



# Bio-Based Thermosetting Resins from Waste Cooking Oil

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In order to face the environmental concern about the use of traditional fossil-based monomers for the production of thermosetting resins, herein this study reports the synthesis of bio-based materials from waste cooking oil (WCO). In this context, this study explores the epoxidation-acrylation strategy for the synthesis of the starting functionalized oil for the production of thermosetting resins composed of only WCO-derived monomers or in combination with terpenic comonomers such as limonene and myrcene. Furthermore, employing myrcene as comonomer produces thermosetting resins that reveal the best properties in terms of mechanical strength if compared to the homopolymer ones.

pollutants (HAP).<sup>[7]</sup> Our group has recently detailed a strategy where acrylated-epoxy monomers obtained from vegetable oils have been used with biobased comonomers such as terpenes to afford thermosetting resins with comparable properties with respect to the ones obtained from comonomers of fossil origin.<sup>[8]</sup> In the context of renewable bio-based materials, waste cooking oil (WCO), defined as oils and fats coming from cooking or frying food ingredients in private, commercial, and industrial settings, is a promising alternative since it is far cheaper and has a greater impact on the waste

valorization and sustainability principles.<sup>[9]</sup> In the current study, we investigate the possibility to substitute vegetable oils with WCOs to improve the overall sustainability and circularity of the process. Herein, we report the functionalization of WCO by an epoxidation-acrylation strategy and the use of the ensuing oil as starting material for the production of thermosetting materials composed of only WCO-derived monomers or in combination with terpenic comonomers such as limonene and myrcene.

## 1. Introduction

The substitution of petroleum-based raw materials with renewable resources has become a significant concern from both an economic and an environmental standpoint.<sup>[1]</sup> Natural sources such as carbohydrates, lipids and oils, terpenes, and a wide range of bio-transformed products like fermentation derivatives or byproducts of microbial activity provide many opportunities for developing novel monomers and functional materials.<sup>[2]</sup> Vegetable oils are one of the most significant class of renewable resources because of their extensive range of chemical usage and global availability. As a matter of fact, chemical industries prefer them over other renewable resources.<sup>[3]</sup> One peculiar feature of these oils is the presence of carbon-carbon double bonds that are amenable to several chemical modifications. For instance, the linseed oil has been functionalized to produce epoxy or epoxy-derived monomers that have been subsequently used to fabricate highly crosslinked thermosetting resins.<sup>[4]</sup> Additionally, these epoxy-monomers can be used in combination with a comonomer that acts as a chain extender, affording a material with enhanced thermal and mechanical properties.<sup>[5,6]</sup> Classically, these comonomers are of fossil origin, such as styrene or divinylbenzene, which raise severe concerns about their toxicity as volatile organic compounds (VOC) and hazardous air

## 2. Results and Discussion

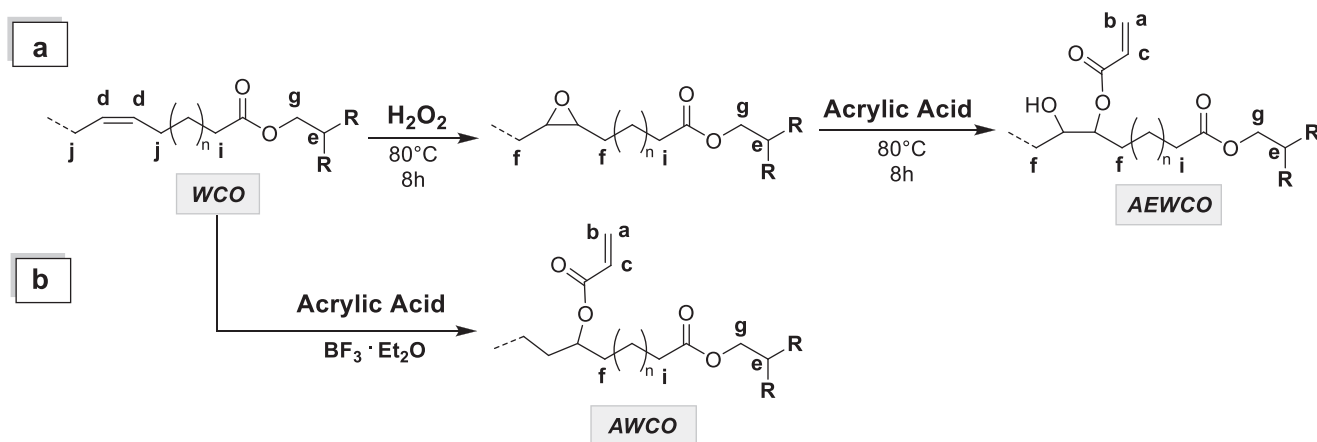
We started our investigation by synthesizing the fatty monomer derived from the WCO according to a two-step sequence based on a procedure reported in the literature consisting of an epoxidation followed by the addition of acrylic acid (**Scheme 1a**). At the outset, we calculated the triglyceride content within the WCO mixture via <sup>1</sup>H NMR spectroscopic analysis of the ratio between the peak area of H<sub>i</sub> and H<sub>g</sub>, which was found to be approximately 3:2.<sup>[10]</sup> This is the ratio expected for oil purely made up of triglycerides.<sup>[11]</sup> Moreover, through the same NMR investigation, we calculated the average number of double bonds per molecule in WCO, which was found to be 3.70.<sup>[10]</sup> WCO was thus converted into its epoxy analogue by treating the oil with H<sub>2</sub>O<sub>2</sub> and formic acid at 60 °C. Subsequently, this derivative was reacted with acrylic acid to yield the corresponding acrylated epoxidized WCO (AEWCO).<sup>[8]</sup> By <sup>1</sup>H NMR analysis, the average number of acrylate groups per triglyceride of the AEWCO sample was found to be 2. In parallel to this approach, inspired by the paper of the group of Simpson, we explored the feasibility of a straightforward BF<sub>3</sub>-promoted strategy to directly add the acrylic acid to the double bonds of WCO (**Scheme 1b**).<sup>[10]</sup>

Two set of reaction conditions were tested in order to achieve high content of acrylated WCO, by using BF<sub>3</sub>·Et<sub>2</sub>O as the catalyst. The first attempts were performed employing six equivalents of acrylic acid and 0.6 for the catalyst, which delivered 1.14 of

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**Scheme 1.** Procedure for the synthesis of a) acrylated epoxidized waste cooking oil (WCO) and b) acrylated WCO.



**Figure 1.** a) Acrylated epoxidized waste cooking oil (AEWCO) cured resin removed from the mould, b) AEWCO dumbbell specimens.

acrylate moiety per molecule of WCO.<sup>[10]</sup> Doubling the amount of acrylic acid and catalyst in a second attempt did not improve the results, thus delivering 1.35 of acrylate group. The acrylated WCO (AEWCO and AWCO) synthesized as described in Scheme 1 were subsequently employed as the monomers for the following curing step with limonene and myrcene as comonomers. The desired amount of acrylated oil (80 wt%) and the corresponding comonomer (20 wt%) were placed into a mold with Luperox<sup>®</sup> as the catalyst. The curing procedure implies a treatment in a high-temperature furnace by applying the following three-step program: 2 h at  $140^\circ C$ , 2 h at  $160^\circ C$ , and 4 h at  $180^\circ C$ . The obtained cured resins are shown in Figure 1.

Table 1 reports the mechanical properties of the samples evaluated by performing tensile test by uni-axial stretching until the

break, namely Young's modulus ( $E$ ), maximum tensile strength ( $\sigma_{max}$ ), and elongation at break ( $\epsilon$ ). The addition of two structurally different comonomers such as the linear myrcene and the cyclic limonene may provide insight into the effect of a linear versus cyclic structure and the availability of double bonds in achieving an efficient reticulation. Among the newly fabricated materials, AEWCO-My exhibited the highest values of Young's modulus and maximum tensile strength proving to possess the best mechanical properties. This finding suggests that the increased number of terminal double bonds encourages stronger copolymerization and cross-linking. Moreover, the elongations at break of AEWCO-derived samples present similar values ranging from 5% to 7%.

When employing AWCO as starting oil, the final resins were extremely fragile and impossible to remove entirely from the mold. This could be explained by the low percentage of carbon-carbon double bonds, which results in a lower degree of cross-linking reactivity, thus a more fragile material. The thermal stability and the degradation mechanism of cured resins were evaluated by thermogravimetric analysis (TGA), monitoring the sample mass loss with increasing temperature. The temperature at which a mass loss of 5% occurs ( $T_d$ ) was chosen as the one corresponding to the beginning of the degradation of the samples (Table 1). The homopolymers and copolymers present good thermal stability and very similar thermal behavior with a decomposition stage that occurs from 300 to  $500^\circ C$ .

**Table 1.** Thermal and mechanical properties of cured resins.

Sample	$T_d$ [ $^\circ C$ ]	$E$ [MPa]	$\sigma_{max}$ [MPa]	$\epsilon$ [%]
AEWCO	325	$99 \pm 17$	$4.4 \pm 0.6$	$6.7 \pm 1.6$
AEWCO-Li	332	$137 \pm 28$	$4.4 \pm 0.4$	$5.2 \pm 0.8$
AEWCO-My	330	$189 \pm 15$	$5.7 \pm 0.3$	$6.5 \pm 0.9$
AWCO	342	–	–	–
AWCO-Li	338	–	–	–

AEWCO, acrylated epoxidized WCO; AWCO, acrylated WCO.

### 3. Conclusion

Biobased thermosetting resins based on WCO and terpenes, such as myrcene and limonene, were successfully prepared. The AEWCO, in combination with 20 wt% of myrcene as a comonomer, produces a cured resin with promising mechanical and thermal properties, compared to the homopolymer. Moreover, employing WCO and terpenes instead of fossil-derived monomers is an economically sustainable choice and has a greater impact on the environment. Our preliminary results on the approach based on the direct acrylation of the WCO have been addressed and proved to be a promising tool for the production of such starting material. Besides, a one-step pathway could improve the sustainability of the overall process, limiting the waste and the additional chemical reaction.

### 4. Experimental Section

**Materials:** WCO was kindly provided by Adriatica Oli Srl (Italy); Amberlyst® IR120 was purchased from Supelco; formic acid ACS puriss., H<sub>2</sub>O<sub>2</sub> solution (34.5%–36.5% vol), acrylic acid anhydrous 99%, DABCO® 32-LV(1,4 diazabicyclo[2.2.2]octane, boron trifluoride etherate (BF<sub>3</sub>·Et<sub>2</sub>O), NaHCO<sub>3</sub>, NaCl, MgSO<sub>4</sub>, Luperox® (*tert*-butylperoxybenzoate, 98%), and hydroquinone (>99.5%) were purchased from Merck. (±) Limonene (Li) (>95%), styrene (St) (99%), and  $\beta$ -myrcene (My) (>70%) were purchased from TCI.

**Methods:** The products were analyzed by a Bruker Advance 400 spectrometer interfaced with a workstation equipped with a topspin software package. TGA investigations were carried out using a Perkin Elmer TGA7 thermogravimetric analyzer. The analysis was performed at a heating rate of 20 °C min<sup>-1</sup> from 50 to 750 °C in nitrogen atmosphere.

The tensile mechanical tests were carried out on dumbbell specimens (overall length 75 mm, gauge length 25 mm, a width of narrow section 4 mm) obtained by cutting the cured resins. The tests were conducted using a Zwick-Roell Z010 dynamometer with a load cell of 2.5 kN operating at a crosshead speed of 5 mm min<sup>-1</sup> until break. The mechanical parameters were averaged on at least three tests per sample and reported with their standard deviations.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

Data available on request from the authors.

### Keywords

biomaterials, cross-linking, terpenes, thermosetting resins, waste cooking oil

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