the other hand, the protons in the carbon atoms where the acrylate groups are hosting (9) show a chemical shift as a multiplet of 4.40 ppm. A group of signals corresponding to the terminal vinyl protons of the acrylate group (10, 11 and 11') are displayed. A double of double can be seen with a chemical shift of 5.85 ppm, corresponding to the protons (11') of the terminal methylene (=CH$_2$) in the acrylate groups, while the 6.14 ppm chemical shift multiplet belongs to the methine protons (10). Finally, another double signal doublet with a chemical shift of 6.42 ppm corresponds to protons of the terminal methylenes in the acrylate groups (11).

For the ^{1}H NMR spectra of MAESO 1 (Figure 5c), signals observed between 5.7 and 6.7 ppm are attributed to the vinyl protons of the acrylate and maleate groups (10, 11, 11' and 12). At 7.20 ppm, the unreacted MA signal is noted. Likewise, it is interesting to see the protons of the C adjacent to the incorporation of maleate/acrylate groups (13) at a displacement of 4.4 ppm. Table 2 shows conversions of molar ratio form SO in successive reactions.

Conversion of SO unsaturation moles in oxirane rings (Figure 1, reaction a) was 77.3%. Incorporation of acrylate and maleate groups for the opening of oxirane rings represents 88.9% of the original unsaturation (Figure 1, reaction b and c). These values arise from the calculation of the double bonds measured for the SO used (4.4 moles C=C) that reacted in different stages of the reaction to generate epoxides, hydroxyls or other types of reaction intermediates serving as an attachment for the reaction of acrylates and maleates.

Table 2. Molar ratio for products obtained from integrated areas on ^{1}H NMR.

	SO	ESO 1	AESO 1	AESO 2	AESO 3	AESO 4	MAESO 1
mol HC=CH/mol TG	4.4	0.31	-	-	-	-	-
mol HCOCH/mol TG	-	3.40	-	-	0.31	-	-
mol CH-OR*/mol TG	-	-	8.24	7.26	5.91	3.15	-
mol HC=CH$_2$/mol TG	-	-	2.82	2.50	2.37	6.97	7.83**
mol MA/mol TG	-	-	-	-	-	-	1.12

*R= acrylates, H-, etc.

** Olefinic protons on maleate and acrylate groups.
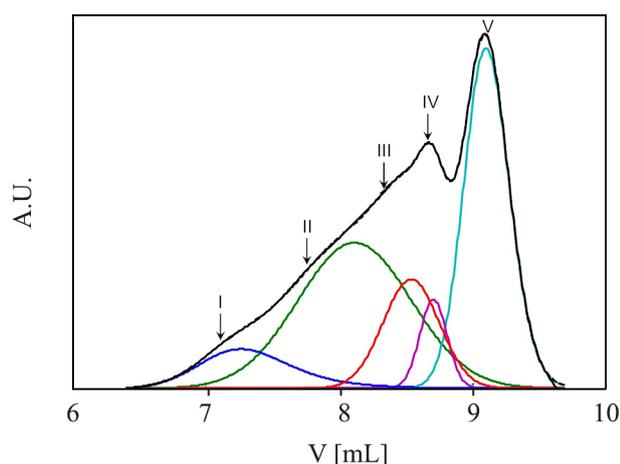
Figure 6. SEC curve of MAESO.

This amount of unsaturation incorporated into the MAESO molecule (reaction c on Figure 1) represents bonds available for polymerization [18]. These results perfectly match those observed in the FT-IR results mentioned above. Values achieved by this molar conversion of unsaturation into reactive vinyl groups are higher than those reported in the literature for commercial AESO maleinization [11, 12].

SEC
The SEC analysis (Figure 6) shows that the MAESO has a molar mass represented by a polydisperse distribution, with an average value M_w=11700, M_n=4575 and D=2.54. Curves in color represent the deconvolution of SEC with the presence of 5 peaks; the original curve is shown in black.

It can be seen that there is a predominance of two oligomers (II and V) whose percentage contributions to the global M_w are similar (37% and 35% respectively), suggesting there are molecules with greater M_w (II) which may involve intermolecular polymerization and growth of chains pending from the TG molecule [13]. Peak number V involves molecules with lower M_w. The average molecular weight achieved by MAESO is similar to the one reported in the literature [14].

Results of the product characterization techniques

in the evaluated conditions show that an adequate control of the variables enables the obtention of a product with good crosslinking potential. This fact supports the idea of greater copolymer incorporation for a subsequent improvement in the mechanical properties. However, the M_n/M_w ratio in the SEC and the absorbance ratio signals reflected in the FT-IR could suggest the presence of different types of polymerization reactions. This could mean that, even with an acceptable M_w [14], early oligomerization affects the final product structure, causing alterations in the mechanical properties of the structures formed from copolymerization.

Mechanical and thermal properties
The mechanical experiments were performed using pure MAESO-St and blends of UP with 25% and 50% of MAESO-St. In Table 3, the results for the mechanical tests are shown. The three-point bending test for the flexural modulus showed no significant differences between UP and its replacement with 25% of MAESO-St. The flexural modulus decreases when the percentage of replacement of MAESO-St increases. Probably, MAESO-St exerts a plasticizing effect with its increasing concentration in the mixtures. Likewise, replacements with 50 and 100% of MAESO-St show modulus values that can be considered statistically equal to each other, and lower than for UP. On the other hand, the average values obtained for the maximum stress in the UP samples, 25% MAESO-St and 50% MAESO-St, were statistically equivalent to each other, and higher for 100% MAESO-St. No significant differences were found between the displacement values for UP and MAESO-St in their different replacements.

The impact resistance test values in the analyzed specimens increased in the following order 25% MAESO-St=UP < 50%MAESO-St < 100%MAESO-St. These results show that a higher MAESO-

Table 3. Average values for mechanical tests.

	Flexure modulus (MPa)	Maximum stress (N/mm²)	Displacement (mm²)	Impact resistance (J/mm²)	Shore-D hardness
UP	2940.95±362.64	76.60±16.33	0.05721±0.00011	0.00012±0.00007	84.67±0.58
25% MAESO-St	2548.94±647.14	82.19±34.54	0.06026±0.00005	0.00013±0.00002	84.00±1.00
50% MAESO-St	1876.24±518.44	72.76±17.28	0.06354±0.00048	0.00018±0.00039	83.00±1.00
100% MAESO-St	1332.66±342.97	47.83±11.96	0.06043±0.00107	0.00046±0.00053	83.00±1.00
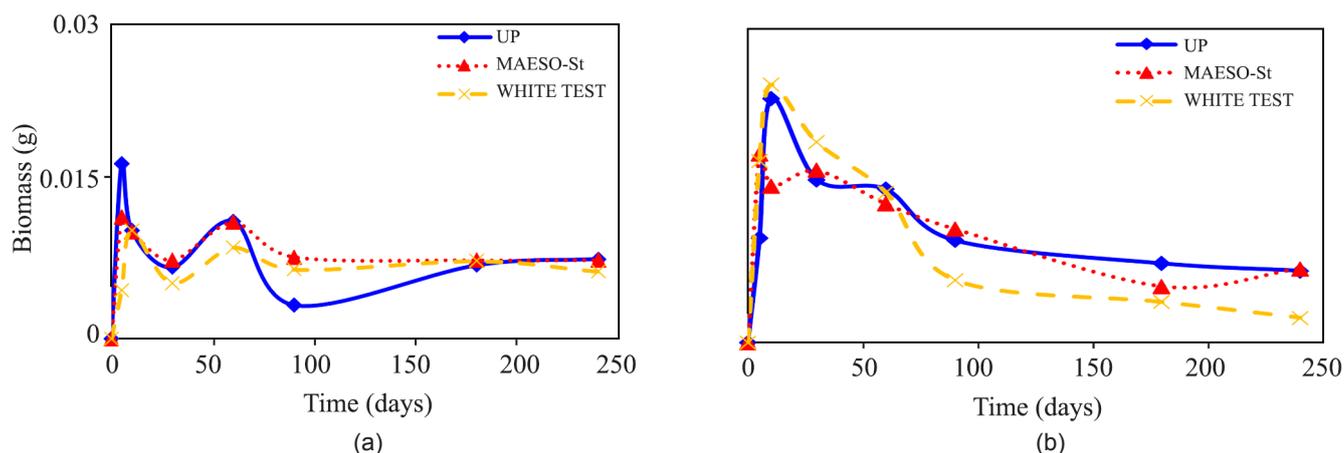
**Figure 7**. Dry biomass growth curves for a) A. niger and b) A. alternata.

St replacement improves the toughness of the structure, which promotes a better impact withstand capacity. This, in turn, correlates with the results of flexibility, where greater replacement implies the same deformation and lower flexure modulus. Both results suggest a more flexible behavior for MAESO-St at 100%, improving its ability to absorb impacts and reduce its stiffness. There were no significant differences between the hardness of UP and MAESO-St samples.

As is better known, small molecules act as self-plasticizing for a main polymeric chain as they are interspersed in the structure occupying intramolecular spaces and reducing secondary binding forces [29, 30]. Major and most effective biobased plasticizers contain ester linkage in their structure, such as SO, ESO and other molecules derived from them [29]. These biobased molecules also act as plasticizers because they can have aliphatic chains of different lengths pending from the main chain, acting as spacers which increase the free volume [31]. This involves an increase in flexibility which translates into a decrease in hardness and elastic modulus, and an increase in impact resistance [29]. These effects are observed in the results for the mechanical properties tests: they show a material with improved resilience as compared with UP and whose replacement in UP at different proportions tends to improve flexibility and impact resistance, showing a "pseudo-plasticizing" effect in the mixture obtained. This behavior is consistent with that found in the previously suggested structural characterization of the polymer (section 3.2).

Degradation tests

Biomass growth can be associated with the reproduction rate of microorganisms [32]. The microorganisms used correspond to species of fungi with high prevalence in the environment, and whose enzymes are capable of degrading fats and esters [33]. They were evaluated as species with the ability to degrade synthetic polyesters [18, 33]. In the dry growth graphs, Figure 7, it was observed that, for both A. niger and A. alternata, the order of biomass growth MAESO-St= UP > WHITE TEST was shown at 240 days.

In Figure 8, the weight for a specimen degraded with A. alternata is shown to decrease rapidly in the first days of degradation; after 10 days, the weight loss remains almost constant at 1.7% and 0.4% for MAESO-St and UP, respectively. Degradation by A. niger is also shown to decrease specimen weight in the same way as with A. alternata, reaching almost constant weight loss values of 2.2% and 0.4% for MAESO-St and UP samples, respectively. Finally,
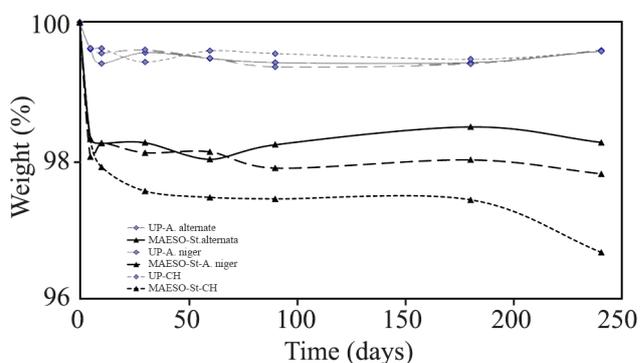
Figure 8. Percent weight evolution for UP and MAESO-St applying A. alternata, A. niger and chemical hydrolysis (CH).

the weight loss caused by chemical hydrolysis under constant temperature conditions is also shown to follow the same degradation evolution, only with lower weight values of 3.3% and 0.4% for MAESO-St and UP, respectively.

In MAESO-St, weight loss was higher due to chemical hydrolysis as compared to the microbial one. This could be attributed to the fact that microorganisms form a thick mycelium layer around the samples, covering them partially or totally, which generates a kind of microbial wall that could isolate the direct contact of the material with water. This was found particularly in A. alternate degradation tests. Polyester degradation is mainly affected by the random hydrolysis of the ester bonds on the exposed surface [34] and is strongly influenced by the physical properties of the polymer and its molecular weight, given that lower molecular weights favor the process [35]. Nonpolar polymers usually show limitations in biodegradation due to the hydrophobic properties of its surfaces; biofilm formation can overcome this restriction [36]. In this aspect, the presence of microbial growths that cover the surface of the polymer, isolating it from water, leads to the development of degradation mechanisms that do not affect the mass reduction of the polymer as much as other physical properties. This, in turn, shows that the effect of microbial enzymes on MAESO-St weight loss was not visible in the period studied. UP specimens showed no weight loss evolution after the first 10 days, maintaining constant values in chemical and microbial hydrolysis, which suggests that the small weight loss effect results from the retained water and not from the attack of microorganisms. However, the micrographic images of the degraded surfaces showed

biomass residues and visibly modified surfaces (Figures 9, 10 and 11). Figure 9 shows the comparison of surfaces degraded by chemical hydrolysis and non-degraded surfaces.

Figures 10 and 11 show the enzymatically degraded surfaces at different magnifications. The spores of A. niger and filamentous structures of both A. niger and A. alternata can be seen adhered to the degraded surfaces, observed in greater proportion on the surfaces of MAESO-St. The presence of fractures can be seen in the micrographs of Alternaria on MAESO, not observed in the chemical hydrolysis, suggesting that the main mechanism of degradation by microbial attack is related to crosslinking. However, in chemical hydrolysis, it is related to the rupture of the main chain, with greater weight reduction when compared to that of the microbial attack.

The results for the mechanical tests after degradation are shown in Table 4. In the case of MAESO-St copolymers, there was an increase in the module values of degradation by A. niger, and a stronger decrease in maximum stress and displacement values (about 80% for displacement values). For A. Alternata, the modulus and maximum stress values remained statistically equal to the ones for the non-degraded resin, but the displacement of the sample during the test decreased by 40% from the original value. Hardness values remained statistically constant in all enzymatic degradations. For UP samples, module values are statistically the same in all the samples, but maximum stress and displacement decrease in A. niger and A. alternate degradation samples, being statistically equal to each other.
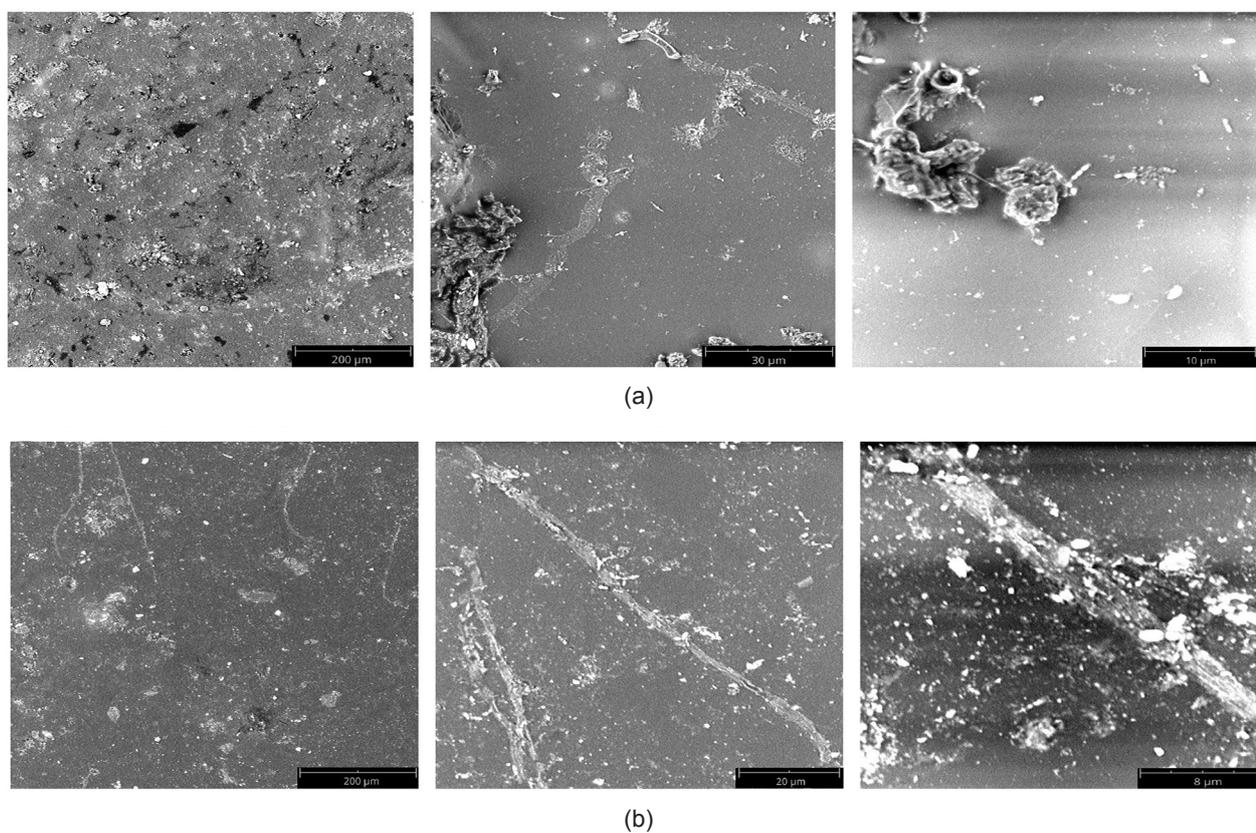
These results indicate that both UP and MAESO-
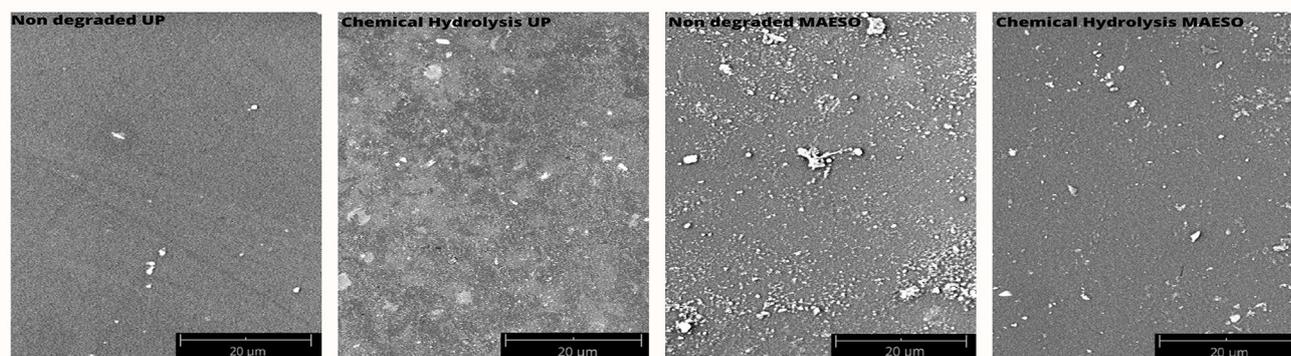
Figure 9. SEM comparison after and before chemical hydrolysis in UP and MAESO at 2940X.
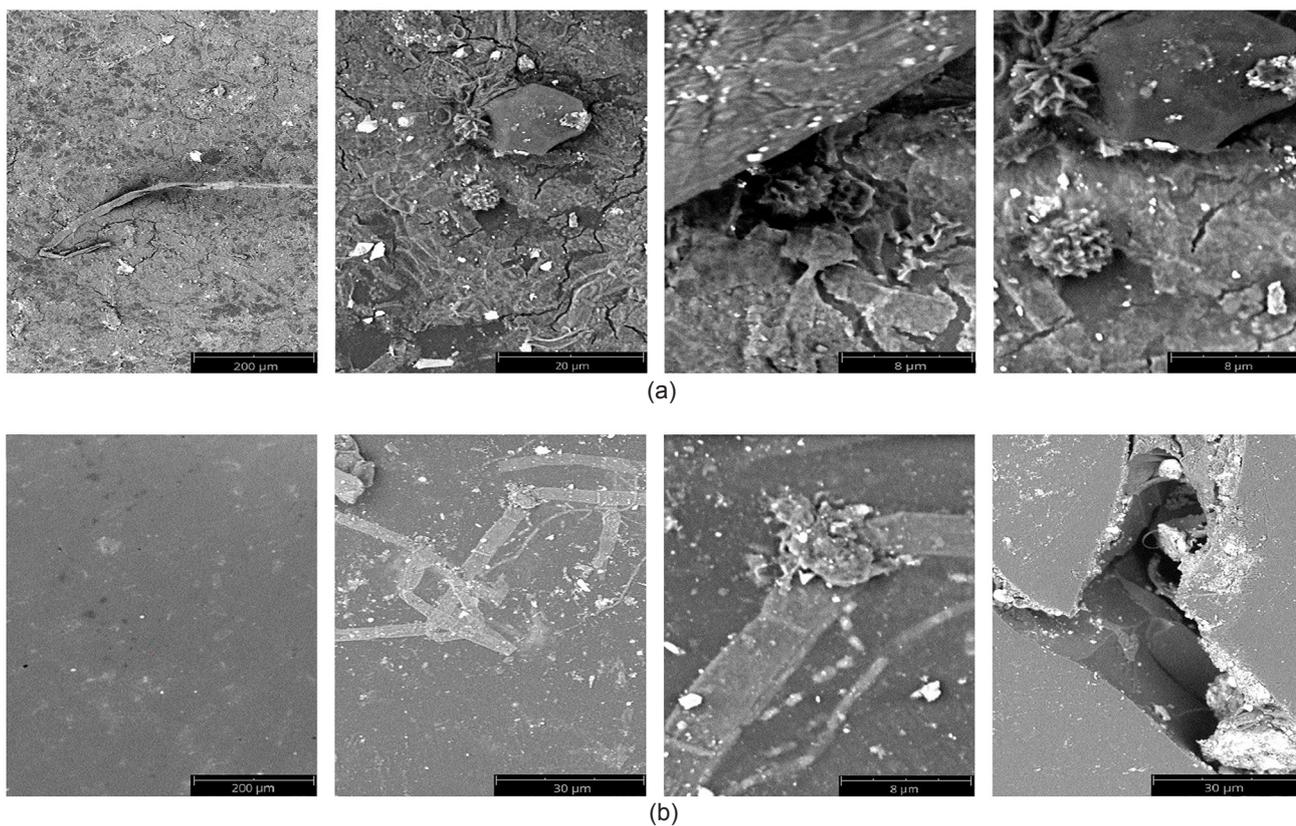
Figure 10. SEM before degradation test on MAESO with a) A. niger and b) A. alternata.

Figure 11. SEM before degradation test on UP with a) A. niger and b) A. alternata.

Table 4. Mechanical test on degradation specimens of UP and MAESO.

		Flexure modulus (MPa)	Maximum stress (N/mm²)	Displacement (mm²)	Shore-D Hardness
UP	Original	2940.95 ± 362.64	76.59 ± 16.33	0.05721 ± 0.00011	84.87 ± 0.58
	A. niger	2940.50 ± 456.82	30.84 ± 6.83	0.02075 ± 0.00002	86.00 ± 1.00
	A. alternata	2638.44 ± 253.22	22.038 ± 4.26	0.01898 ± 0.00001	87.52 ± 1.15
MAESO	Original	1332.66 ± 342.97	47.83 ± 11.96	0.06043 ± 0.00001	83.00 ± 1.00
	A. niger	2872.01 ± 271.44	24.47 ± 2.11	0.01209 ± 0.00002	84.00 ± 1.00
	A. alternata	1910.48 ± 314.13	48.22 ± 1.26	0.03807 ± 0.00007	81.00 ± 1.00

St specimens exhibited a decrease in their mechanical properties. Yet, flexibility after degradation decreased more significantly in samples generated from SO, as compared to non-degraded materials. This could be the result of the loss of the pseudo-plasticizing effect provided by the presence of small molecules interpenetrated in the polymeric structure, which could result in an increase in the crosslinking density. These results agree with those described for the major weight loss in MAESO-St and with the presence of a high fraction of low M^w molecules, as shown in SEC. This also correlates with cracks and microfractures seen in the MAESO-St micrographs. When degradation is low or incipient, as in UP samples, structural changes are not detected by a weight loss test, due to the low sensitivity of this test.

It is precisely this behavior, evidenced in the degradation, which promotes the idea that the use of MAESO-St as a partial replacement for UP provides a pseudo-plasticizing effect to the mixture. These results agree with the flexure data found in the study of mechanical properties of pure and blends of MAESO-St and UP.

The description above enables the proposal of MAESO-St as a potentially degradable material which can be degraded by different mechanisms and which will be enhanced in a suitable composting environment where exposure to a microbial consortium, high humidity, radiation and several atmospheric conditions should tend to reduce decomposition time.

CONCLUSION

This work aimed to optimize the modification of industrial SO through an epoxidation-acrylation-maleinization process. The results found showed an improvement in the development of industrial applications that promote the increase of SO production and its by-products, in addition to obtaining a material with improved degradation properties for its later disposal. This could enable a partial or total replacement of UP by MAESO-St regarding desired mechanical properties. Specifically, for products requiring the preservation of hardness and scratch resistance, a 100% replacement could be formulated, while a replacement of up to 75% would be adequate to preserve bending resistance. Mechanical properties demonstrate that the handling of the chemical reaction parameters would enable the production of a material suitable to reduce or replace the use of plasticizers usually added in the copolymerization process.

In terms of biodegradation, the results showed that UP resins under in vitro conditions showed no degradation over a period of 240 days, while MAESO-St resins showed weight loss of at least 1.7% under different conditions, enzymatically degraded surfaces and decrease in mechanical properties, even in the presence of fossil fuel derivates like St. Degradation is expected to be even greater under more extreme conditions in a suitable compost.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

Data availability: The raw/processed data required to reproduce these findings cannot be shared at this time as the data also form part of an ongoing study.

SYMBOLS AND ABBREVIATIONS

AA: acrylic acid

AI: acidity index

DGC: Di Rienzo, Guzmán and Casanoves test

ESO: epoxidized soybean oil

FT-IR: Fourier-transform infrared spectroscopy

^{1}H NMR: proton nuclear magnetic resonance

MA: maleic anhydride

MAESO: maleinated acrylated epoxidized soybean oil

SEC: size exclusion chromatography

SEM: scanning electron microscopy

SO: soybean oil

St: styrene

TG: triglyceride

UP: unsaturated polyester

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