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Epoxidized oleic acid-based polymethacrylates as viscosity index improvers

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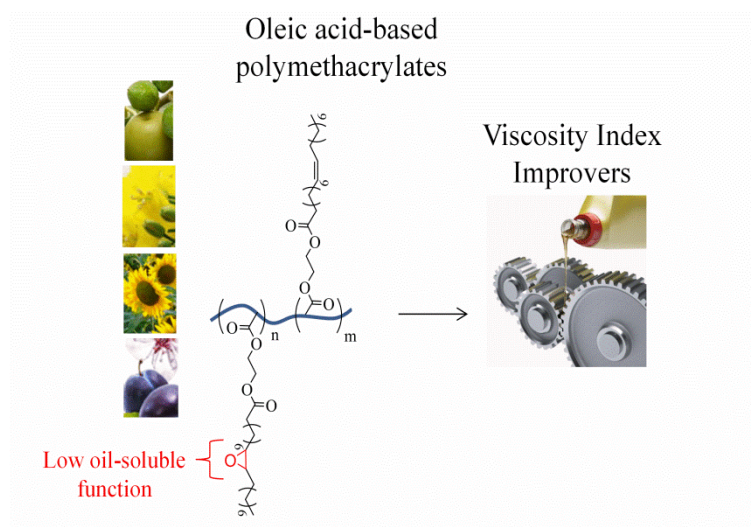
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Keywords: Oleic acid; Epoxidation; Radical polymerization; Rheology; Lubricant; Viscosity Index Improver

Abstract

This study reports two routes for the synthesis of epoxidized oleic acid-based polymethacrylates. The first one consisted in the synthesis followed by epoxidation of the oleic acid-based methacrylate, 2-(methacryloyloxy)ethyl oleate (MAEO) prior its radical polymerization. In the second pathway, MAEO was firstly homopolymerized to afford poly(2-(methacryloyloxy)ethyl oleate) (PMAEO) and, then, the internal double bonds of the oleate were epoxidized at different yields ranging from 20 to 100 %. All polymeric structures were confirmed by ^1H NMR, and characterized through SEC, TGA and DSC analyses. The resulting polymers were then blended at 5 wt. % in a mineral paraffinic (MPO) oil and in a biobased organic triglyceride oil (OTO) in order to be evaluated as VII. The partially epoxidized polymers up to 40 % were soluble in MPO. According to a rheological study, the oil-soluble epoxidized polymers resulting from the epoxidation of PMAEO exhibited a much higher influence on oil viscosities at high than at low temperatures compared to the low epoxidized PMAEO molecular weight obtained by the first strategy. Additionally, the viscosity index of both lubricating oils were significantly improved with the addition of the epoxidized oleic acid-based polymers resulting from the epoxidation of PMAEO which confirmed their efficiency as VII.

Graphical abstract:



1. Introduction

Multi-grade engine lubricating oils are subject to a wide range of operating temperatures.^{1,2} Therefore, one of the most essential requirements for such lubricating oils is to exhibit a low enough viscosity at low temperatures to maintain pumpability as well as a high enough viscosity at high temperatures to provide a sufficient film strength.³ In the lubricant field, the variation of viscosity with temperature is expressed by the value of the viscosity index (VI).⁴ The method consists in comparing the kinematic viscosity of the fluid to that of two reference fluids at 40 and 100 °C.⁵ Oils with a high VI exhibit a much smaller viscosity-temperature dependence than oils with a lower VI.

For many decades, the VI of mineral oils which have low VI, has been improved by adding polymeric viscosity index improvers (VII) in lube oils which ensured a proper oil viscosity at high temperature.⁶⁻⁸ The most commonly used polymers in lubricant applications are poly(alkyl methacrylate)s (PMA)s.⁹⁻¹¹ Such polymers are less soluble than hydrocarbon polymers in mineral oils due to their polar ester functions and are known to raise the viscosity of the mineral oil proportionately more at high than at low temperatures which results in the lube oil VI improvement.^{10,12,13} Their widely reported mechanism of action is based on the coil polymer expansion in mineral oil which is assimilated to the gradual improvement of polymers solubility in temperature and therefore to a gradual polymer thickening power in oil.¹⁴⁻¹⁶ Despite their extensive use in lubricant applications, the monomers used to afford PMAs belong to the second generation of petrochemical products. Indeed, PMAs are mainly

copolymers based on low oil-soluble alkyl methacrylates ($< C_7$) and long oil-soluble alkyl alcohol methacrylates (C_{12} - C_{20}). All these monomers are mostly issued from petro-based resources, which can lead to environmental concerns in the next few years.^{17,18} Recently, due to their specific structure with long aliphatic chains combined with a polar head, VO-based polymers resulting from direct radical polymerization have shown promising properties as VII in various mineral lube oils²⁸⁻³⁰. However, even if they demonstrated good properties to enhance the field service performance of engine oil, VO generally showed poor reactivity in radical process.³¹ In most of the cases, VO required to be radically copolymerized with more reactive petrosourced comonomers to perform radical polymerization which decreases the ecological advantage of the resulting VO-based additives.³²⁻³⁴

Hence, beyond the functionalization of VO for the synthesis of reactive building blocks for step growth polymerization, some teams have design new fatty-acid based radically polymerizable mono-functional monomers³⁵. These new VO-based monomers allowed the preparation of biobased polyacrylates with well-defined architectures which is not possible with conventional polylcondensation. Indeed, recently, Maiti *et al.* reported a new method of functionalization involving Steglich esterification of various FA (caprylic, capric, lauric, myristic, palmitic, stearic and oleic acids) to provide partially biobased methacrylate monomers in a one-step method.^{36,37} Another synthetic route based on a two-step method through amidation followed by (meth)acrylation has been recently reported by Yuan *et al.* to provide monomers for radical polymerization.³⁸ Similarly, in order to find other bioalternative, our previous work focused on the synthesis of oleic acid- based monomer, the 2-(methacryloyloxy)ethyl oleate (MAEO), which was successfully involved in free radical polymerization (FRP) and evaluated as VII.¹⁹ The resulting homopolymer (PMAEO) has demonstrated good VII properties when blended (1-10 wt. %) in a paraffinic mineral oil (MPO). However, when PMAEO was blended in an organic biobased triglyceride oil (1-10 wt. %), the lubricating oil acted as a too “good solvent” at low temperature which prevented the coil polymer to further expand with temperature. It resulted in a similar thickening effect on oil viscosity at low and high temperatures instead of expected VII properties.³⁹

Considering the growing production of biobased lubricants in the recent years, the use of PMAEO has been also extended in a triglyceride organic oil (OTO) to evaluate its efficiency as VII in a biolubricant. However, the polymer behaved as a simple thickener additive due to its too good solubility in the triglyceride oil at low temperature which prevented the coil polymer to further expand with temperature. By consequence, a same polymer will not

necessarily be a good VII for oils with different compositions. Therefore, there is a major challenge in developing suitable VII for all types of lubricants and more especially for biolubricants.^{20–23}

This study proposes to improve PMAEO properties as VII in MPO and, more especially, to extend its VII properties in a triglyceride oil (OTO). The strategy consists to customize the PMAEO with low oil-soluble function in order to decrease its initial solubility in both lube oils at low temperature. Thus, it may promote the coil polymer expansion by improving the difference of polymer solubility in lube oils at low and high temperatures and therefore may result in higher VII performances. For this purpose, two synthetic routes were investigated to afford a modified PMAEO with a reduced solubility in lube oils. In a first strategy, MAEO was epoxidized with hydrogen peroxide and formic acid and then involved in radical polymerization. The second strategy consisted in the direct fully and partially epoxidation of the polymer PMAEO. Finally, the resulting epoxidized polymers were evaluated and compared as VII in both OTO and MPO lubricating oils by measuring the dynamic viscosity of oil-polymer blends versus temperature. Further calculations of oil-polymer blends viscosity index were also conducted and compared to those of pure oils.

2. Materials and methods

2.1 Reagents

Oleic acid (OA, 98 %) was obtained from Fisher Scientific. Dicyclohexylcarbodiimide (DCC, 99 %), 4-dimethylaminopyridine (DMAP, 99 %), 2-hydroxyethyl methacrylate (HEMA, 98 %), hydrogen peroxide solution 30 % in H₂O (H₂O₂), *p*-toluenesulfonic acid monohydrate (p-TsOH, 98 %), benzoyl peroxide (BPO, with 25 % H₂O), and deuterated chloroform (CDCl₃, 99.8 %) were purchased from Sigma-Aldrich. All solvents including tetrahydrofuran (THF, 99 %), toluene (99.5 %), methanol (MeOH, 99.8 %), ethyl acetate (EtOAc, 98 %) and cyclohexane (CY, 98 %) were purchased from VWR. Formic acid solution 60 % in H₂O was purchased from ICKOWICZ manufacturer. Based oils including an organic triglyceride oil (OTO) and a mineral paraffinic oil (MPO) were kindly supplied by ITERG and CHEVRON and their characteristics are detailed in Table 1. All products were used as received.

Table 1: Base oils properties

Properties	OTO	MPO
Density at 20 °C (g.cm ⁻³)	0.9273	0.8503
Kinematic viscosity at 40 °C (mm ² .s ⁻¹)	26.50*	26.92*
Kinematic viscosity at 100 °C (mm ² .s ⁻¹)	5.58*	4.87*
Viscosity Index	156	102
Pour Point (°C)	-30	-15

*measured through rheological measurements (see instrumentation part below)

2.2 Instrumentations

Nuclear magnetic resonance (NMR)

¹H NMR spectra were acquired using a Bruker Avance 400 MHz spectrometer equipped with a QNP z-gradient probe at room temperature. NMR samples were prepared as follows: 10 mg of product for ¹H experiment in around 0.4 mL of CDCl₃. The chemical shifts were reported in part per million relative to tetramethylsilane. Spin multiplicity is expressed by s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet

Size exclusion chromatography (SEC)

Molar mass and molar mass distribution (dispersity, Đ) of polymers were determined by size exclusion chromatography using a GPC 50 Varian equipped with an RI refractive index detector. The system used two PLgel 5 µm Mixed D columns with THF as eluent with a flow rate of 1 mL.min⁻¹. Poly(methyl methacrylate) (PMMA) standards were used for the calibration. The typical sample concentration was 5 mg.mL⁻¹.

Thermogravimetric analysis (TGA)

Thermogravimetric analyses (TGA) were performed using a TGA Q50 (TA instrument) at a heating rate of 10 °C.min⁻¹. Approximately 10 mg of sample were placed in an aluminum pan and heated from room temperature to 500 °C under nitrogen atmosphere (60 mL.min⁻¹).

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) analyses were carried out using a NETZSCH Maia DSC200F3 calorimeter. Constant calibration was performed using indium, *n*-octadecane and *n*-octane standards. Nitrogen was used as the purge gas. 10–15 mg samples were sealed in aluminum pans. The thermal properties were analyzed at 20 °C.min⁻¹ between -100 and 100 °C.

Rheometer

Rheological investigations are executed by using a MCR 302 rheometer by Anton-Paar in plate-plate geometry with a diameter of $d = 25$ mm. The dynamic viscosity of oil-polymer blends was measured from 0 to 100 °C at a shear rate of 100 s^{-1} and the relative viscosity (RV) in function of temperature was calculated by using the equation below:

$$RV = \frac{\mu}{\mu_0} \quad \text{Equation 1}$$

where μ and μ_0 correspond respectively to the dynamic viscosity of the polymer solution and the dynamic viscosity of the pure solvent.

Densimeter

Density measurements of all formulations were performed on the DMA 4100M densimeter of Anton Paar at 40 and 100 °C. Before starting the test, the oil-polymer blends were all stirred at 100 °C during 1 hour to ensure a good homogenization. Then, samples were cooled at the temperature of measurement and approximatively 1 mL is loaded into the densimeter to start the test. The kinematic viscosity of oil-polymer blends at 40 and 100 °C were then deducted by following the equation:

$$\nu = \frac{\mu}{\rho} \quad \text{Equation 2}$$

where ν , μ , and ρ correspond respectively to the fluid kinematic viscosity ($\text{mm}^2.\text{s}^{-1}$), the fluid dynamic viscosity (Pa.s^{-1}), and the fluid density (g.cm^{-3}). Finally, the viscosity indexes of the formulations were calculated according to the ASTM D2270-10 method by using the values of kinematic viscosity of polymer solutions at 40 and 100 °C.

2.3 Preparation of methacrylate monomers from oleic acid and their resulting polymers

2.3.1 2-(methacryloyloxy)ethyl oleate (MAEO)

The synthesis procedure is exactly the same than described in our previous study.¹⁹

δ (ppm): 6.12 and 5.59 ($-\text{C}=\text{CH}_2$, 2H, s), 5.38-5.29 ($-\text{CH}=\text{CH}-$, 2H, m), 4.36-4.3 ($-\text{OCH}_2\text{CH}_2\text{O}$, 4H, m), 2.32 ($\text{O}=\text{CCH}_2$, 2H, t, $J = 7.5$ Hz), 2.05-1.98 ($-\text{CH}_2\text{CH}=\text{CHCH}_2$, 4H, m), 1.95 ($-\text{CH}_2=\text{C}-\text{CH}_3$, 3H, s), 1.66-1.58 ($\text{O}=\text{CCH}_2\text{CH}_2$, 2H, m), 1.29-1.26 ($\text{CH}_3-(\text{CH}_2)_6-$, 20H, m), 0.87 ($-\text{CH}_2\text{CH}_3$, 3H, t, $J = 6.9$ Hz). Its chemical

structure was confirmed by ^1H NMR (400 MHz, CDCl_3). All peaks have been assigned as illustrated in Figure 1, (A).

2.3.2 Epoxidized 2-(methacryloyloxy)ethyl oleate (MAEO-E):

MAEO (25.3 mmol, 10.0 g), 60 % formic acid (27.8 mmol, 2.08 g), *p*-TsOH (0.9 mmol, 0.15 g) and toluene (12 mL) were introduced into a 50 mL round bottom flask equipped with a magnetic stirrer and reflux condenser. Then, the reaction mixture was heated at 50 °C and 30 % aqueous hydrogen peroxide solution (252.5 mmol, 8.6 g) was slowly added to the reaction. After complete addition of hydrogen peroxide, the reaction was slowly heated up to 65 °C during 4 h. At the end of the reaction, the crude product was filtered and washed with a 5 wt.% sodium bicarbonate solution and distilled water, respectively. Then, the organic phase was dried under vacuum at 65 °C for 3 h (yield = 64 %). The resulting monomer chemical structure was confirmed by ^1H NMR. All peaks have been assigned as illustrated in Figure 1,(B).

δ (ppm): 6.12 and 5.59 ($-\text{C}=\text{CH}_2$, 2H,s), 4.36-4.30 ($-\text{OCH}_2\text{CH}_2\text{O}$, 4H, m), 2.90-2.88 ($\text{CH}-\text{O}-\text{CH}-$, 2H, m), 2.32 ($\text{O}=\text{CCH}_2$, 2H, t, $J = 7.5$ Hz), 1.95 ($-\text{CH}_2=\text{C}-\text{CH}_3$, 3H, s), 1.58-1.66 ($\text{O}=\text{CCH}_2\text{CH}_2$, 2H, m), 1.50-1.45 ($\text{CH}_2-\text{CH}-\text{O}-\text{CH}-\text{CH}_2$, 4H, m), 1.29-1.26 ($\text{CH}_3-(\text{CH}_2)_6-$ $\text{CH}_2-\text{CH}-\text{O}-\text{CH}-\text{CH}_2-(\text{CH}_2)_4-$, 20H, m), 0.87 ($-\text{CH}_2\text{CH}_3$, 3H, t, $J = 6.9$ Hz).

2.3.3 Poly(2-(methacryloyloxy)ethyl oleate) (PMAEO)

The synthesis procedure is exactly the same than described in our previous study.¹⁹

δ (ppm): 5.38-5.29 ($-\text{CH}=\text{CH}-$, 2H, m), 4.25-4.13 ($-\text{OCH}_2\text{CH}_2\text{O}-$, 4H, m), 2.37-2.27 ($\text{O}=\text{CCH}_2$, 2H, m), 2.05-1.94 ($-\text{CH}_2\text{CH}=\text{CHCH}_2-$, 4H, m), 1.82-1.61 ($-\text{CH}_2-\text{C}$, 2H, m), 1.62-1.59 ($\text{O}=\text{CCH}_2\text{CH}_2$, 2H, m), 1.31-2.27 ($-(\text{CH}_2)_6-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-(\text{CH}_2)_4-$, 20H, m), 1.03-0.87 ($-\text{CH}_3$, 3H, m), 0.87 ($-\text{CH}_2\text{CH}_3$, 3H, t, $J = 6.8$ Hz). Its chemical structure was confirmed by ^1H NMR. All peaks have been assigned as illustrated in Figure 3, (A).

2.3.4 Epoxidized poly(2-(methacryloyloxy)ethyl oleate) (PMAEO-E)

MAEO-E (12.70 mmol, 5.00 g) and BPO (0.25 mmol, 61.00 mg) were dissolved in toluene (25.0 mL) in a two necked flask purged with N_2 gas for 20 min. The reaction mixture was heated at 90 °C. After 24 h, the polymerization was quenched by cooling the reaction mixture

in liquid nitrogen. Then, the resulting fully epoxidized polymer was purified by several precipitations in cold MeOH and dried under vacuum for 5 h at 80 °C to get a viscous liquid (yield = 60 %). Its chemical structure was confirmed by ^1H NMR. All peaks have been assigned as illustrated in Figure 1, (B).

δ (ppm): 4.25-4.15 ($-\text{OCH}_2\text{CH}_2\text{O}-$, 4H, m), 2.91-2.86 ($\text{CH}-\text{O}-\text{CH}-$, 2H, m), 2.34-2.30 ($\text{O}=\text{CCH}_2$, 2H, m), 1.82-1.61 ($-\text{CH}_2-\text{C}$, 2H, m), 1.62-1.59 ($\text{O}=\text{CCH}_2\text{CH}_2$, 2H, m), 1.50-1.45 ($\text{CH}_2-\text{CH}-\text{O}-\text{CH}-\text{CH}_2$, 4H, m), 1.34-1.26 ($-(\text{CH}_2)_6-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-(\text{CH}_2)_4-$, 20H, m), 1.02-0.89 ($-\text{CH}_3$, 3H, m), 0.89 ($-\text{CH}_2\text{CH}_3$, 3H, t, $J = 6.8$ Hz).

2.3.5 Post-polymerization epoxidation of PMAEO

PMAEO (20.20 mmol, 8 g, 1eq), 60 % aqueous HCOOH solution, p -TsOH (0.019 eq) and toluene (12 mL) were charged into a 50 mL round bottom flask equipped with a magnetic stirrer and reflux condenser. Then, the reaction mixture was heated at 50 °C and 30 % aqueous hydrogen peroxide (H_2O_2) solution was slowly added to the reaction. After complete addition of hydrogen peroxide, the reaction was slowly heated up to 65 °C. Five molar ratios of PMAEO: HCOOH : H_2O_2 were conducted (1:0.28:0.28; 1:0.38:0.38; 1:0.45:0.45; 1:0.58:0.58; 1:1.1:1.1;) to target various yields of epoxidation ; 20, 30, 40, 50 and 100 % respectively. The resulting polymers, respectively PMAEO-E₂₀, PMAEO-E₃₀, PMAEO-E₄₀, PMAEO-E₅₀, PMAEO-E₁₀₀ were obtained respectively at 75 %, 82 %, 81 %, 84 % and 84 % yields. Their chemical structures were all confirmed by ^1H NMR as illustrated in Figure 3, (A).

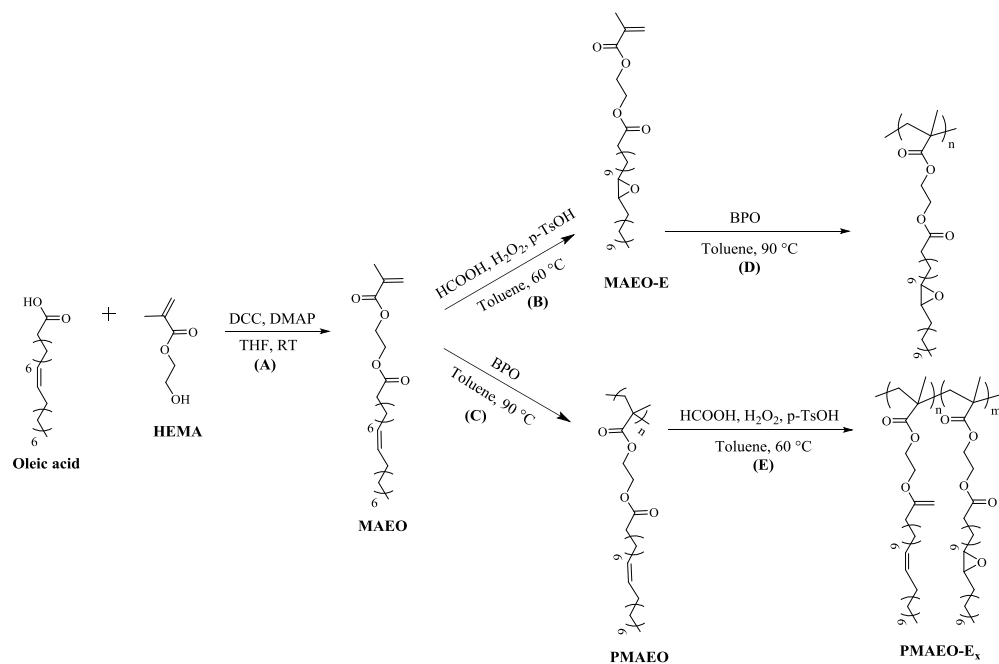
δ (ppm): 5.38-5.29 ($-\text{CH}=\text{CH}-$, 2H, m), 4.25-4.13 ($-\text{OCH}_2\text{CH}_2\text{O}-$, 4H, m), 2.91-2.86 ($-\text{CH}-\text{O}-\text{CH}-$, 2H, m), 2.37-2.29 ($\text{O}=\text{CCH}_2-$, 2H, m), 2.07-1.95 ($-\text{CH}_2\text{CH}=\text{CHCH}_2-$, 4H, m), 1.82-1.61 ($-\text{CH}_2-\text{C}$, 2H, m), 1.62-1.59 ($\text{O}=\text{CCH}_2\text{CH}_2$, 2H, m), 1.50-1.45 ($-\text{CH}_2-\text{CH}-\text{OCH}-\text{CH}_2-$, 4H, m), 1.34-1.26 ($-(\text{CH}_2)_6-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-(\text{CH}_2)_4-$, 20H, m), 1.02-0.80 ($-\text{CH}_3$, 3H, m), 0.91-0.87 ($-\text{CH}_2\text{CH}_3$, 3H, t, $J = 6.8$ Hz).

3. Results and discussion

3.1 Synthesis of methacrylate FA-based monomers

Oleic acid was functionalized *via* Steglich esterification with 2-hydroxyethylmethacrylate (HEMA) in the presence of DMAP as catalyst and DCC as coupling agent at room temperature to afford the monomer MAEO (Scheme 1, (A)). The resulting oleic acid-based methacrylate monomer was obtained with 100 % conversion and its structure was further confirmed by using ^1H NMR spectroscopy where all peaks have been assigned in Figure 1, (A). In the ^1H NMR spectrum of MAEO, the characteristic signal at 4.33 ppm corresponds to the $\alpha\text{-CH}_2$ of the ester functions while the vinyl protons of the methacrylate function are assigned to the peaks located at 6.12 and 5.59 ppm and confirmed the efficiency of the functionalization. No side reaction from the oleate double bond at 5.34 ppm has been observed.

MAEO was further epoxidized in toluene at 50 °C with formic acid, *p*-TsOH as catalyst and H_2O_2 as oxidizing agent (30 % aq.) (Scheme 1, (B)). The peracids are formed *in situ* by reaction of formic acid with hydrogen peroxide.⁴⁷ H_2O_2 was added dropwise to the solution mixture in order to avoid substantial increase of temperature due to the exothermic reaction between H_2O_2 and HCOOH .⁴⁸ The ^1H NMR spectrum of the epoxidized MAEO is presented in Figure 1, (B). The complete disappearance of the ethylene protons at 5.34 ppm as well as the α -protons of the internal unsaturation of MAEO at 2.01 ppm and finally the apparition of the CH protons adjacent to the epoxy group at 2.89 ppm confirmed the successful epoxidation reaction.



Scheme 1: (A) Synthesis of MAEO by Steglich esterification of oleic acid, (B) Epoxidation of MAEO, (C) Synthesis of PMAEO by free radical polymerization, (D) Polymerization of MAEO-E, (E) Post-polymerization epoxidation of PMAEO with $x=20, 30, 40, 50, 100$ corresponding to the conversion of internal unsaturations into epoxy groups

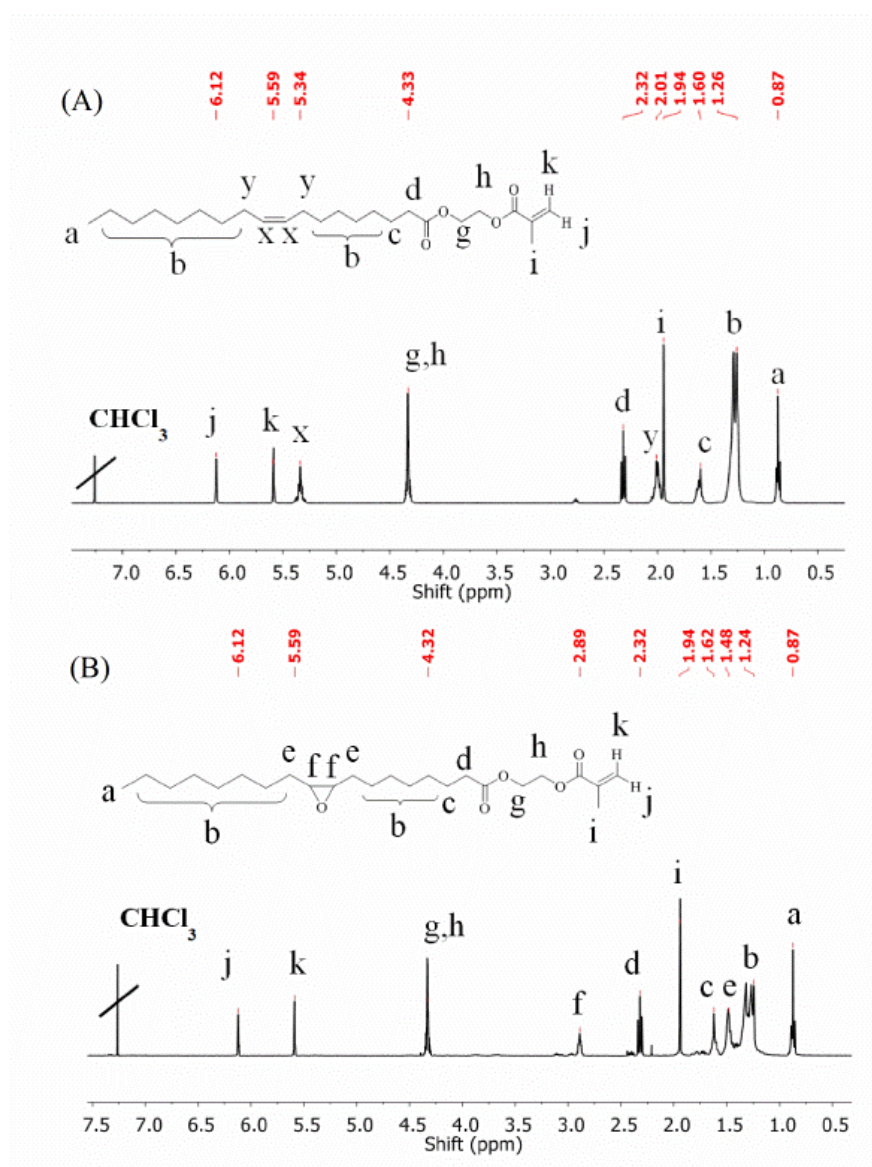


Figure 1: ^1H NMR spectra of (A) MAEO and (B) MAEO-E in CDCl_3

3.2 Free radical polymerization of FA-based polymers

The polymerization of MAEO was conducted in toluene at 90 °C with BPO as thermal initiator (Scheme 1, (C)). The rate of polymerization was monitored by ^1H NMR spectroscopy by following the decrease in intensity of the methacrylate signal. The monomer was converted into polymer at 87 % after 7 h of reaction (Figure 2). After precipitation of the resulting polymer (PMAEO) in cold MeOH, its structure was confirmed by ^1H NMR (Figure 3, (A)). The peaks corresponding to the vinyl protons of the methacrylate function have completely disappeared, which confirmed the efficiency of the purification procedure. In the meantime, the signal assigned to the internal unsaturation of PMAEO at 5.33 ppm remains constant

revealing its unreactivity during the radical polymerization. The repeating unit protons O-CH₂-CH₂-O (g and h) from the polymer side chain appear at 4.13 and 4.25 ppm. In addition, the spectrum indicates that chiral centers of the polymer chain present tacticity as shown by the split of the signal assigned to the methyl protons i.²⁴ The resulting polymer exhibits a broad dispersity (3.6) and a weight average molecular weight of 160 kg.mol⁻¹ determined by size-exclusion chromatography (SEC) in THF according to PMMA standards.

MAEO-E was involved in similar radical polymerization conditions than MAEO (Scheme 1, (D)). After 7 h of reaction, a monomer conversion of 70 % was reached (Figure 2). The lower monomer conversion compared to MAEO conversion may be related to the increasing viscosity of the system as polymerization proceeds resulting in the decrease of the polymerization rate. This increasing viscosity was mainly due to the steric hindrance of the bulky and rigid pendant chains with epoxy function which are contained in the resulting polymer (PMAEO-E). Thus, PMAEO-E demonstrated lower weight average molecular weight (25 kg.mol⁻¹) and dispersity (1.5) than its analogous without epoxy function in the pendant aliphatic chains. However, a previous study has revealed that low polymer molecular weight did not show enough contribution on oil viscosity to show interesting VII properties in lube oils. As a result, PMAEO-E may show limited properties as VII.¹⁹ Its chemical structure was confirmed through ¹H NMR as shown in Figure 3, (B).

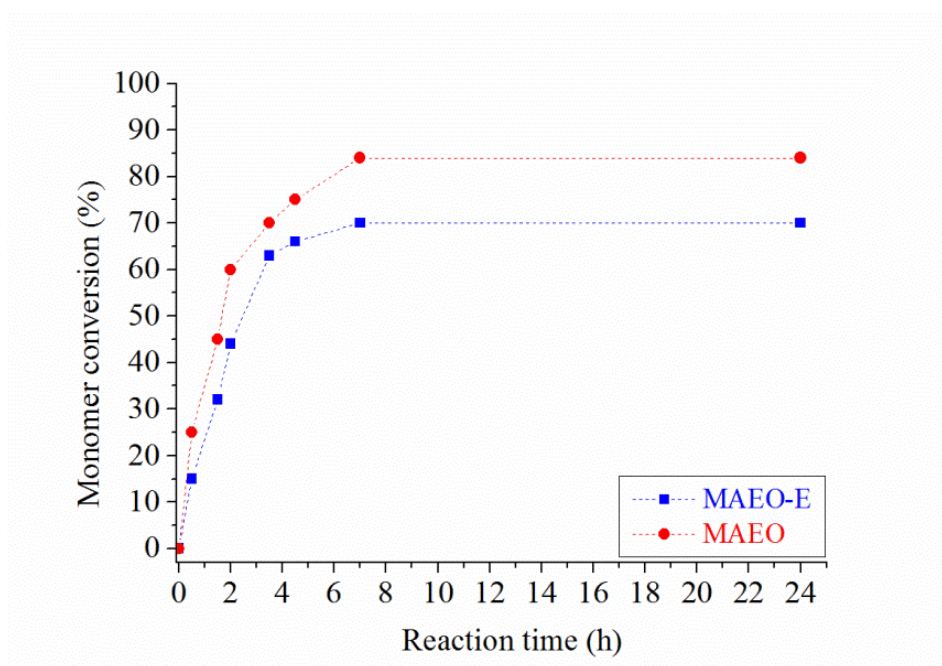


Figure 2: MAEO and MAEO-E conversion versus time during the radical polymerization

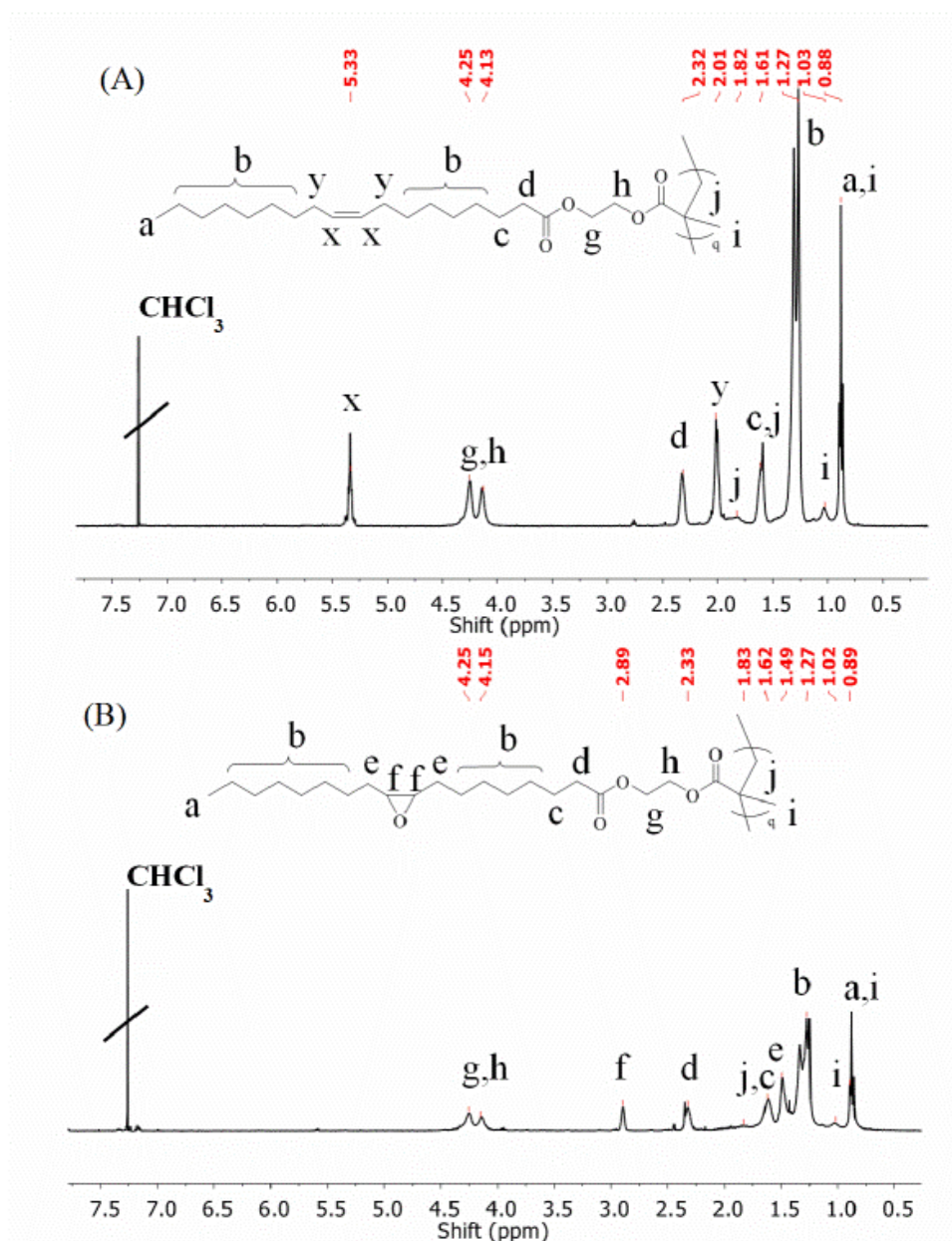


Figure 3: ^1H NMR spectra of PMAEO (A) and PMAEO-E (B) in CDCl_3

3.3 Post-polymerization epoxidation

As the carbon-carbon double bond in PMAEO structure is unreactive during the radical polymerization, this reactive site is still available for further functionalizations. Therefore, epoxidation of double bonds of PMAEO has been performed to afford epoxidized polymers with different epoxy contents (Scheme 1, (E)). The double bonds of side-chains of PMAEO have been easily either partially or totally converted into epoxide groups owing to the reaction time and the amount of peracids formed in the reaction mixture. For this purpose, five molar

ratios of PMAEO:HCOOH:H₂O₂ were studied (1:1.1:1.1; 1:0.58:0.58; 1:0.45:0.45; 1:0.38:0.38; 1:0.28:0.28). The ¹H NMR spectra of PMAEO-Ex with various epoxy contents are shown in Figure 4 except PMAEO-E₁₀₀ which demonstrated the same NMR ¹H than PMAEO-E in Figure 3, (B). The epoxy protons appear around 2.9 ppm while unreacted double bonds are assigned to the peak around 5.3 ppm confirming the partial epoxidation of PMAEO. The epoxy protons (–CH–O–CH–) relative to the unsaturation signal (–CH=CH–) was used to calculate the degree of epoxidation (DOE) during the performed reactions according to the equation below:

$$\text{DOE} = \frac{A(-\text{CH}-\text{O}-\text{CH}-)2.9 \text{ ppm}}{A(-\text{CH}-\text{O}-\text{CH}-)2.9 \text{ ppm} + A(-\text{CH}=\text{CH}-)5.3 \text{ ppm}} \quad \text{Equation 3}$$

The resulting conversions of internal unsaturations into epoxy groups were approximately 20, 30, 40, 50 and 100 % for PMAEO-E₂₀, PMAEO-E₃₀, PMAEO-E₄₀, PMAEO-E₅₀ and PMAEO E₁₀₀ respectively. No side reactions like ring-opening reactions occurred during epoxidation.

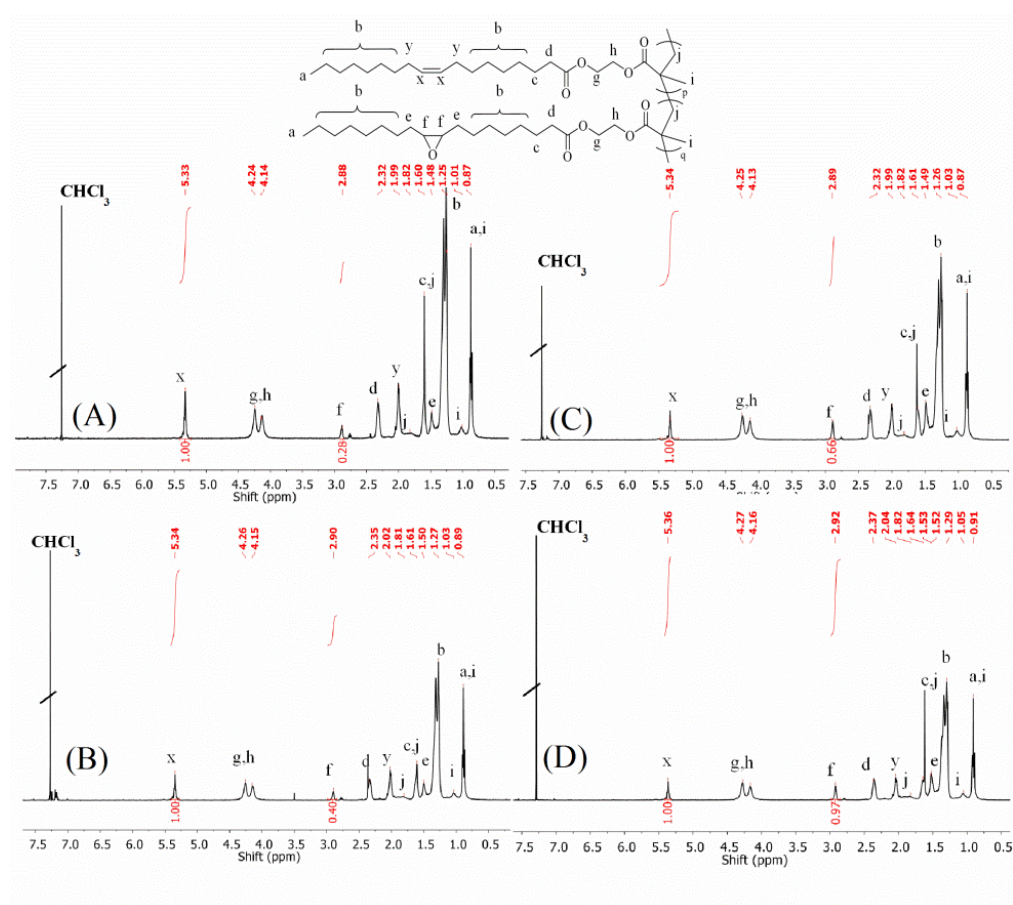


Figure 4: ¹H NMR spectra in CDCl₃ of partial epoxidized PMAEO with (A) PMAEO-E₂₀ (B) PMAEO-E₃₀ (C) PMAEO-E₄₀ (D) PMAEO-E₅₀

3.4 Thermal properties

The purpose of this study was to show the suitability of the synthesized epoxidized polymers from oleic acid as VII for lubricant application. Hence, as VII are supposed to be frequently subjected to high local temperatures due to their use in engine oils, the polymer thermal properties have been evaluated.

The thermal stability of all synthesized polymers were determined by TGA (Figure SI-1). Results indicated that the temperature at 5 % weight loss ($T_{d5\%}$) of epoxidized polymers increased with the epoxy content. Indeed, the $T_{d5\%}$ of PMAEO is 270 °C, while they are 284, 291, 296, 302 and 321 °C for PMAEO-E₂₀, PMAEO-E₃₀, PMAEO-E₄₀, PMAEO-E₅₀, and PMAEO-E₁₀₀ respectively (Table 2). These results show that the presence of the epoxy ring confers higher thermal stability to the molecules in respect to alkene groups. The improvement of thermal stability of the resulting polymers with the incorporation of epoxy groups was already reported in literature.⁵⁰ Moreover, for the fully epoxidized polymer, the molecular weight is not a powerful parameter since a similar thermal stability with a $T_{d5\%}$ around 320 °C was observed for both PMAEO-E (25 kg.mol⁻¹) and PMAEO-E₁₀₀ (160 kg.mol⁻¹).

Table 2: Thermal characterizations of the synthesized polymers

Polymers	Td5% a) (°C)	Tg b) (°C)
PMAEO	270	-80
PMAEO-E20	284	-76
PMAEO-E30	291	-72
PMAEO-E40	296	-70
PMAEO-E50	302	-63
PMAEO-E100	321	-48
PMAEO-E	318	-50

a): values determined by ATG; b): values determined by DSC

Complementary, DSC analyses have been performed on all the polymers (Figure 5). Despite the difference of molecular weight, PMAEO-E, resulting from the homopolymerization of MAEO-E, has a similar T_g value than PMAEO-E₁₀₀. PMAEO-E₁₀₀ showed a slightly higher glass transition temperature than the other partially epoxidized

polymers as shown in Table 2. According to the results, the higher the epoxy content, the higher the rigidity of the polymer aliphatic pendant chain and the higher the T_g value.

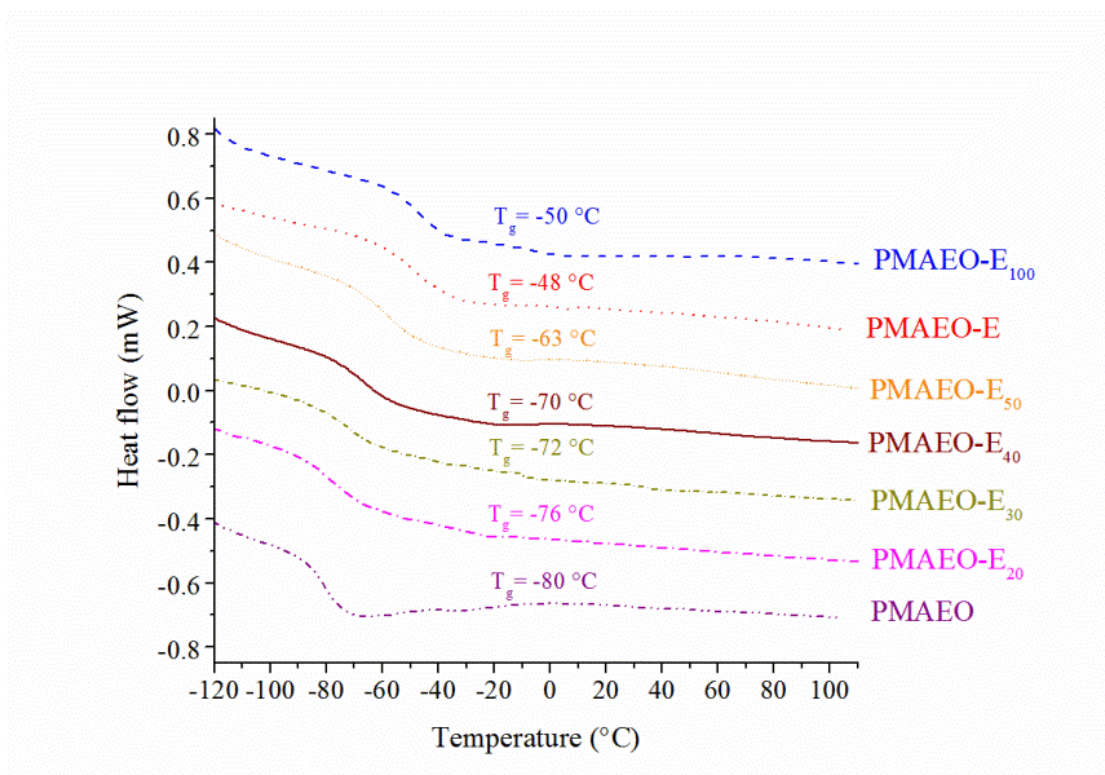


Figure 5: DSC analyses of the synthesized polymers

3.5 Evaluation of the epoxidized oleic acid-based polymers as VII in lubricating oils

3.5.1 Solubility test of the resulting polymers in lube oils

The homopolymers PMAEO-E and PMAEO-E₁₀₀ were blended at 5 wt. % in both organic triglyceride oil (OTO) and mineral paraffinic oil (MPO). After 1 h at 80 °C, it was observed that they were both soluble in OTO while they were found to be totally insoluble in MPO. This difference of solubility was related to the high polarity of their epoxidized aliphatic chains which had no affinity with the high aliphatic content of MPO. Nevertheless, the insolubility of these polymers in MPO confirmed the efficiency of the epoxidation strategy; the functionalization of PMAEO with epoxy group lead to a decrease of the initial polymer solubility in MPO. On the other hand, as the triglyceride oil is less apolar than the MPO due to the presence of ester functions, it explains why the fully epoxidized polymers (PMAEO-E

and PMAEO-E₁₀₀) were found to be enough soluble in this oil. In order to provide epoxidized polymers with a minimum of solubility in MPO, partially epoxidized polymers (20, 30, 40 and 50 %) were blended at 5 wt. % in MPO and heated at 80 °C for 1 h. In this case, PMAEO-E₂₀, PMAEO-E₃₀ and PMAEO-E₄₀ were found enough soluble in MPO to be evaluated as additives while PMAEO-E₅₀ was still not soluble in the oil due to its high polarity. Nevertheless, the addition of PMAEO-E₂₀, PMAEO-E₃₀ and PMAEO-E₄₀ provided turbid oil solutions at room temperature which reflected their reduced solubility in the lube oil at low temperature. However, by heating the oil-epoxidized polymer formulations at 80 °C, they became limpid and suggested a higher solubility of the partially epoxidized polymers in oil at high temperature.

3.5.2 Rheological polymer behaviors with temperature in lubricating oils

Rheological measurements were performed in order to evaluate the suitability of the synthesized epoxidized oleic acid-based polymers as VII for lubricating oils. For this purpose, the relative viscosity (RV) between lube oils and lube oil-polymer (5 wt. %) blends were calculated and plotted in respect to temperature. As the calculated RV represents the influence of the polymer on oil's viscosity, the RV should increase with temperature in case of coil copolymer expansion as previously reported.¹⁷ The rheological FA-based polymers properties were compared to those previously reported for PMAEO.

3.5.2.1 Mineral lube oil

According to Figure 6, the rheological study has suggested a difference in the size of polymer coil between low and high temperatures as all the RV values of MPO-polymer blends were improved with temperature. In addition, this improvement was more significant for PMAEO-E₄₀ and PMAEO-E₃₀ compared to PMAEO. For instance, the difference of RV between 0 and 100 °C was 0.22, 0.35 and 0.55 for PMAEO, PMAEO-E₃₀ and PMAEO-E₄₀ respectively. These results were mostly explained by the higher thickening power of PMAEO-E₄₀ and PMAEO-E₃₀ at 80 and 100 °C (where polymers are more probably in an expanded coil conformation) compared to PMAEO when blended in MPO. Indeed, the RV value of PMAEO was 1.43 at 100 °C while it was 1.55 for PMAEO-E₃₀ and 1.75 for PMAEO-E₄₀ at the same temperature. These results were mostly related to the presence of epoxy functions which are known to confer rigidity to the polymers chains.²⁵ The current literature devoted to biolubricants based on epoxidized vegetable oils report that they exhibit high VI and are

generally used on a wide temperature range due to their higher viscosity compared to the raw oil, especially at high temperature.^{22,26} Our results are in total accordance with these observations. However, for low epoxy content such as the polymer PMAEO-E₂₀, no significant rheological behavior differences were observed related to PMAEO. In summary, PMAEO-E₄₀ and PMAEO-E₃₀ represent interesting alternatives to PMAEO as VII since they have a lower effect on oil viscosity at low temperature and a higher contribution on oil viscosity at high temperature.

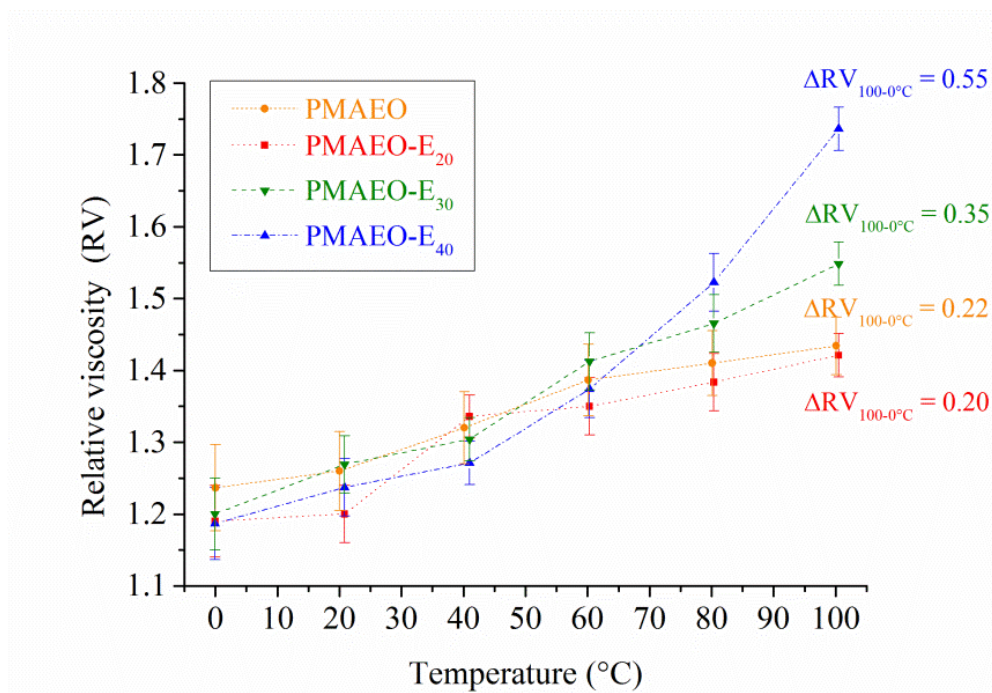


Figure 6: RV of oil-polymer blends vs temperature in MPO

3.5.2.2 Organic triglyceride oil

In a previous study, PMAEO has only demonstrated a similar thickening power with increasing temperature when added in OTO suggesting a similar coil size dimension at low and high temperatures.¹⁹ This result was explained by the good polymer solubility in OTO as they both have similar structure with long aliphatic chain and ester functions. Therefore, it may have prevented the coil expansion with temperature as the polymer was already swollen in oil at low temperature. However, when the fully epoxidized polymer PMAEO-E₁₀₀ was blended in OTO, a different polymer rheological behavior on oil viscosity was clearly observed as shown in Figure 7. Indeed, while the RV remained constant with temperature for PMAEO, it was increased from 1.74 at 40 °C to 1.96 at 100 °C with PMAEO-E₁₀₀. This result indicates that the epoxidized polymer has higher influence on oil viscosity at high temperature

than at low temperature. Therefore, it suggests that the coil polymer size was improved by increasing temperature, inducing good polymer VII properties in OTO. Indeed, as PMAEO-E₁₀₀ contains non-negligible polar epoxy functions, it inherently provides less solubility in the oil at low temperature as confirmed the temperature behavior of PMAEO-E₁₀₀ in OTO which can be interpreted as a gradual increase of polymer solubility in temperature. Nevertheless, even if PMAEO-E₁₀₀ may displayed a lower solubility in OTO than PMAEO, its effect on oil viscosity was high at low temperature. This result underlined that the presence of a high content of epoxy function in the polymer backbone has also improved its thickening power compared to PMAEO.

In the meantime, the epoxidized polymer obtained via the homopolymerization of MAEO-E only has shown a low and similar thickening power at low and high temperatures according to Figure 7. Indeed, the calculated RV remains constant (around 1.25) despite the increasing temperature. The difference of coil polymer behavior between PMAEO-E and PMAEO-E₁₀₀ was directly related to their high difference of molecular weights. As PMAEO displayed only a low polymer molecular weight of 25 kg.mol⁻¹, it induced a reduced coil size and a low thickening power which have limited the coil dimension improvement with temperature. Therefore, it explained the low polymer influence on oil viscosity either at low or high temperatures. These results are in accordance with our previous work where the importance of the molecular weight polymer on its VII properties were also demonstrated.¹⁹

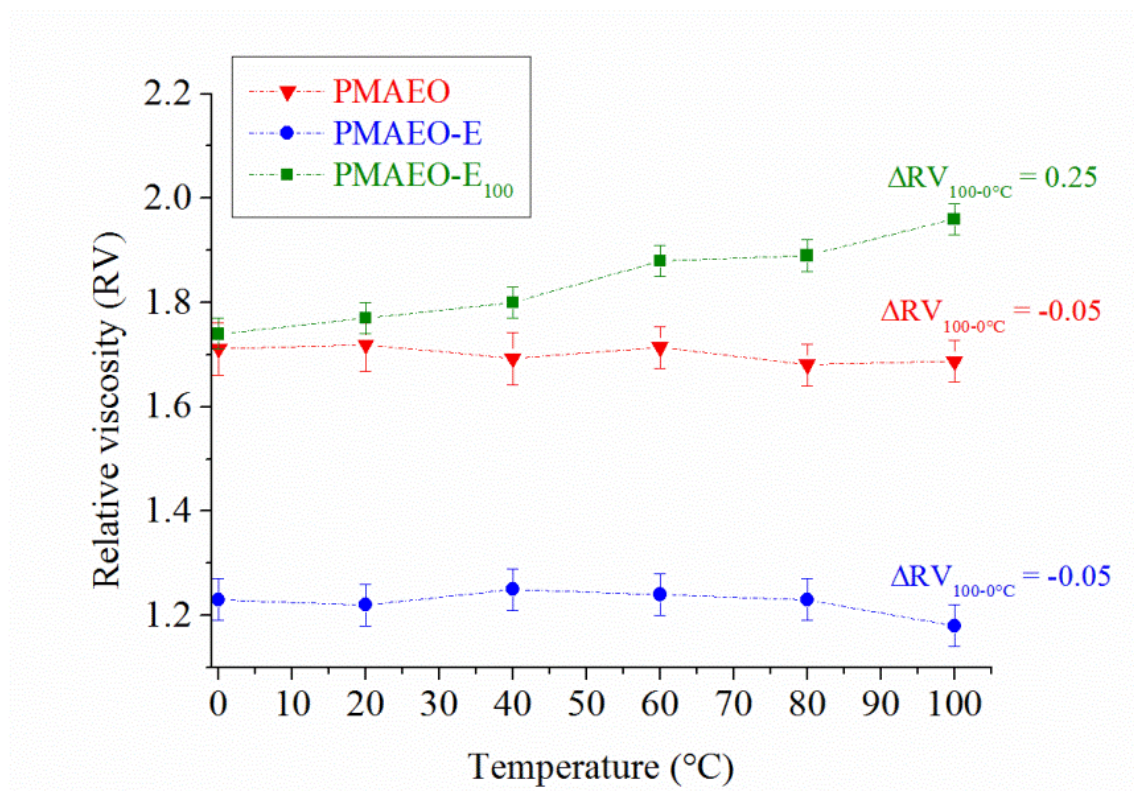


Figure 7: RV of oil-polymer blends vs temperature in OTO

3.5.3 Viscosity Index calculations

Viscosity Index of oil-polymer blends were measured according to the ASTM D2270-10 and compared to the initial lube oils VII. The results of Table 3 indicated that epoxidized polymers, except PMAEO-E₂₀, demonstrated a better ability to improve the viscosity index of MPO than PMAEO. Indeed, while the addition of 5 wt. % of PMAEO in MPO improved the VI from 102 to 154, the addition of 5 wt. % of PMAEO-E₃₀ or PMAEO-E₄₀ in MPO allowed to reach a VI of 192 and 240 respectively. These results underlined the good correlation between polymers ability to have a more significant effect on oil viscosity at high than at low temperatures ($\Delta RV_{100-0\text{ }^{\circ}\text{C}}$) and the polymer's ability to increase the oil VII. Indeed, as previously mentioned, the addition of 5 wt. % of PMAEO-E₄₀ in MPO demonstrated a higher increase of RV with temperature ($\Delta RV_{100-0\text{ }^{\circ}\text{C}} = 0.55$) compared to PMAEO ($\Delta RV_{100-0\text{ }^{\circ}\text{C}} = 0.20$) and therefore demonstrated the best improvement of MPO's viscosity index. Consequently, the partially epoxidized polymers PMAEO-E₃₀ and PMAEO-E₄₀ exhibit better VII properties than PMAEO for MPO.

Table 3: Viscosity index data of MPO blended with 5 wt. % of copolymers

Oil-polymer blends	KV 40 °C (mm ² .s ⁻¹)	KV 100 °C (mm ² .s ⁻¹)	Viscosity Index	$\Delta RV_{100-0\text{ }^{\circ}\text{C}}$
Pure MPO	26.92	4.87	102	-
MPO + PMAEO	35.80	6.91	154	0.20
MPO +PMAEO-E ₂₀	35.81	6.91	154	0.20
MPO +PMAEO-E ₃₀	34.99	7.54	192	0.35
MPO +PMAEO-E ₄₀	34.18	8.45	240	0.55

Similarly, the addition of 5 wt. % of PMAEO-E₁₀₀ in OTO revealed a better effect than PMAEO on the improvement of the oil's VI (Table 4). Indeed, the calculated VI were 196 and 230 for respectively PMAEO and PMAEO-E₁₀₀ while the pure oil was 156. It can be noticed that despite the similar high thickening power of PMAEO on the lube oil viscosity at low and high temperatures, the polymer was still able to improve the VI of OTO. Thus, the viscosity index should not be used as the only argument to confirm the nature of an additive as suitable VII since thickener additives also have the ability to improve the oil VI without following the coil expansion theory.²⁷ Otherwise, the addition of PMAEO-E in OTO did not affect significantly the oil viscosity index which was increased from 156 to only 162. This observation can be directly related to the very low polymer thickening power on oil viscosity inducing low VII properties.

Table 4: Viscosity index data of OTO blended with 5 wt. % of copolymers

Oil-polymer blends	KV 40 °C (mm ² .s ⁻¹)	KV 100 °C (mm ² .s ⁻¹)	Viscosity Index	$\Delta RV_{100-0\text{ }^{\circ}\text{C}}$
Pure OTO	26.50	5.58	156	-
OTO + PMAEO	45.32	9.27	196	-0.05
OTO PMAEO-E ₁₀₀	46.38	10.88	230	0.25
OTO + PMAEO-E	32.60	6.58	160	-0.05

4. Conclusion

The purpose of this study was to incorporate epoxy functions in the poly(2-(methacryloyloxy)ethyl oleate) (PMAEO) backbone and evaluate the influence of such polar functions on its efficiency as viscosity index improver (VII) in both MPO and OTO lubricating oils. In a first strategy, the 2-(methacryloyloxy)ethyl oleate (MAEO) was successfully epoxidized and then polymerized through conventional radical polymerization. However, the resulting polymer (PMAEO-E) was obtained with a too low molecular weight for VII application (25 kg.mol⁻¹). Thus, a second strategy was performed using the direct

epoxidation of double bonds of a previously reported PMAEO which displayed a suitable molecular weight for VII application (160 kg.mol^{-1}) and which has already shown promising VII properties in MPO. Partially (20, 30, 40 and 50 % of converted unsaturations) and fully epoxidized PMAEO were successfully obtained (PMAEO-E₁₀₀). All the resulting polymers were firstly added at 5 wt. % in MPO and have shown different solubilities in oil according to their epoxy content. Polymers with 50 % and 100 % of epoxidized unsaturations were completely insoluble in MPO while polymers PMAEO-E₂₀, PMAEO-E₃₀ and PMAEO-E₄₀ were found to be enough soluble in oil to be evaluated as VII. These results firstly indicated that the incorporation of polar functions in PMAEO backbone decreased its initial solubility in MPO as it was expected. Moreover, the polymers PMAEO-E₃₀ and PMAEO-E₄₀ have demonstrated a more significant improvement of their thickening power on oil with temperature compared to PMAEO. Thus, it suggested that the lower solubility of partially epoxidized polymers at low temperature in MPO compared to PMAEO allowed to improve their coil expansion with temperature and therefore their VII properties. In the meantime, the addition in OTO of 5 wt. % of PMAEO-E₁₀₀ with a high molecular weight has shown promising VII properties that the non-epoxidized polymer did not show initially. Nevertheless, PMAEO-E showed only low properties as VII in OTO and this observation was related to its too low molecular weight for the targeted application. In summary, this study demonstrated that the control of the epoxidation rate of a high enough PMAEO molecular weight for VII application represents a promising strategy to improve its initial VII properties in mineral paraffinic oils or even to turn it into a suitable VII for triglyceride oils.

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