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Comparison of the thermal behaviour of some fatty esters and related ethers by TGA–DTA analysis

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Abstract

The thermal behaviour of cuts of 2-ethyl hexyl oleate, octyl oleate, 2-ethyl hexyl oleyl oxide and octyl oleyl oxide were determined by TGA–DTA analysis, after characterisation of the products to determine purity. Most of the acyl chains of those fatty esters and fatty ethers were oleic chain and the products were fluid.

The thermal stability of each liquid was very good as all decomposed at temperatures between 250°C and 300°C. All evaporated before reaching their decomposition temperature. They are new molecules which could be used as lubricants.

Keywords: Alkyl oleates; Alkyl oleyl oxides; 2-Ethyl hexanol; Fatty esters; Fatty ethers; Octanol; Physical properties; TGA–DTA analysis; Thermal behaviour

1. Introduction

A new range of ecologically correct molecules, with new and varied properties, can be obtained from oils and fats obtained from the biomass. The production of monoalcoholic fatty esters by transesterification of oils [1] and of monoalcoholic fatty ethers by etherification of fatty alcohols [2] notably gives rise to functional molecules which respond to the requirements of numerous fields of application which include the ‘‘sensitive’’ sectors of energy, cosmetology, additives for plant protection and lubricants [3–9]. We propose two new range of linear and ramified esters and ethers whose general structures are presented in Fig. 1. The carboxyl and ether groups confer these compounds specific physico-chemical properties. Their linear or ramified alkyl chain also influence the thermal behaviour of these products.

The carboxyl group permits the formation of intermolecular London electrostatic bonds. This reduces the vapour tension of the product, increases its viscosity and confers a high viscosity index. Esters dissolve a large number of polar additives (anticorrosive additives, high pressure additives, anti-wear additives) on account of the polarity of the carboxyl groups. Due to the presence of carbon chains, most of them are miscible with other solvents and/or mineral oils [3]. Unsaturated esters are liable to attack by oxygen with the initial formation of peroxides on the double bond. The use of molecules with saturated fatty chains would then limit such oxidation but these latter have a low flow point with a tendency to crystallise at

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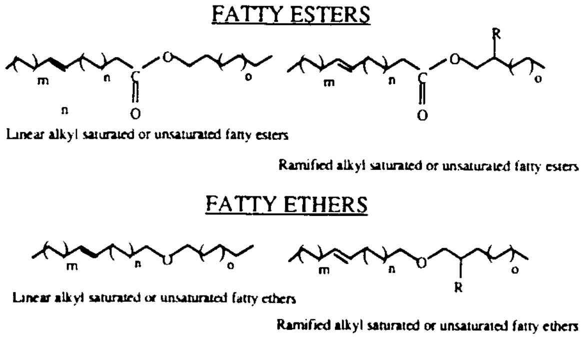

Fig. 1. General structures of the fatty esters and fatty ethers tested.

ambient temperature. Using monounsaturated fatty chains, that gives fluid products, is the best arrangement as their oxidation rate, relative to saturated chain, is about 10, compared to 100 for diunsaturated chains and to 200 for triunsaturated fatty chains [10]. The hydrolytic stability of esters depends essentially on the manufacturing process and geometry of the molecule: a high acid number and the presence of traces of catalyst and/or water diminish the stability of an ester to hydrolysis. Esters exhibit high biodegradability. Microbial attack generally occurs in two simultaneous stages with initial hydrolysis of the ester being followed by oxidation of the long carbon chains [3].

The resistance of ethers to chemical cleavage is good because of the high stability of the ether bond. The polar ether group confers compatibility with numerous additives and, when associated with good fluidity, confers solvent properties. Due to their carbon chains, the fatty ethers have very low flow points. These chains also enable them to be miscible with most organic solvents and mineral oils. They are thermally stable [9].

The thermal behaviour of fatty esters and fatty ethers is of prime importance in the field of lubrication. The products are generally used in the presence of air, and are therefore subjected to oxidative and thermal decomposition. This may be evaluated by thermogravimetric analysis (TGA) which provides a quantitative measure of all the changes which occur in the weight of a sample as a function of temperature [11–14]. Thermogravimetric analysis may be coupled with differential thermal analysis (DTA) to distinguish the physical phenomena of changes in state from the chemical phenomena responsible for the changes in sample weight.

The objective of this article is to study four cuts of fatty esters and fatty ethers with linear or branched eight-carbon alkyl radicals. We chose four products rich in oleic chains that are therefore fluid. A comparative analysis of the thermal behaviour of 2-ethyl hexyl and octyl oleates and of 2-ethyl hexyl and octyl oleyl oxides is therefore carried out.

2. Materials and methods

2.1. Materials

The raw oleic oil was obtained by expression of oleic sunflower seeds in a twin screw extruder used as a press [15]. The triglycerides contained 89% of oleic acid, 5% of linoleic acid, 3% of palmitic acid and 2.5% of stearic acid (NF T60-23 and NF T60-233). 2-Ethyl hexanol (99%) was purchased from prolabo (Gradignan, France) and octanol (99%) from Sigma (St Quentin Fallavier, France). Phosphoric acid (85%) was supplied by Prolabo (Gradignan, France). The resin IRA93SP type was purchased from Rohm and Hass (Paris, France).

1-Bromoalkanes (2-bromo-2-ethylhexane (95%), 1-bromooctane (99%)), oleyl alcohol (85%), potassium hydroxide (15% humidity) and tetrabutylammonium bromure (TBAB, 99%) were obtained from Aldrich (St Quentin Fallavier, France).

2.2. Transesterification procedure

200 g of oil (0.23 mol triglycerides) are introduced in a 2 l flask equipped with a mechanical stirrer (500 rpm) and a condenser. 1.2 mol alcohol (2-ethyl hexanol or octanol) and 0.20 mol of phosphoric acid are added. The mixture is heated unter nitrogen for 7 h at 130°C. At the end of the reaction time, the product is cooled in a water bath and there is separation of two phases. The upper lipidic phase containing the esters and alcohol is deacidified by elution on a resin column [1]. The esters are then distilled under partial vacuum.

2.3. Etherification procedure

This is a two-step procedure. 44.8 g of potassium hydroxide (0.80 mol) and 44.8 g of water are placed in a 500 ml flask equipped with a mechanical stirrer (500 rpm) and a condenser. The catalyst is immedially dissolved and 0.04 mol of oleyl alcohol, 0.004 mol of TBAB and 0.16 mol of the bromoalkane are added. The flask is heated at 90°C for 2 h in an oil bath. The aqueous phase and the basic catalyst are then changed and the mixture is then heated again for 2 h. After cooling, potassium bromure deposits in the flask in the aqueous phase. The upper organic phase is separated, washed twice with 50 ml water and dried on sodium sulphate. The ethers are distilled under partial vacuum.

2.4. Characterisation

The products were characterised by infrared spectroscopy on a Perkin-Elmer Spectrometer (model 1600) and by ^{1}H-NMR and ^{13}C-NMR spectroscopy on a Bruker AC200 Spectrometer at, respectively, 200 and 50 MHz in $CDCl_3$.

2.5. TGA–DTA analysis

The TGA–DTA determinations were carried out on a TP-DTG 92 apparatus (Setaram, Lyon, France) and involved two different tests. A stream of nitrogen or helium was used as inert atmosphere and a stream of air as the reactive atmosphere. The analytical crucibles were made of alumina. The samples weighed between 30 and 70 mg. The temperature was programmed to remain at a constant temperature of 20°C for 120 s and then to increase to 600°C at a rate of 10°C/min. Data were collected every 0.8 s.

3. Results and discussion

The fatty substrates used to produce the esters and ethers were compounds derived from vegetable sources. The triglycerides of the oil were rich in oleic acid (89%) and also contained palmitic acid (3%), stearic acid (2.5%) and linoleic acid (5%). The oleyl alcohol was of technical grade (purity: 85%). The esters were cuts rich in octyl or 2-ethyl hexyl oleate and the ethers produced were cuts rich, respectively, in octyl or 2-ethyl hexyl oleyl oxide. These cuts were mixtures but the oleic compounds were predominant. Their properties could therefore be compared.

3.1. Characterisation of fatty esters and fatty ethers

3.1.1. Characterisation of the octyl oleate cut

The infrared spectra of esters (Table 1) exhibit absorption bands, characteristic of the carboxyl group at 1738.8 cm^{-1} (C=O stretching) and 1172.2 cm^{-1} (C–O stretching). The infrared band at a wavelength of 811.2 cm^{-1} represents the oscillation of the linear alkyl $(CH_2)_n$ chain ($n > 4$).

On the ^{1}H-NMR analysis spectra, the chemical shift of the ethylenic protons is of 5.33 ppm, resulting from the strongly inducive shielding effect of the methylen groups of the acyl chain. The double bond of the acyl chain is of *cis* form ($J = 14$ Hz). Chemical shifts of 129.79 and 130.02 ppm are obtained from the carbon ^{13}C-NMR analysis.

Protons H_d and H_e of the alkyl resonate at 4.05 ppm and the carbons C_d and C_e resonate at 64.45 and 31.83 ppm.

3.1.2. Characterisation of the 2-ethyl hexyl oleate cut

The carboxyl group is not affected by the branching of the alkyl chain as the wavelenghts of its absorptions bands are at 1738.2 and 1174.2 cm^{-1} and are similar to those of the octyl oleate.

Similar chemical shifts for protons H_a, H_b and carbons C_a, C_b, C_c are also observed on the

Table 1
Characterisation of the octyl and 2-ethyl hexyl oleate cuts ((x): numbering of the carbon atom)

Cuts	IR (cm^{-1})	^{1}H-NMR (ppm)	^{13}C-NMR (ppm)
$CH_3–(CH_2)_7C_aH_a=C_bH_b–(CH_2)_7–C_c(O)–O–C_dH_{2d}–C_eH_{2e}–(CH_2)_5–CH_3$	1738.8, 1172.2, 811.2	a,b: 5.33; d: 4.05	a,b: 129.90; c: 174.04; d: 64.45; e: 31.83
$CH_3–(CH_2)_7C_aH_a=C_bH_b–(CH_2)_7–Cc(O)–O–C_dH_{2d}–C_eH_e–(CH_2)_3–CH_3CH_2–CH_3$	1738.2, 1174.2, –	a,b: 5.33; d: 3.97	a,b: 129.90; c: 174.14; d: 66.66; e: 38.79

^{1}H-NMR and ^{13}C-NMR spectra (δ ($H_{a,b}$) = 5.33 ppm, δ ($C_{a,b}$) = 129.79–130.02 ppm, δ (C_c) = 174.14 ppm). The *cis* form of the double bond is noticed (J = 14 Hz).

Branching increases the chemical shift of the carbons H_d and H_e of the alkyl chain (shielding effect of the branching) which resonates at 66.66 and 38.79 ppm.

3.1.3. Characterisation of the octyl oleyl oxides cut

The ether group produces an infrared absorption band at 1123.1 cm^{-1} for the linear ether. On the ^{1}H-NMR spectra, the chemical shift of the ethylenic protons is of 5.33 ppm and exhibit a coupling constant of 14 Hz which is characteristic of the *cis* form of the double bond. Protons H_c and H_d resonate at 3.33 and 3.40 ppm and carbons C_c and C_d resonate at 70.98 ppm (Table 2).

3.1.4. Characterisation of the 2-ethyl hexyl oleyl oxides cut

The absorption band associated with the streching of the ether group is noted at 1112.9 cm^{-1} because of the branching of the alkyl chain. This is also observed on the chemical shift associated with protons H_d in ^{1}H-NMR which resonates at 3.25–3.27 ppm. The chemical shifts associated with carbons C_c and C_d are of 73.8 and 71.1 ppm. Branching induces a differentiation of these carbons for the 2-ethyl hexyl oleyl oxide, which is not the case for the octyl oleyl oxides.

3.2. Thermal behaviour

Figs. 2 and 3 show two typical thermograms recorded under nitrogen and air for the analysis of the cut of octyl oleate. Differential thermal analysis under inert atmosphere (nitrogen, helium) exhibits an endothermic peak resulting from thermal degradation of the compound. Under air, the oxygen produces oxidation reactions (exothermic peak) and superimposition of the endothermic peaks which may correspond to loss of the different volatile products created during oxidation and thermal degradation of the analysed compound (by evaporation, for example) should be noted.

As all the products had a similar thermal profile, Tables 3 and 4 give the results obtained from the thermogravimetric curve (onset, 1%, 50% and end of loss in weight) for each sample tested together with the temperature associated with the tops of the endothermic and exothermic peaks.

For the esters cuts, the temperature values at the onset of loss in weight obtained in the presence of nitrogen are 166°C and 155°C and 175–155°C under air depending on the nature of the alkyl radicals. The

Table 2
Characterisation of the octyl and 2-ethyl hexyl oleyl oxide cuts ((x): numbering of the carbon atom)

Cuts	IR (cm^{-1})	^{1}H-NMR (ppm)	^{13}C-NMR (ppm)
$CH_3–(CH_2)_7CaHa=C_bH_b–(CH_2)_7–C_cH_{2c}–O–C_dH_{2d}–(CH_2)_6–CH_3$	1123.1	a,b: 5.33; c: 3.33; d: 3.40	a,b: 129.85; c,d: 70.98
$CH_3–(CH_2)_7C_aH_a=C_bH_b–(CH_2)_7–C_cH_{2c}—O–C_dH_{2d}–CH–(CH_2)_3–CH_3CH_2–CH_3$	1112.9	a,b: 5.33; c: 3.33–3.39; d: 3.24–3.27	a,b: 129.85; c: 73.80; d: 71.10

Table 3
TGA–DTA analyses of the cuts of octyl and 2-ethyl hexyl oleate

Cut	Atmosphere	Onset of weight loss (°C)	1% of weight loss (°C)	50% of weight loss (°C)	Top of the peaks (°C)	End of weight loss (°C)
Octyl oleate	Nitrogen	166	200	373	400	416
	Air	175	200	356	357	480
2-Ethyl hexyl oleate	Nitrogen	155	177	342	400	500
	Air	155	180	360	379	423

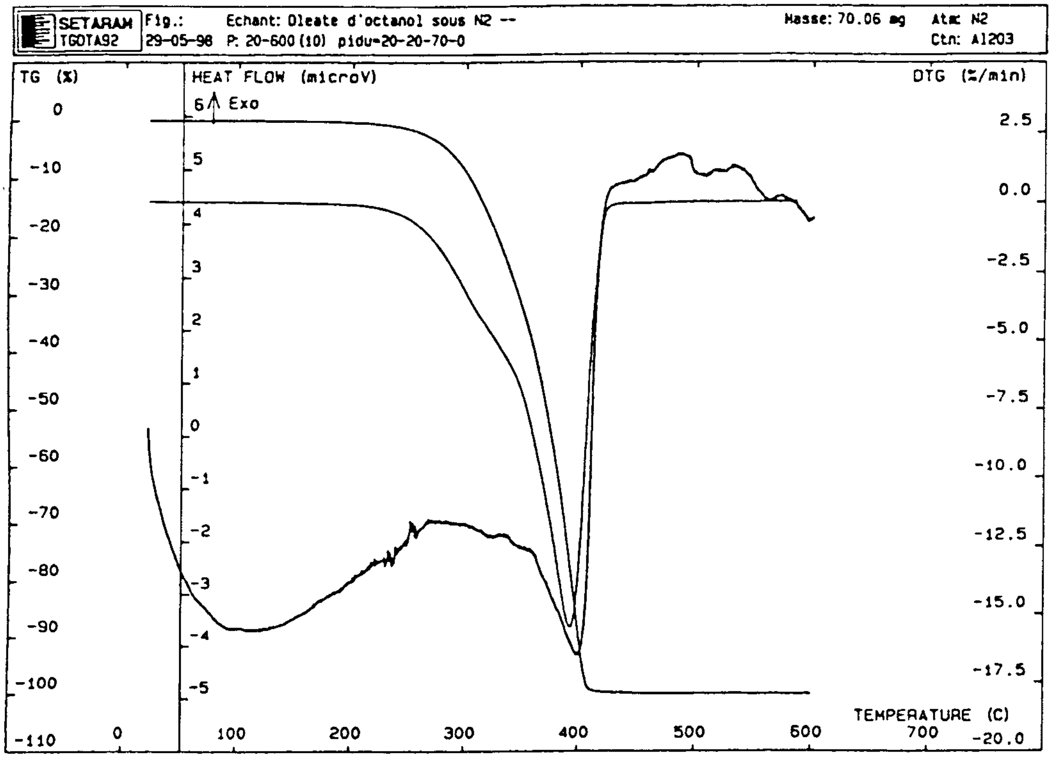

Fig. 2. Thermogram of the octyl oleate cut under nitrogen.

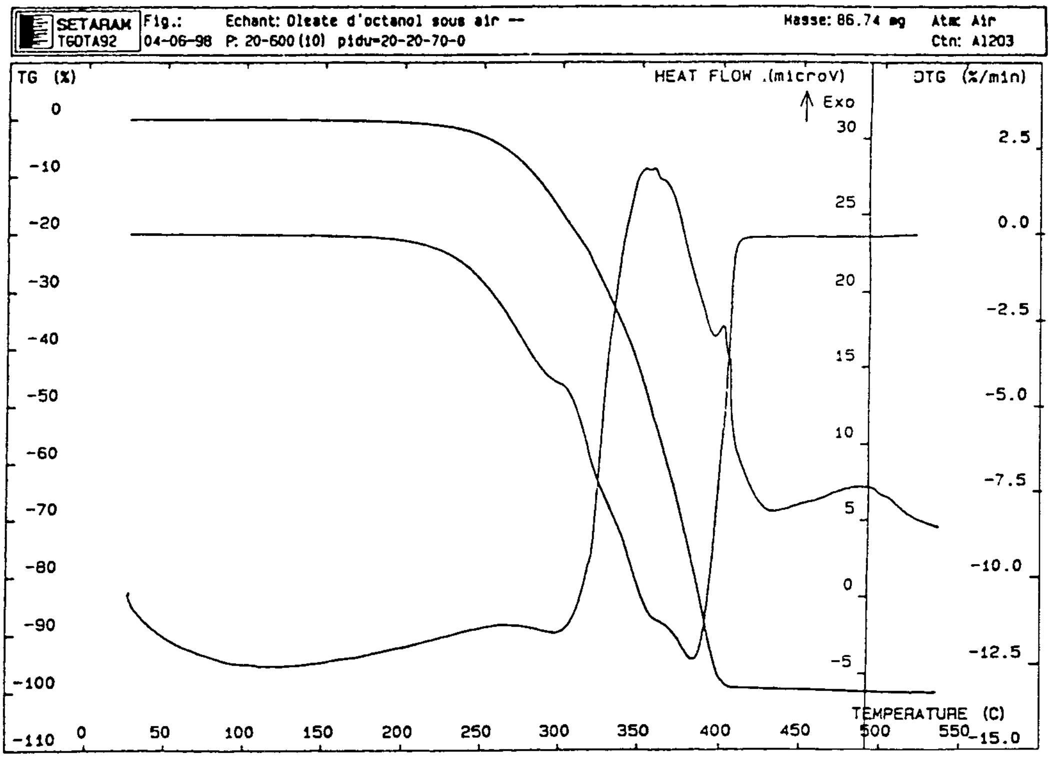

Fig. 3. Thermogram of the octyl oleate cut under air.

Table 4
TGA–DTA analyses of the cuts of octyl and 2-ethyl hexyl oleyl oxide

Cut	Atmosphere	Onset of weight loss (°C)	1% of weight loss (°C)	50% of weight loss (°C)	Top of the peaks (°C)	End of weight loss (°C)
Octyl oleyl oxide	Helium	160	183	343	366	435
	Air	135	150	343	210, 343	500
2-Ethyl hexyl oleyl oxide	Helium	177	214	313	260, 300, 359	380
	Air	164	200	340	339, 383	500

higher values are associated to the octyl oleate cut. Evaporation is slow and constant for all the liquids at temperatures below the temperature of decomposition because the temperature associated with a 1% loss in weight is greater by 30–40°C than the temperature at the onset of loss in weight. Branching on the alkyl radical increases volatility of the ester. These esters with eight linear or branched carbons alkyl chain exhibit good thermal stability because they are stable up to 300°C. End of weight loss is associated with temperature exceeding 420°C. The presence of the double bond confers thermal stability to these compounds.

As the ether cuts are concerned, the temperature values at the onset of the loss in weight obtained in the presence of helium are 160°C and 177°C and those obtained under air are 135°C and 164°C. Branching of the alkyl chain decreases the volatility of the ether. Evaporation occurs before the degradation of such products and temperatures exceeding 150°C are associated with a loss of weight of 1%. The onset of denaturing of these long fatty chain ethers occurs at a relatively high temperature, in order of 250°C. The curves exhibit several peaks, associated with several top temperature, indicative of successive degradations. The thermal behaviour of these fatty ether cuts is good.

If the relative stabilities of esters and ethers (similar fatty chains and alkyl chains) are compared, the different cuts exhibit a similar thermal profile and are stable at the high temperatures tested. In an inert atmosphere, the products had a noteworthy stability. Both also exhibit a good thermal behaviour in an oxidative atmosphere (air).

The different fields of application of these molecules will be determined by their physical properties [1,2].

4. Conclusion

Four products derived from chemical modifications of fats were characterised by infrared, ^{1}H-NMR and ^{13}C-NMR spectroscopy. The results confirmed that cuts of 2-ethyl hexyl and octyl oleates and 2-ethyl hexyl and octyl oleyl oxides were obtained. TGA–DTA analyses were used to determine their thermal behaviour under both an inert and oxidising atmosphere. Fatty esters and fatty ethers exhibit a similar thermal profile. All the compounds analysed were thermally stable as they decomposed at temperatures around 250°C for the ether cuts and 300°C for the ester cuts. They evaporated at temperatures around 150°C before reaching their degradation temperature. The results revealed the influence of the chemical structure of the alkyl chain. A branched alkyl chain increases the volatility of the oleic esters and decreases those of the oleyl oxydes.

The products show good promise. According to their fluidity at ambient temperature, high boiling points, and their filmogenic and surfactant properties, they are destined for use as base oils or additives in active lubricating formulations [1,2].

Acknowledgements

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