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Synthesis of plant oil-based amide copolymethacrylates and their use as viscosity index improvers

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Abstract

Polymeric materials derived from fatty acids (FA)s were synthesized through free radical polymerization and evaluated as viscosity index improvers (VII) in an organic triglyceride lube oil (OTO). For this purpose, various FA-based copolymers were designed to own a reduced solubility at low temperature in OTO which can be gradually improved by increasing temperature. Different fatty amide methacrylates were chosen for their poorly oil-miscible repeating units while fatty ester methacrylates, 2-(methacryloyloxy)ethyl oleate (MAEO) and 2-(methacryloyloxy)ethyl 4-(dodecylthio)oleate (MAEO_{SC12}), were used as oil-miscible comonomers for providing copolymers with a minimum of solubility in the lube oil. All copolymers were synthesized with a 50:50 molar feed ratio and were fully characterized through ¹H NMR, SEC, DSC, and TGA analyses. Then, rheological study of oil-copolymer blends revealed that copolymers containing -NH function were able to have a higher impact on oil viscosity at high than at low temperatures suggesting the coil copolymer expansion. This improvement of thickening power with temperature in OTO was further optimized by increasing the copolymer molecular weight, dispersity, concentration, pendant aliphatic chain length or by adding an additional aliphatic chain in the copolymer backbone. Moreover, copolymer additions in OTO did not disturb the initial Newtonian behavior of OTO at -30 °C which corresponds to the lube oil pour point.

Graphical abstract:

1. Introduction

In order to limit the decrease of viscosity with temperature, mineral oils are generally blended with viscosity index improver (VII) additives which have the ability to expand the base oil operating temperature range.^{1,2} These additives are well-known to reduce the lube oils viscosity-temperature dependency but also their cold flow properties.³ The main polymers used for this application are poly(alkyl)methacrylates (PMA)s. They typically have long oil soluble hydrocarbon (nonpolar) tails and smaller hydrophilic (polar) head groups which provide them specific conformation in mineral oils according to the temperature.⁴ Indeed, as the two parts of the polymer show different affinities in the hydrophobic base oil, it results in a coil polymer expansion with temperature inducing a limited contribution on base oil viscosity at low temperature (coil up) and a high thickening effect on base oil viscosity at high temperature (expanded coil conformation).⁵ Thus, the addition of PMAs in mineral oil provides, since many years, an interesting way of considerably limiting the variation of their viscosity with increasing temperature. Although the conventionally used PMAs exhibit satisfactory performances as VII additives, they originated from petroleum resources which induce environmental concerns toward their inherent toxicity. These conventional methacrylate copolymers used as viscosity modifiers in the industry are constituted of long aliphatic chain methacrylates and short aliphatic chain methacrylates which mostly come from petroleum resources (methyl methacrylate for instance).^{7,8} Even if some long aliphatic chain methacrylates could be obtained from fatty alcohols by oleochemistry, the industry is

currently still using petroleum route such the Ziegler process to provide most of fatty alcohols.⁶ Moreover, In the meantime, the development of biolubricants are currently encouraging the design of innovative biobased VII with similar rheological properties than current PMAs in mineral oils.⁹ 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 oils.^{10–12} However, even if they demonstrated good properties to enhance the field service performance of engine oil, VO generally showed poor reactivity in radical process.¹³ 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.^{14–16}

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 monomers²³. 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.^{19, 20} 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.²¹ 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.¹⁷ 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.¹⁸

Hence, in order to provide suitable VII for a triglyceride oil (OTO), new copolymers were designed to promote the globular conformation in oil at low temperature and to exhibit the ability to undergo coil expansion with increasing temperature. For this purpose, lower oil-soluble comonomers were designed by using suitable functionalizations of fatty esters. Hence, this current study aims at the synthesis of new VO-based comonomers with lower solubility in OTO. In a first part, both methyl oleate and methyl erucate were functionalized by amidation with ethanolamine to add high polar amide functions which may have few affinities with the

hydrophobic content of OTO. In addition, the methyl oleate was also functionalized with *N*-methylethanolamine in order to provide a less polar derivative bearing a *N*-substituted amide by a methyl group unable form H-bonds. Then, the *N*-hydroxyalkyl fatty amide derivatives were reacted with the methacrylic anhydride through *trans*-esterification to afford suitable monomers for free radical polymerization (FRP).

The resulting monomers were involved in copolymerization with MAEO by fixing a 50:50 feed monomers molar ratio to provide copolymers with a minimum of solubility in OTO. Additionally, further copolymers were designed under the same conditions by using another oil-soluble comonomer, the 2-(methacryloyloxy)ethyl 4-(dodecylthio)oleate (MAEO_{SC12}) instead of MAEO. Finally, characterizations and performances of the resulting FA-based (co)polymers were evaluated as VII in OTO and then compared in terms of VII properties to the previously reported PMAEO as well as to a commercial PMA additive. The influence of several parameters such as the copolymer polarity/solubility in oil, the molecular weight, the concentration, and the aliphatic chain length were evaluated for the resulting copolymers VII properties. Additionally, cold flow behavior was also studied for the most promising FA-based copolymers as VII.

2. Materials and methods

2.1 Reagents

Methyl erucate (80 %) and methyl oleate (83 %) were kindly supplied by ITERG. Ethanolamine (99 %), *N*-methylethanolamine (98 %), dimethylaminopyridine (DMAP, 99 %), methacrylic anhydride (94 %), deuterated chloroform (CDCl₃) were used as received except azobis(isobutyronitrile) (AIBN, 98 %) which was recrystallized by methanol. A commercial PMA-based viscosity index improver (Viscoplex 10-250) was purchased at Evonik. All solvents including tetrahydrofuran (THF, 99 %), toluene (99 %), methanol (MeOH, 99 %) were purchased from VWR and were used without further purification. Organic biobased triglyceride oil (OTO) were kindly supplied by ITERG. The lubricating oil characteristics are detailed in Table 1.

Table 1: Organic triglyceride oil (OTO)

Properties	
Density at 20 °C (g.cm ⁻³)	0.9273

Kinematic viscosity at 40 °C (mm².s⁻¹)	26.5*
Kinematic viscosity at 100 °C (mm².s⁻¹)	5.58*
Viscosity Index	156
Pour Point (°C)	-30

*: calculated through rheological measurements (see instrumentation part below).

2.2 Instrumentations

Nuclear magnetic resonance (NMR) spectroscopy

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 (ppm) 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 OTO and OTO-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 (1) below:

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

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

The rheological cold flow behavior of oil-polymer blends was determined through measurements of shear stress (Pa) and dynamic viscosity ($\text{Pa}\cdot\text{s}^{-1}$) at various shear rates ranging from 1 to 1000 s^{-1} . The additive concentration used was 5 wt. %. The value of the yield stress can be obtained by extrapolating the shear stress to zero shear rate on a linear curve of the relationship between shear rate and shear stress.

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 (2) below:

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

where ν , μ , ρ correspond respectively to the fluid kinematic viscosity ($\text{mm}^2\cdot\text{s}^{-1}$), the fluid dynamic viscosity ($\text{Pa}\cdot\text{s}^{-1}$), and the fluid density ($\text{g}\cdot\text{cm}^{-3}$). 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 Synthesis of *N*-hydroxyalkyl fatty amides

- ***N*-(2-hydroxyethyl)oleamide (HEOA)** was prepared as followed:

Methyl oleate (1 eq, 0.1 mol, 30.0 g) and ethanolamine (2 eq, 0.2 mol, 12.4 g) were charged in bulk in a 250 mL two neck round bottom flask and stirred at 100 °C. After 24 h of reaction, the complete conversion of amidation process was confirmed by ^1H NMR and the reaction was stopped. The crude product was poured in chloroform and washed twice with a 0.1 M solution of acetic acid. Then, the chloroform was removed using a rotary evaporator to obtain pure HEOA (yield = 84 %). Its chemical structure was confirmed by ^1H NMR (Figure 1, (A)).

HEOA: δ (ppm, 400 MHz, CDCl_3): 6.01 (NH, 1H, s), 5.40-5.28 (HC=CH, 2H, m), 3.73-3.71 ($\text{CH}_2\text{-OH}$, 2H, m), 3.44- 3.40 (HN- CH_2 , 2H, m), 2.21 ($\text{H}_2\text{C-C=O}$, 2H, t), 1.97-2.01 ($\text{H}_2\text{C-}$

CH=CH-CH₂, 4H, m), 1.59-1.66 (H₂C-H₂C-C=O, 2H, m), 1.24-1.26 (-(CH₂)₆-CH₂-CH=CH-CH₂-(CH₂)₄-, 20H, m), 0.87 (CH₂-CH₃, 3H, t).

- **(Z)-N-(2-Hydroxyethyl)docos-13-enamide (HEDA)** was prepared by following the same previous conditions with methyl erucate instead of methyl oleate (yield= 89 %). Its structure was confirmed by NMR ¹H (Figure S1, (A)).

HEDA: δ(ppm, 400 MHz, CDCl₃): 6.05-5.98 (NH, 1H,m), 5.33-5.36 (HC=CH, 2H, m), 3.72-3.75 (H₂C-OH, 2H, m), 3.41-3.45 (HN-CH₂, 2H,m), 2.21 (H₂C-C=O, 2H, t), 1.99-2.04 (H₂C-CH=CH-CH₂, 4H, m), 1.59-1.66 (H₂C-H₂C-C=O, 2H, m), 1.26-1.30 (-(CH₂)₆-CH₂-CH=CH-CH₂-(CH₂)₈, 28H, m), 0.87 (CH₂-CH₃, 3H, t).

- **N-(2-hydroxyethyl)-N-methyloleamide (HEMOA)** was prepared by following the same procedure than HEOA with N-methylethanolamine instead of ethanolamine (yield = 90 %). Its chemical structure was confirmed by ¹H NMR (Figure S2, (A)).

HEMOA: δ (ppm, 400 MHz, CDCl₃): 6.05-5.98 (NH, 1H,m), 5.32-5.34 (HC=CH, 2H, m), 3.74-3.77 (H₂C-OH, 2H, m), 3.52-3.55 (HN-CH₂, 2H, m), 3.05 (CH₃-N,3H,s), 2.32 (H₂C-C=O, 2H, t), 1.97-2.04 (H₂C-CH=CH-CH₂, 4H, m), 1.58-1.65 (H₂C-H₂C-C=O, 2H, m), 1.24-1.30 (-(CH₂)₆-CH₂-CH=CH-CH₂-(CH₂)₄, 20H, m), 0.87 (CH₂-CH₃, 3H, t).

2.4 Synthesis of methacrylate monomers

- Synthesis of fatty ester 2-(methacryloyloxy)ethyloleate (MAEO)

The synthesis procedure is exactly the same than described in our previous study.¹⁷

- **Synthesis of fatty ester 2-(methacryloyloxy)ethyl 4-(dodecylthio)oleate (MAEO_{SC12})** was prepared in a two-step method as follows:

Oleic acid (1 eq, 0.106 mol, 30.0 g) was charged in bulk in a 200 mL two neck round bottom flask. Then, AIBN (0.2 eq, 21 mmol, 3.5 g) and dodecanethiol (3 eq, 0.319 mol, 64.5 g) was added into the reaction mixture and stirred at 70 °C. After 24 h of reaction, a second addition of AIBN is added to the solution and the reaction is continued 24 h more. After the complete conversion of the intern unsaturation of oleic acid by thiol-ene coupling, the resulting oleic acid-based thiol derivative (OA_{SC12}) was purified through flash chromatography using silica gel as stationary phase and CY-EtOAc (95:5, v/v) as eluent (yield = 83 %). Its structure was confirmed by ¹H NMR (Figure SI3, (A)).

OA_{SC12}: δ (ppm, 400 MHz, CDCl₃): 2.54-2.52 (-S-CH-, 1H, m), 2.47-2.43 (-CH₂-S-, 2H, m), 2.33-2.30 (O=C-CH₂, 2H, m), 1.63-1.59 (H₂C-H₂C-C=O, 4H, m), 1.56-1.54 (-CH₂-CH-CH₂,

4H, m), 1.30-1.26 ($-(\text{CH}_2)_7\text{-CH}_2\text{-CH-CH}_2\text{-(CH}_2)_4$ and $\text{S-CH}_2\text{-(CH}_2)_{10}\text{-CH}_3$, 42H, m), 0.87 ($-\text{CH}_2\text{-CH}_3$ and $\text{S-CH}_2\text{-(CH}_2)_{10}\text{-CH}_3$, 6H, t).

In a second step, OA_{SC12} , DMAP and HEMA were put into a two neck round bottom flask with 200 mL of THF and stirred at room temperature. The reaction mixture was then put in an ice-water bath with a purge of N_2 gas through it. In a separate beaker, DCC (350 mmol, 72.3 g) was dissolved in a minimum of THF and was added dropwise to the solution mixture. The ice-water bath was removed after the complete addition of DCC. After 24 h, the white urea precipitate was filtered off and THF was removed by rotary evaporator. Then, the resulting ester was purified by column chromatography using silica gel as stationary phase and CY-EtOAc (95:5, v/v) as eluent to obtain pure monomer $\text{MAEO}_{\text{SC12}}$ (yield: 70 %). Its chemical structure was confirmed by ^1H NMR (Figure S3, (B))

$\text{MAEO}_{\text{SC12}}$: δ (ppm, 400 MHz, CDCl_3): 6.13 and 5.59 (C=CH_2 , 2H, s), 4.35-4.32 ($\text{OCH}_2\text{-CH}_2\text{O}$, 4H, m), 2.54-2.52 ($-\text{S-CH-}$, 1H, m), 2.47-2.43 ($-\text{CH}_2\text{-S-}$, 2H, m), 2.33-2.30 (O=C-CH_2 , 2H, m), 1.95 ($\text{CH}_3\text{-C}$, 1H, s), 1.63-1.59 ($\text{H}_2\text{C-H}_2\text{C-C=O}$, 4H, m), 1.56-1.54 ($-\text{CH}_2\text{-CH-CH}_2$, 4H, m), 1.30-1.26 ($-(\text{CH}_2)_7\text{-CH}_2\text{-CH-CH}_2\text{-(CH}_2)_4$ and $\text{S-CH}_2\text{-(CH}_2)_{10}\text{-CH}_3$, 42H, m), 0.87 ($-\text{CH}_2\text{-CH}_3$ and $\text{S-CH}_2\text{-(CH}_2)_{10}\text{-CH}_3$, 6H, t).

- **2-oleamidoethyl methacrylate (OAEM)** was prepared as follows:

HEOA (1 eq, 0.08 mol, 25,0 g), methacrylic anhydride (1 eq, 0.08 mol, 11.9 g) and DMAP (0,01 eq, 0.8 mmol, 94 mg) were mixed together in bulk into a 250 mL two neck round bottom flask equipped with a magnetic bar and purged with N_2 gas for 20 min. The reaction mixture was then put into an oil bath set at 60°C overnight. After complete conversion of methacrylate synthesis, 15 mL of deionized water was added into the mixture and stirred for 1 h. The, the solution was poured in dichloromethane and washed with saturated solution of sodium bicarbonate. After the removing of solvent with rotary evaporator, an orange liquid, was obtained (yield = 92 %). Its chemical structure was confirmed by ^1H NMR (Figure 1, (B)).

OAEM: δ (ppm, 400 MHz, CDCl_3): 6.12-6.11 and 5.60-5.59 (C=CH_2 , 2H, s), 5.76-5.73 (NH , 1H, s), 5.35-5.32 (HC=CH , 2H, m), 4.26-4.24 ($\text{H}_2\text{C-OH}$, 2H, m), 3.59-3.55 (HN-CH_2 , 2H, m), 2.20 ($\text{H}_2\text{C-C=O}$, 2H, t), 2.02-1.98 ($\text{H}_2\text{C-CH=CH-CH}_2$, 4H, m), 1.94-1.92 ($\text{CH}_3\text{-C}$, m), 1.65-1.58 ($\text{H}_2\text{C-H}_2\text{C-C=O}$, 2H, m), 1.30-1.26 ($-(\text{CH}_2)_6\text{-CH}_2\text{-CH=CH-CH}_2\text{-(CH}_2)_4$, 20H, m), 0.87 ($\text{CH}_2\text{-CH}_3$, 3H, t).

The same procedure was applied on HEDA and HEMOA to obtain respectively (Z)-2-(docos-13-enamido)ethyl methacrylate (DAEM) (yield= 83 %) and 2-(N-methyloleamido)ethyl methacrylate (MOAEM) (yield= 75 %). The resulting monomers structures were confirmed by ^1H NMR (Figure S1, (B) and Figure S2, (B) respectively).

DAEM: δ (ppm, 400 MHz, CDCl_3): 6.12-6.11 and 5.60-5.59 ($\text{C}=\text{CH}_2$, 2H, s), 5.76-5.73 (NH , 1H, m), 5.35-5.33 ($\text{HC}=\text{CH}$, 2H, m), 4.26-4.24 ($\text{H}_2\text{C}-\text{OH}$, 2H, m), 3.59-3.55 ($\text{HN}-\text{CH}_2$, 2H, m), 2.20 ($\text{H}_2\text{C}-\text{C}=\text{O}$, 2H, t), 2.03-1.98 ($\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2$, 4H, m), 1.94-1.92 (CH_3-C , m), 1.65-1.57 ($\text{H}_2\text{C}-\text{H}_2\text{C}-\text{C}=\text{O}$, 2H, m), 1.30-1.25 ($-(\text{CH}_2)_6-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-(\text{CH}_2)_8-$, 28H, m), 0.87 (CH_2-CH_3 , 3H, t).

MOAEM: δ (ppm, 400 MHz, CDCl_3): 6.10-6.08 and 5.57-5.55 ($\text{C}=\text{CH}_2$, 2H, s), 5.34-5.31 ($\text{HC}=\text{CH}$, 2H, m), 4.29-4.25 ($\text{H}_2\text{C}-\text{OH}$, 2H, m), 3.67-3.64 ($\text{HN}-\text{CH}_2$, 2H, m), 3.05 (CH_3-N , 3H, s), 2.29 ($\text{H}_2\text{C}-\text{C}=\text{O}$, 2H, t), 2.05-1.97 ($\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2$, 4H, m), 1.94-1.92 (CH_3-C , m), 1.66-1.57 ($\text{H}_2\text{C}-\text{H}_2\text{C}-\text{C}=\text{O}$, 2H, m), 1.33-1.24 ($-(\text{CH}_2)_6-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-(\text{CH}_2)_8-$, 28H, m), 0.87 (CH_2-CH_3 , 3H, t).

2.5 Synthesis of (co)polymers through FRP

2.5.1 Homopolymers of *N*-hydroxyalkyl methacrylate fatty amides

Homopolymerization of OAEM was carried out as follows : OAEM (7 mmol, 3 g) and AIBN (0.08 mmol, 12 mg) were dissolved in 10 mL of THF at 60 °C. The reaction mixture was then added into a two necked flask equipped with a magnetic bar and purged with N_2 gas for 20 min. Then, after reaching a maximum of monomer conversion, the mixture was quenched by cooling with liquid nitrogen and purified by precipitation in MeOH at least two times to yield a viscous liquid. The obtained polymer (POAEM) was dried under vacuum for 5 h at 80 °C (yield= 82 %). Its chemical structure was confirmed by ^1H NMR spectroscopy (Figure 1, (C)).

POAEM: δ (ppm, 400 MHz, CDCl_3): 5.35-5.33 ($-\text{HC}=\text{CH}-$, 2H, m), 4.03-3.48 ($\text{HN}-\text{CH}_2-\text{CH}_2-\text{OH}$, 4H, m), 2.22-2.20 ($\text{H}_2\text{C}-\text{C}=\text{O}$, 2H, m), 2.03-2.01 ($\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2$, 4H, m), 1.63-1.59 ($\text{H}_2\text{C}-\text{H}_2\text{C}-\text{C}=\text{O}$, 2H, m), 1.29-1.26 ($-(\text{CH}_2)_6-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-(\text{CH}_2)_4-$, 20H, m), 1.03-0.87 ($\text{C}-\text{CH}_3$, 3H, m), 0.87 ($-\text{CH}_2-\text{CH}_3$, 3H, t).

DAEM and MOAEM monomers were polymerized by following the same conditions and were obtained in 80 % and 60 % yields respectively. The structures of the resulting polymers were confirmed by ^1H NMR (Figure S1, (C) and Figure S2 (C) respectively).

PDAEM: δ (ppm, 400 MHz, CDCl_3): 5.39-5.29 ($-\text{HC}=\text{CH}-$, 2H, m), 4.03-3.48 ($\text{HN}-\text{CH}_2-\text{CH}_2-\text{OH}$, 4H, m), 2.22-2.19 ($\text{H}_2\text{C}-\text{C}=\text{O}$, 2H, m), 2.03-1.98 ($\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2$, 4H, m), 1.62-1.58 ($\text{H}_2\text{C}-\text{H}_2\text{C}-\text{C}=\text{O}$, 2H, m), 1.29-1.26 ($-(\text{CH}_2)_6-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-(\text{CH}_2)_8-$, 28H, m), 1.03-0.87 ($\text{C}-\text{CH}_3$, 3H, m), 0.87 ($-\text{CH}_2-\text{CH}_3$, 3H, t).

PMOAEM: δ (ppm, 400 MHz, CDCl_3): 5.39-5.29 ($-\text{HC}=\text{CH}-$, 2H, m), 4.04-3.62 ($\text{HN}-\text{CH}_2-\text{CH}_2-\text{OH}$, 4H, m), 3.10-2.93 ppm ($\text{N}-\text{CH}_3$, 3H, m), 2.35-2.30 ($\text{H}_2\text{C}-\text{C}=\text{O}$, 2H, m), 2.03-1.98 ($\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2$, 4H, m), 1.62-1.58 ($\text{H}_2\text{C}-\text{H}_2\text{C}-\text{C}=\text{O}$, 2H, m), 1.29-1.26 ($-(\text{CH}_2)_6-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-(\text{CH}_2)_4-$, 20H, m), 1.03-0.87 ($\text{C}-\text{CH}_3$, 3H, m), 0.87 ($-\text{CH}_2-\text{CH}_3$, 3H, t).

2.5.2 Copolymers of *N*-hydroxyalkyl fatty amides methacrylate and fatty ester methacrylate monomers

MAEO was copolymerized with the different methacrylate monomers including OAEM, DAEM and MOAEM with a molar ratio of 50:50 and purified under the same conditions than for the homopolymerization. The copolymerization between MAEO and OAEM was also performed by varying the amount of initiator (1 and 2 % molar) and by using also fractional initiator additions to provide copolymers with different molecular weights and dispersities. All chemical structures were confirmed by ^1H NMR. (Figure 3, (A) PMAEO-co-POAEM and Figure S4, (A) and (B) for PMAEO-co-PDAEM and PMAEO-co-PMOAEM respectively).

PMAEO-co-POAEM (yields ranging from 65 and 80 %): δ (ppm, 400 MHz, CDCl_3): 5.39-5.29 ($-\text{CH}=\text{CH}-$, 4H, m), 4.24-4.16 ($\text{OCH}_2-\text{CH}_2\text{O}$, 4H, m), 4.02-3.50 ($\text{HN}-\text{CH}_2-\text{CH}_2-\text{OH}$, 4H, m), 2.33-2.30 ($\text{O}=\text{C}-\text{CH}_2$ from ester function, 2H, m), 2.22-2.19 ($\text{H}_2\text{C}-\text{C}=\text{O}$ from amide function, 2H, m), 2.05-1.98 ($\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2$, 8H, m), 1.63-1.59 ($\text{H}_2\text{C}-\text{H}_2\text{C}-\text{C}=\text{O}$, 4H, m), 1.31-1.27 ($-(\text{CH}_2)_6-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-(\text{CH}_2)_4-$, 40H, m), 1.05-0.87 ($\text{C}-\text{CH}_3$, 6H, m), 0.87 ($-\text{CH}_2-\text{CH}_3$, 6H, t).

PMAEO-co-PDAEM (yield = 59 %): δ (ppm, 400 MHz, CDCl_3): 5.39-5.29 ($-\text{CH}=\text{CH}-$, 4H, m), 4.25-4.15 ($\text{OCH}_2-\text{CH}_2\text{O}$, 4H, m), 4.03-3.50 ($\text{HN}-\text{CH}_2-\text{CH}_2-\text{OH}$, 4H, m), 2.34-2.30 ($\text{O}=\text{C}-\text{CH}_2$ from ester function, 2H, m), 2.22-2.19 ($\text{H}_2\text{C}-\text{C}=\text{O}$ from amide function, 2H, m), 2.03-1.98 ($\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2$, 8H, m), 1.64-1.60 ($\text{H}_2\text{C}-\text{H}_2\text{C}-\text{C}=\text{O}$, 4H, m), 1.30-1.26 ($-(\text{CH}_2)_6-\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2-(\text{CH}_2)_8-$, and $-(\text{CH}_2)_6-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-(\text{CH}_2)_4-$, 48H, m), 1.03-0.88 ($\text{C}-\text{CH}_3$, 6H, m), 0.88 ($-\text{CH}_2-\text{CH}_3$, 6H, t).

PMAEO-co-PMOAEM (yield = 53 %): δ (ppm, 400 MHz, CDCl_3): 5.39-5.29 ($-\text{CH}=\text{CH}-$, 4H, m), 4.25-4.15 ($\text{OCH}_2-\text{CH}_2\text{O}$, 4H, m), 4.03-3.50 ($\text{HN}-\text{CH}_2-\text{CH}_2-\text{OH}$, 4H, m), 3.04-2.96 ($\text{N}-\text{CH}_3$, 3H, m), 2.34-2.30 ($\text{O}=\text{C}-\text{CH}_2$, 4H, m), , 2.03-1.98 ($\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2$, 8H, m), 1.64-1.60 ($\text{H}_2\text{C}-\text{H}_2\text{C}-\text{C}=\text{O}$, 4H, m), 1.30-1.26 ($-(\text{CH}_2)_6-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-(\text{CH}_2)_4-$, 40H, m), 1.03-0.88 ($\text{C}-\text{CH}_3$, 6H, m), 0.88 ($-\text{CH}_2-\text{CH}_3$, 6H, t).

MAEO_{SC12} was copolymerized with OAEM and DAEM by following the protocol described for the homopolymerization. Both copolymer structures were confirmed by ^1H NMR (Figure 3, (B) for PMAEO_{SC12}-co-POAEM and Figure S5 for PMAEO_{SC12}-co-PDAEM).

PMAEO_{SC12}-co-POAEM (yield = 60 %): δ (ppm, 400 MHz, CDCl₃): 5.39-5.29 (–CH=CH–, 2H, m), 4.24-4.16 (OCH₂–CH₂O, 4H, m), 4.02-3.50 (HN–CH₂–CH₂–OH, 4H, m), 2.54-2.52 (–S–CH–, 1H, m), 2.47-2.43 (–CH₂–S–, 2H, m), 2.33-2.30 (O=C–CH₂ from ester function, 2H, m), 2.22-2.19 (H₂C–C=O from amide function, 2H, m), 2.05-1.98 (H₂C–CH=CH–CH₂, 4H, m), 1.63-1.59 (H₂C–H₂C–C=O, 4H, m), 1.56-1.54 (–CH₂–CH–CH₂, 4H, m), 1.30-1.26 (–(CH₂)₆–CH₂–CH=CH–CH₂–(CH₂)₄–, –(CH₂)₇–CH₂–CH–CH₂– (CH₂)₄ and and S–CH₂–(CH₂)₁₀–CH₃, 62H, m), 1.05-0.87 (C–CH₃, 6H, m), 0.87 (–CH₂–CH₃ and S–CH₂–(CH₂)₁₀–CH₃, 9H, t).

PMAEO_{SC12}-co-PDAEM (yield = 56 %): δ (ppm, 400 MHz, CDCl₃): 5.37-5.29 (–CH=CH–, 2H, m), 4.25-4.15 (OCH₂–CH₂O, 4H, m), 4.00-3.50 (HN–CH₂–CH₂–OH, 4H, m), 2.55-2.52 (–S–CH–, 1H, m), 2.43-2.47 (–CH₂–S–, 2H, m), 2.34-2.30 (O=C–CH₂ from ester function, 2H, m), 2.22-2.19 (H₂C–C=O from amide function, 2H, m), 2.03-1.98 (H₂C–CH=CH–CH₂, 4H, m), 1.64-1.60 (H₂C–H₂C–C=O, 4H, m), 1.56-1.54 (–CH₂–CH–CH₂, 4H, m), 1.30-1.26 (–(CH₂)₆–CH₂–CH=CH–CH₂–(CH₂)₈–, –(CH₂)₇–CH₂–CH–CH₂– (CH₂)₄ and and S–CH₂–(CH₂)₁₀–CH₃, 70H, m), 1.03-0.88 (C–CH₃, 6H, m), 0.88 (–CH₂–CH₃ and S–CH₂–(CH₂)₁₀–CH₃, 9H, t).

3. Results and discussion

3.1 From fatty esters to fatty amide derivatives

Amidation of fatty esters was carried out in bulk at 100 °C by mixing fatty esters with an excess of amino alcohol (1:2) without using catalyst. The process is generally based on consecutive transesterification and rearrangement via O–N intramolecular acyl migration to form amides. Three fatty derivatives were prepared through this process by using different amino alcohols including ethanolamine and *N*-methylethanolamine (Scheme 1, (A)). In all the cases, the amidation of fatty esters was performed in quantitative conversion after 24 h of reaction. The resulting fatty amide derivatives structures were confirmed by using ¹H NMR spectroscopy (in CDCl₃) where all peaks have been assigned. (Figure 1, (A) for HEOA and Figure S1, (A) and Figure S2, (A) for HEDA and HEMOA respectively). The spectra show the disappearance of the methyl protons of the ester at 3.66 ppm and the appearance of peaks at 3.42 (–NH–CH₂–) and 3.72 ppm (–CH₂–OH–) for HEOA and HEDA, and 3.75 and 3.54 ppm for HEMOA corresponding to methylene protons in the *N*-hydroxyalkyl groups. The N–H peak was assigned at 6.01 ppm while the protons of N–CH₃ was attributed to the peak at 3.05 ppm for HEMOA. The complete disappearance of the methyl protons at 3.66 ppm of the fatty esters confirmed their complete conversion into *N*-hydroxyalkyl fatty amides.

Scheme 1: Amidation of fatty esters with amino alcohols (A) and preparation of methacrylate monomers through esterification with the methacrylic anhydride with the aid of DMAP (B)

Figure 1: ^1H NMR spectra of HEOA (A) OAEM (B) and POAEM (C) in CDCl_3

3.2 From fatty amide derivatives to methacrylate monomers

N-hydroxyalkyl fatty amides were then converted into radically polymerizable monomers using an efficient transesterification reaction catalyzed by DMAP in bulk in the presence of the methacrylic anhydride (Scheme 1, (B)). The reaction was successfully performed with

complete conversion with a ratio 1:1 between the *N*-hydroxyalkyl fatty amide and the methacrylic anhydride. The methacrylation of *N*-hydroxyalkyl fatty amides was confirmed by ¹H NMR spectroscopy as illustrated in Figure 1, (B) for the monomer OAEM. The shift toward higher ppm of the α-CH₂ of amine and hydroxyl functions to respectively 3.58 and 4.25 ppm indicated the formation of the ester group and thus, the effectiveness of the synthesis procedure. The vinylic protons of the methacrylate group were assigned to the peaks located at 6.12 and 5.60 ppm while methyl protons next to the ester group appear at 1.95 ppm. No side reaction from the internal double bonds contained in the aliphatic chain of the methacrylate monomers was observed.

3.3 (Co)polymerization of *N*-hydroxyalkyl fatty amide methacrylate monomers

N-hydroxyalkyl fatty amide methacrylates were firstly involved in FRP in order to confirm their ability to polymerize according to a radical route. Then, they were copolymerized with the methacrylate derivative of oleic acid, the 2-(methacryloyloxy)ethyl oleate (MAEO) or the 2-(methacryloyloxy)ethyl 4-(dodecylthio)oleate (MAEO_{SC12}), which both are triglyceride oil-soluble monomers as previously reported. All experimental conditions and data from the resulting (co)polymers are summarized in Table 2.

Table 2: (Co)polymerization conditions and resulting data from the (co)polymers

(Co)polymers	Composition					%initiator (mol)	Conv. (%) ***	SEC****	
	MAEO	OAEM	DAEM	MOAEM	MAEO _{SC12}			$\overline{M}_w$ (kg.mol ⁻¹)	Đ
PMAEO	100	-	-	-	-	1% BPO*	84	160	3.6
POAEM	-	100	-	-	-	1% AIBN	90	22	2.2
PDAEM	-	-	100	-	-		90	20	2.1
PMOAEM	-	-	-	100	-		71	65	2.3
PMAEO-co-POAEM₁₆₀	50	50	-	-	-		70	160	2.8
PMAEO-co-PDAEM	50	-	50	-	-		68	110	2.8
PMAEO-co-PMOAEM	50	-	-	50	-		60	90	2.5
PMAEO_{SC12}-POAEM	-	50	-	-	50		70	170	3.0
PMAEO_{SC12}-PDAEM	-	-	50	-	50		70	190	3.0
PMAEO-co-POAEM₂₄₀	50	50	-	-	-	2** % AIBN	90	240	5.8
PMAEO-co-POAEM₁₁₀	50	50	-	-	-	2 % AIBN	80	110	2.5

*: Previous work¹⁷

**: Successive additions of 1% mol of AIBN at t=0 h and at t=7 h

***: Overall conversion of both monomers

****: PMMA calibration in THF at 35 °C

3.3.1 Homopolymerization

OAEM, DAEM and MOAEM were homopolymerized by using AIBN as radical source at 60 °C in THF as shown in Scheme 2, (A).

Scheme 2: Homopolymerization of *N*-hydroxyalkyl fatty methacrylate amide monomers in THF at 60 °C with AIBN (A), Copolymerizations of MAEO with *N*-hydroxyalkyl fatty methacrylate amide monomers in THF at 60 °C with AIBN (B), Copolymerizations of MAEO_{SC12} with either OAEM or DAEM in THF at 60 °C with AIBN (C)

Polymerization of OAEM and DAEM were achieved in 90 % conversion after 7 h of reaction which confirmed their good reactivity through radical process (Figure 2). Hence, the difference of chain length did not change the reactivity of polymerization. On the other hand, the substitution of the N atom by a methyl group of MOAEM reduced the reactivity by inducing more steric hindrance and thus, resulted in lower conversion (70 %) compared to OAEM and DAEM in the same polymerization conditions.

Figure 2: *N*-hydroxyalkyl fatty methacrylate amide monomer conversion (%) vs reaction time (h)

The ^1H NMR spectrum of POAEM is shown in Figure 1, (C) while that of PDAEM and PMOAEM are shown in Figure S1, (C) and Figure S2, (C) respectively. In the ^1H NMR spectra of the resulting polymers, the disappearance of peaks assigned to the vinyl protons of the methacrylate group indicated the complete removal of unreacted monomer after precipitation in cold methanol. The methylene protons of the *N*-hydroxyalkyl groups bearing in the polymer side chain appeared at 4.04 and 3.48 ppm while methyl protons of the polymer backbone are assigned to the peak between 1.02 and 0.88 ppm. According to the ^1H NMR spectra, the internal unsaturation contained in the monomer aliphatic chain remains stable during the polymerization process as no side reaction was observed. Table 2 summarizes all data related to the resulting *N*-hydroxyalkyl fatty methacrylate amides-based homopolymers including their conversions, yields and molecular weights.

3.3.2 Copolymerization with fatty ester methacrylate monomers

The *N*-hydroxyalkyl fatty amide methacrylates were firstly copolymerized in THF at 50:50 molar ratio with the fatty methacrylate ester, MAEO according to the homopolymerization procedure described in the experimental section (THF, 1 % molar of AIBN, 60 °C) (Scheme 2, (B)). Similarly, OAEM and DAEM were also copolymerized at 50:50 molar ratio with the highly hydrophobic oleic acid-comonomer, MAEO_{SC12} (Scheme 2, (C)). The resulting copolymers were obtained between 60 and 90 % of conversion after 24 h with a lower rate than their respective homopolymers (Table 2). Figure 3 showed ^1H NMR spectra of PMAEO-co-POAEM (A) and PMAEO_{SC12}-co-POAEM (B) where all peaks have been assigned. The

other copolymers spectra are reported in Figure S4, (A) for the copolymers PMAEO-co-PDAEM, Figure S4, (B) for the copolymer PMAEO-co-PMOAEM and in Figure S5 for the copolymer PMAEO_{SC12}-co-PDAEM.

The reactivity of the comonomers through radical polymerization was monitored by ¹H NMR spectroscopy. In a first step, aliquots of each copolymer solution were taken at periodic time intervals and analyzed by ¹H NMR. Only the total monomer conversions were calculated by this method as methacrylate proton peaks of all monomers have similar shifts (6.13-6.09 and 5.60-5.56 ppm). Thus, the previous aliquots were also reprecipitated in cold methanol and analyzed through ¹H NMR in order to evaluate the copolymer composition at periodic times. For this purpose, the integral value of the α -CH₂ peak at 2.32 ppm belonging to the ester of the poly(2-(methacryloyloxy)ethyl oleate) (PMAEO) or the poly(2-(methacryloyloxy)ethyl 4-(dodecylthio)oleate) (PMAEO_{SC12}) moieties was compared to that of the α -CH₂ peak of the amide function at 2.20 ppm belonging to poly(*N*-hydroxyalkyl fatty amide methacrylates). For copolymerizations with MOAEM, the copolymer composition was monitored by comparing the integral value of CH₃-N at 3.08-2.99 ppm of PMOAEM and the ethylene protons (CH=CH₂) at 5.34 ppm contained in both copolymer moieties. Hence, by knowing both the total monomer conversions and copolymer compositions at times *t*, the conversion of each monomer has been deducted. The results revealed that the FA-based monomers showed similar reactivity by radical polymerization which have induced more likely statistic copolymers. Figure S6 shows the similar kinetic reactivity between MAEO and either OAEM, DAEM or MOAEM. Moreover, despite an additional grafted alkyl chains, MAEO_{SC12} have demonstrated similar reactivity than OAEM and DAEM (Figure S7). Finally, all the final copolymer compositions were in accordance with the theoretical monomer feed (50:50 molar ratio).

The resulting copolymer molecular weights were measured by SEC and summarized in Table 2. Focusing on PMAEO-co-POAEM copolymers, higher molecular weights were reached by using lower initiator amounts. For instance, with 1 and 2 % molar of AIBN, the weight average molecular weight attained 160 and 110 kg.mol⁻¹, respectively. Additionally, the synthesis of this copolymer was also performed by adding 1 % molar of AIBN at the beginning of the reaction and after 7 h of reaction. The resulting copolymer was characterized by an average molecular weight of 240 kg.mol⁻¹ as well as a broad dispersity of 5.8. Thus, fractional initiator addition allowed to increase the heterogeneity in the chain polymer length during the polymerization.

Figure 3: ^1H NMR spectrum of PMAEO-co-POAEM (A) and of PMAEO_{sCl2}-co-POAEM (B) in CDCl_3

3.4 Thermal properties of the homo- and copolymers

As the purpose of the FA-based (co)polymers is to be used as viscosity index improvers in lubricating oils, they will be frequently subjected to high local temperatures due to friction at gears, roll -contacts, bearings etc. Thus, in order to confirm their ability of being used over a wide range of temperatures, thermal properties of FA-based (co)polymers have been evaluated. The thermal degradation of homopolymers derived from *N*-hydroxyalkyl fatty

amide methacrylates was monitored by thermogravimetric analysis (TGA) and revealed two degradation stages (Figure 4). The first degradation temperature of POAEM, PDAEM and PMOAEM occurred around 280 °C which may be related to the ester function degradation contained in the homopolymer structures. The second degradation temperature was observed around 375 °C for POAEM and PDAEM and 390 °C for PMOAEM. This latter may corresponded to the amide function degradation which is known to have a better thermal stability than ester function.¹⁹ Moreover, the higher thermal stability of PMOAEM than POAEM or PDAEM can be attributed by the substitution of nitrogen atom of amide group (N-CH₃) related to N-H bond. In the meantime, all the FA-based copolymers showed good thermal stability up to 300 °C which is slightly higher than their analogous homopolymers (Figure S8). Hence, according to the TGA results, the methacrylate (co)polymers have shown enough thermal stability to be used as VII in lube oils operating at a temperature range below 300 °C.

Figure 4: TGA analysis of homopolymers derived from *N*-hydroxyalkyl fatty amide methacrylate monomers

The thermal behavior of the (co)polymers and the evaluation of the glass transition temperature (T_g) have been also performed by DSC analyses. The homopolymers demonstrated different T_g depending on the aliphatic chain length contained in the backbone (Figure 5). For instance, a T_g was observed around -80 °C for POAEM (C-18) and PMOAEM (C-18) while PDAEM (C-22) showed a T_g at -60 °C. In a previous study, the T_g of PMAEO (C-18) was noticed at -80 °C.¹⁸

Figure 5: DSC analysis of homopolymers derived from *N*-hydroxyalkyl fatty amide methacrylates and PMAEO

Despite their different molecular weights, copolymers PMAEO-co-POAEM have showed a similar low T_g at -80 °C. As PMAEO-co-PMOAEM has a similar chain length, its T_g was also around -80 °C while PMAEO-co-PDAEM showed a T_g around -70 °C (Figure 6). Crystalline behaviors at around -45 °C were observed for PMAEO_{SC12}-co-POAEM and PMAEO_{SC12}-co-PDAEM copolymers due to their additional C-12 saturated pendant side chain. As the pour point of the lubricating oil is around -30 °C and thus, much above the copolymer crystallization temperatures, their use as additives should not affect the oil flow behavior at cold temperature.

Figure 6: DSC analyses of the FA-based copolymers

3.5 Evaluation of the FA-based copolymers as VII

3.5.1 Solubility test of the resulting (co)polymers in an organic triglyceride oil (OTO)

The resulting homopolymers derived from *N*-hydroxyalkyl fatty amide methacrylates were blended at 5 wt. % in an organic triglyceride oil (OTO) and mixed at 100 °C for 1 h. While PMOAEM was soluble in OTO, POAEM and PDAEM were both insoluble in the lube oil. This difference of oil affinity was related to the ability of POAEM and PDAEM to form hydrogen bonds through their -NH functions which induced high polarity and therefore made the polymers insoluble in an apolar oil such as OTO. On the other hand, substitution of the -NH group with a -NCH₃ group in PMOAEM backbone was sufficient to afford an oil-soluble polymer. Thus, even if amide is a high polar function and may decrease the polymer affinity with OTO, the long alkyl chains contained in PMOAEM are enough compatible with triglyceride compounds to obtain a minimum of solubility in OTO.

Then, the synthesized *N*-hydroxyalkyl fatty amide methacrylates have been used as low oil-soluble or oil-insoluble comonomers with either MAEO or MAEO_{SC12} in order to decrease the solubility of their respective homopolymers PMAEO and PMAEO_{SC12} in OTO. It is expected that the resulting copolymers may present a reduced solubility in OTO at low temperature and therefore it may promote the coil copolymer expansion with temperature. However, the FA-based copolymers must be a minimum soluble in oil before being evaluated as VII. Several ratios of oil-soluble and oil-insoluble monomers were evaluated for the study. When the methacrylate amide monomer content was higher than 50 % molar in copolymers, the copolymers were only partially soluble or completely insoluble in the triglyceride oil even by mixing the solution at 100 °C for several hours. Therefore, as the purpose of the project was to provide copolymers with a minimum solubility in lubricating to promote its coil contraction at low temperature, the ratio 50:50 feed molar ratio (low oil-soluble moiety and oil: oil-soluble moiety) was chosen. All FA-based copolymers showed enough solubility in OTO, so they could have been evaluated as VII in the following part.

3.5.2 Dynamic viscosity measurements of oil-polymers blends

Rheological measurements were performed to evaluate the FA-based copolymer coil behavior in OTO with the temperature and confirm their effectiveness as VII. For this

purpose, the relative viscosity (RV) between OTO and FA-based copolymer blends were calculated and plotted against temperature. The calculated RV represents the influence of the copolymer on oil's viscosity and should increase with the temperature in case of coil copolymer expansion.²⁰

3.5.2.1 Influence of additive concentration

PMAEO-co-POAEM₂₄₀ copolymer was evaluated as VII in OTO with various concentrations (Figure 7). At 5 wt. % of PMAEO-co-POAEM₂₄₀ in OTO, the RV improved by 0.55 between 0 and 100 °C while it only improved by 0.27 and 0.21 for 3 and 1 wt. % of copolymeric additive, respectively. Therefore, the greater the additive concentration, the higher the improvement of RV with temperature and the higher the copolymer thickening power. However, the use of high additive concentration in OTO also induced a non-negligible effect on the oil viscosity at low temperature. For instance, the RV was 1.92 at 0 °C with the addition of 5 wt. % of PMAEO-co-POAEM₂₄₀ in OTO. Therefore, according to the desired application, the additive concentration must be adjusted to reach the appropriate viscosity at a specific temperature. In the following tests, 5 wt. % of additives in OTO were used in order to evaluate the efficiency of the other copolymers as VII.

Figure 7: RV vs temperature for various PMAEO-co-POAEM₂₄₀ copolymer concentrations in OTO

3.5.2.2 Influence of the copolymer molecular weight and dispersity

As illustrated in Figure 8, PMAEO-co-POAEM₁₆₀ demonstrated a higher increase of RV with the temperature ($\Delta RV_{100-0\text{ }^{\circ}\text{C}} = 0.21$) compared to PMAEO-co-POAEM₁₁₀ ($\Delta RV_{100-0\text{ }^{\circ}\text{C}} = 0.13$). Thus, the higher the copolymer molecular weight, the higher the improvement of its

thickening power in oil with temperature. Indeed, as mentioned in our previous work, the ability of a polymeric additive to have VII properties depends greatly of its molecular weight.¹⁷ Low polymer molecular weight generally induce a limited influence on oil viscosity either at low or high temperature which is mostly due to their reduced coil size dimension. Hence, it limits considerably the increase of the polymer thickening power with temperature and therefore its efficiency as VII. Moreover, the dispersity seems to play an important role in the properties of the copolymer as VII. As shown in Figure 8, PMAEO-co-POAEM₂₄₀, which had a high dispersity ($\bar{D}$ =3.6), have demonstrated a much significant ability to reduce the viscosity-temperature dependency than both copolymers PMAEO-co-POAEM₁₆₀ ($\bar{D}$ =2.3) and PMAEO-co-POAEM₁₁₀ ($\bar{D}$ =2.3). However, when the molecular weight and dispersity of the additive are too high, the polymer thickening power is not negligible at low temperature in the lube oil and may disturb the oil flow. The resulting higher lube oil viscosity may therefore require more energy to put the oil in motion. However, as previously shown, the thickening power of a polymeric additive can be easily adjusted by varying its concentration in oil according to the targeted application.

Figure 8: RV versus temperature for different molecular weights of PMAEO-co-POAEM (5 wt. % in OTO)

3.5.2.3 Influence of the copolymer composition

The rheological FA-based copolymer properties were compared to those previously reported for PMAEO in OTO at 5 wt. % and they were also compared to a commercial VII-based PMA additive in this study.¹⁷ In a previous work, it was shown that PMAEO has a similar thickening power on oil viscosity at each temperature as the calculated RV between

OTO and OTO-PMAEO blend remained constant with the increasing temperature. This observation was related to a good polymer swelling in the triglyceride oil at low temperature preventing it to further expand in oil with temperature. In this study, similar observation was noticed by using a petroleum poly(alkyl methacrylate) additive (PMA) in OTO. The RV stayed around a value of 1.50 between 0 and 100 °C meaning that even a commercial polymeric additive does not seem to be a suitable VII for OTO (Figure 9). On the opposite, the addition of PMAEO-co-POAEM₁₆₀ copolymer in OTO induced an improvement of RV with the temperature. For instance, the RV between OTO and OTO-PMAEO-co-POAEM₁₆₀ blend increased from 1.50 at 0 °C to 1.70 at 100 °C meaning that the copolymer had a higher effect on oil viscosity at high temperature than at low temperature. These results underlined the better copolymer PMAEO-co-POAEM₁₆₀ ability to reduce the viscosity-temperature dependency of OTO compared to the homopolymer PMAEO. Indeed, PMAEO-co-POAEM₁₆₀ had a considerably lower contribution on OTO viscosity at 0 °C ($RV_{0\text{ °C}} = 1.50$) than PMAEO ($RV_{0\text{ °C}} = 1.70$) but had a similar thickening power in OTO at 100 °C than PMAEO ($RV_{100\text{ °C}} = 1.70$). This specific behavior may be explained by the coil copolymer expansion in oil with temperature which made the copolymer a suitable VII. On the other hand, the addition of PMAEO-co-PMOAEM in OTO didn't induce any improvement of RV with temperature since the RV remains around 1.55 between 0 and 100 °C. The difference of RV tendency with temperature between the addition of PMAEO-co-POAEM₁₆₀ and PMAEO-co-PMOAEM copolymers in OTO have been related to the polarity of their respective *N*-hydroxyalkyl fatty amide methacrylate moieties. As mentioned in the solubility analyzes part, POAEM was insoluble in OTO due to the formation of polar hydrogen bonds via the –NH group. On the contrary, as PMOAEM bearing –NCH₃ group was previously found soluble in OTO, it may not be an enough low-oil soluble moiety to promote the coil expansion of PMAEO-PMOAEM in OTO with temperature.

Figure 9: RV versus temperature for PMAEO, PMA, PMAEO-co-POAEM₁₆₀ and PMAEO-co-PMOAEM (5 wt. % in OTO)

3.5.2.4 Influence of the pendant aliphatic chain length

The influence of the aliphatic chain length on VII additives for OTO was studied on FA-based copolymers having similar molecular weight ($110 \text{ kg}\cdot\text{mol}^{-1}$) as shown in Figure 10. The RV was increased by 0.25 between 0 and 100 °C with PMAEO-co-PDAEM (C-22) while it was only increased by 0.13 with PMAEO-co-POAEM₁₁₀ (C-18). This result confirmed that the increasing of the aliphatic chain length of a comonomer contained in the copolymer can promote the thickening copolymer power as well as its coil expansion with temperature. Indeed, the longer the copolymer aliphatic chain, the more copolymer-OTO interactions there are. This resulted in an improvement of the copolymer contribution on oil viscosity and more especially at high temperature when the copolymer is more likely in an expanded conformation.

Figure 10: RV versus temperature for copolymers containing different aliphatic chain lengths (5 wt. % in OTO)

3.5.2.5 Influence of an additional pendant chain length

Copolymers containing MAEO_{SC12} instead of MAEO as oil-soluble comonomer and either OAEM or DAEM as oil-insoluble moieties had shown a better ability to reduce the viscosity-temperature dependency of OTO between 0 and 100 °C using 5 wt. % of additive (Figure 11). For instance, the RV improved twice more for PMAEO_{SC12}-co-POAEM between 0 and 100°C ($\Delta RV_{100-0^{\circ}\text{C}} = 0.41$) than for PMAEO-co-POAEM₁₆₀ ($\Delta RV_{100-0^{\circ}\text{C}} = 0.20$) at similar copolymer molecular weight. Moreover, oil-polymers blend containing PMAEO_{SC12}-co-PDAEM have shown a higher improvement of RV ($\Delta RV_{100-0^{\circ}\text{C}} = 0.56$) with temperature than those containing PMAEO_{SC12}-co-POAEM ($\Delta RV_{100-0^{\circ}\text{C}} = 0.41$). This results confirmed the first observation about the positive aliphatic chain length influence on the coil copolymer expansion. Thus, the use of MAEO_{SC12} as oil-soluble comonomer allowed to prepare copolymers with a higher thickening power improvement in OTO with temperature. In the meantime, the use of a comonomer with an additional grafted aliphatic pendant chain induced a non-negligible thickening power of copolymers in OTO at low temperature compared those containing MAEO. For example, at 0 °C, the RV was 1.67 with PMAEO_{SC12}-co-POAEM while the RV was 1.50 with PMAEO-co-POAEM₁₆₀. As previously said, the thickening power of the polymeric additive can be easily modulated by varying its concentration in the lube oil.

Figure 11: RV versus temperature for copolymers containing a moiety with an additional grafted C-12 chain length (5 wt. % in OTO)

3.5.3 Viscosity Index calculations

Viscosity Index of OTO-copolymer blends were measured according to the ASTM D2270-10. This value is mainly used by industrial to evaluate the viscosity-temperature dependency of a lubricant. The higher the VI of a lubricant, the lower change in viscosity with temperature.

The results of the VI calculations confirmed the relationship between the coil polymer expansion in oil with temperature and the polymer efficiency as viscosity index improver. As it shown in Table 3, the higher the coil expansion with the temperature, the better the OTO viscosity index improvement. For instance, the addition of PMAEO-co-POAEM₂₄₀ in OTO induced the higher increase of relative viscosity with the temperature ($\Delta RV_{100-0\text{ }^{\circ}\text{C}} = 0.55$) and therefore demonstrated the better effect on OTO viscosity index which was increased from 137 to 285. However, the calculation of viscosity index also revealed the gap of this industrial scale. Despite it was demonstrated that the copolymer PMAEO-co-PMOAEM did not show coil expansion with the temperature, the calculation of the oil-copolymer blend viscosity index revealed that the copolymer was still able to improve OTO's VI from 156 to 200. Thus, the calculation of VI is not enough as argument to confirm the nature of the additive as viscosity index improver since thickeners can also increase the VI.²¹

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

OTO + 5 wt. % of copolymer	KV 40 °C (mm ² .s ⁻¹)	KV 100 °C (mm ² .s ⁻¹)	Viscosity Index	$\Delta RV_{100-0\text{ }^{\circ}\text{C}}$
--	26.5	5.58	156	-
PMAEO-co-PDAEM	38.40	9.50	245	0.25
PMAEO-co-PMOAEM	44.47	9.29	200	0
PMAEO _{SC12} -co-POAEM	44.10	11.62	270	0.41
PMAE _{SC12} -co-PDAEM	46.75	12.96	285	0.55
PMAEO-POAEM ₁₁₀	38.12	8.74	220	0.13
PMAEO-POAEM ₁₆₀	39.81	9.53	235	0.20
PMAEO-co-POAEM ₂₄₀	51.05	13.84	285	0.55

3.5.4 Rheological behavior of oil-copolymer blends at low temperature

The triglyceride oil used in this study has the advantage to display a low pour point at -30 °C which means that the lube oil can flow properly until this specific temperature without requiring yield stress. This rheological behavior is characteristic of a Newtonian fluid. In order to confirm that the addition of 5 wt. % FA-based copolymers in OTO did not disturb the oil cold flow properties, the rheological behavior of OTO and oil-copolymer blends which have demonstrated the best VII properties have been studied at -30 °C. According to Figure 12, the addition of PMAEO-co-POAEM₂₄₀, PMAEO-co-PDAEM and PMAEO_{SC12}-co-PDAEM induced a non-negligible effect on OTO viscosity at -30 °C. For instance, at 200 s⁻¹, the dynamic viscosity of oil-PMAEO-co-POAEM₂₄₀ blend is 1065 mPa.s⁻¹ while 630 mPa.s⁻¹ for pure OTO. This improvement of oil's viscosity may induce some issues on the oil flow at low temperature.

Figure 12: Dynamic viscosity versus shear rate of OTO and OTO-copolymer blends at -30 °C

However, despite this improvement of oil viscosity with the addition of FA-based copolymers, the Newtonian behavior of OTO was not affected. Indeed, as illustrated in Figure 13, the dynamic viscosity remained approximatively constant with the shear rate for all oil-copolymer blends which is characteristic of Newtonian Fluid. Moreover, the plot of shear stress versus shear rate showed a straight line that passed through the origin with a constant slope for all formulations (Figure 13). This behavior is also characteristic of Newtonian fluids as they do not require any yield stress to flow (intercept of y-axis closed to zero Pa). Therefore, it can be deduced that blended OTO with FA-based copolymer additives did not negatively affect the oil flow behavior at -30 °C.

Figure 13: Shear stress vs shear rate of OTO- copolymer blends at -30 °C

4. Conclusion

This work reported the preparation of suitable VII derived from FA for a biolubricant organic triglyceride oil (OTO). Those additives were synthesized by free radical copolymerization of poorly oil-miscible fatty amide methacrylate comonomers and oil-soluble fatty ester methacrylate comonomers (MAEO and MAEO_{SC12}) with a feed monomers molar ratio of 50:50. The resulting FA-based copolymers were blended at 5 wt. % in OTO and then evaluated as VII. The results indicated that FA-based the copolymer containing $-NH_3$ have shown a similar thickening power with increasing temperature while those containing $-NH$ functions were able to have more influence on oil viscosity at high than at low temperatures realign their high VII properties. Their performance as VII was mostly related to the formation of H-bonding through $-NH$ functions inducing high polarity at low temperature which decreased the oil copolymer solubility in the hydrophobic oil. In the meantime, increasing temperature have improved the copolymer-OTO interactions through their respective aliphatic chains inducing more effect on oil viscosity at higher temperature. The improvement of the copolymer thickening power in oil with increasing temperature was optimized by increasing the copolymer molecular weight, dispersity, the concentration, the aliphatic pendant chain length of the polymer moieties or by using MAEO_{SC12} instead of MAEO as oil-soluble monomer. Finally, the rheological behavior of OTO with the best VII FA-based copolymers indicated that the additives did not disturb the initial Newtonian behavior of the pure oil at -30 °C. Hence, the high cold flow properties of formulations coupled with the good thermal stability of FA-based copolymers (up to approximately 280 °C) demonstrated that the synthesized FA-based copolymers can be used over a wide range of operating temperatures. Therefore, considering the current environmental context, the use of those novel biobased viscosity index improvers in OTO represent a promising “green” lubricant formulation displaying both excellent cold flow properties and high viscosity index.

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