

Synthesis and Characterization of Oleic Succinic Anhydrides: Structure–Property Relations

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ABSTRACT: Alkenyl succinic anhydrides (ASA) were prepared by an -ene reaction of *n*-alkyl (C₁ to C₅) oleates with maleic anhydride. The purified compounds were characterized by FTIR, ¹H NMR, and MS analytical methods to elucidate their structures. Their physicochemical properties were systematically studied and found to depend on the length of the alkyl radical. Structure–property relations were established for viscosity, m.p., and density. The combination of a long hydrophobic chain and a highly polar group with density values close to that of water implied good emulsification properties for some of these molecules. Comparison of the thermal properties of alkyl oleates and their respective ASA demonstrated that the grafting of maleic anhydride allowed the synthesis of compounds with very low melting temperatures (less than –60°C) and good stability at high temperatures (greater than 350°C) under both air and helium atmospheres. All these properties suggest a strong potential for application in the biolubricant or surfactant fields. The combined influences of the succinic part and variable ester moieties imply that each ASA molecule has its own characteristics, based on which applications could be developed.

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KEY WORDS: Alkenyl succinic anhydride, degradation temperature, density, dynamic viscosity, fatty acid ester, maleinization, melting temperature, renewable resources.

Alkenyl succinic anhydrides (ASA) are widely used in several fields, for example, as additives in lubricants (1), intermediates in organic chemistry (2), wood-preservation agents (3), or paper-sizing agents (4,5). They are obtained by an -ene reaction (6) between maleic anhydride (enophile) and an alkene having an allylic hydrogen (-ene). During the reaction, a new bond is created between two unsaturated termini, with an allylic shift of the -ene double bond and transfer of the allylic hydrogen to the enophile. Usually, the alkene is a petrochemical olefin, but TG or vegetable oil derivatives such as FA also have been used; in this case, the reaction is commonly named maleinization (7). The -ene reaction requires a Lewis acid and/or high temperature (>200°C) since its activation energy (E_a) is high (>80 kJ/mol) (8). Even though the conversion rate is improved at higher temperatures, various

side reactions can take place: enophile polymerization, alkene oligomerization, copolymerization between the enophile and alkene, and thermal decomposition of the ASA (retroene reaction). Secondary products are black, waxy solids unsuitable for the major uses of ASA.

Literature concerning the reaction between maleic anhydride and unsaturated molecules can be divided in three periods. First, the reaction mechanism was studied during the 1940s and up to the early 1950s by using ASA from FA or FA esters. Demonstration of the -ene reaction mechanism was debated and finally established during this period (9–11). Second, the strong development of petrol resources in the early 1950s favored the production of ASA from straight or branched olefins or even from polyolefins (4,12). From then up to the 1990s, the studies aimed at limiting secondary products by adding reaction catalysts, polymerization inhibitors (8), or an aromatic solvent (13). Third, with the increased interest in renewable resources clearly observed since the 1990s, new ASA have again been synthesized from vegetable oils and their derivatives. They have essentially been used as monomers for the fabrication of thermosets (14), as the anhydride moiety can react with diamines, diols and polyols, or epoxy resins to yield unsaturated polyester-like resins. Among these works, only a few have been concerned with the fundamentals of vegetable ASA compounds, such as the one carried out by Metzger and Biermann (15), who studied the stereochemistry of ASA obtained from methyl oleate by ¹H and ¹³C NMR. No study has been concerned with the physicochemical properties of vegetable ASA compounds. Our purpose was therefore to synthesize, purify, and characterize ASA compounds obtained from oleic acid esters with different alkyl groups (Fig. 1). The main objective was to study the influence of ester chain length on some physicochemical properties to establish structure–property relations useful for defining potential fields of application. With this study, we intend to favor the replacement of fossil resources by renewable resource-derived ASA.

EXPERIMENTAL PROCEDURES

Materials. Methyl oleate (>96%) was supplied by Fluka (St Quentin Fallavier, France). Oleic acid and oleoyl chloride (both technical grade >85%), as well as maleic anhydride, ethanol, propanol, butanol, and pentanol (all >99%), were

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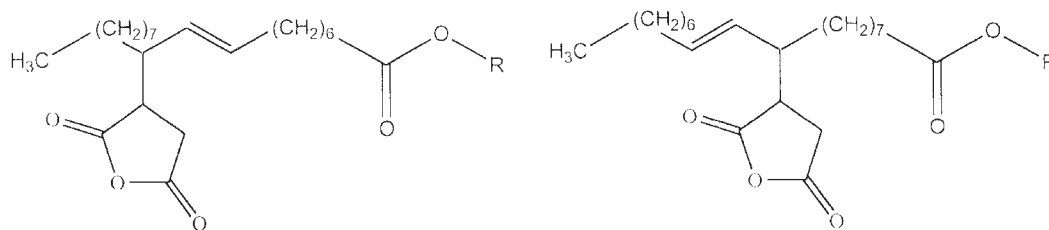


FIG. 1. Alkenyl succinic anhydrides (ASA) compounds derived from alkyl oleates ($R = -C_nH_{2n+1}$, $n = 1-5$). Two isomers are possible.

purchased from Sigma (St Quentin Fallavier, France). 4-Toluene-sulfonic acid (*p*-TSA, >99%) was supplied by Fluka. All reagents were used as received without further purification.

Preparation of butyl and pentyl oleates. The syntheses of butyl and pentyl oleates were based on the complete esterification of oleic acid with the corresponding alcohol. Butanol or pentanol (2 mol), oleic acid (1 mol), and *p*-TSA (0.1% based on total weight) were placed in a 500-mL three-necked reactor and heated to 95°C. The reactor was equipped with a magnetic stirrer, a thermometer, and a distillation column followed by a condenser. The azeotropic mixture formed by water and alcohol was distilled off to shift the equilibrium. Esterification was monitored by quantification of the acid value of the medium according to ISO Standard 660:1996. The reaction was stopped when no more azeotropic mixture was distilled and when the acidity of the medium was minimal. The cooled reaction medium was washed with a NaCl-saturated aqueous solution and then vacuum distilled. FA esters were distilled between 170 and 190°C under 1 mmHg and used immediately for the -ene reaction.

Preparation of ethyl and propyl oleates. These esters were synthesized by acylation of the alcohol with a FA chloride. Ethanol or propanol (1 mol) was placed in a 500-mL three-necked reactor equipped with a nitrogen input, a mechanical stirrer, and a condenser followed by two NaOH solution washers to trap the HCl formed. Oleoyl chloride (0.5 mol) was added to the reactor under nitrogen at room temperature. As the HCl evolved, the equilibrium shifted. The temperature was gently raised to 90°C to complete the reaction. The medium was then washed with a NaCl-saturated aqueous solution and vacuum distilled. Ethyl and propyl oleates were distilled between 160 and 170°C under 1 mmHg and used immediately for the -ene reaction.

Synthesis and purification of ASA. Alkyl oleate (100 g) and maleic anhydride (1.2 mol/mol of alkyl oleate) were heated at 220°C for 8 h under a static nitrogen atmosphere in a three-necked reactor equipped with a magnetic stirrer and a condenser heated at 60°C to reflux the liquid maleic anhydride. At the end of the reaction, the medium was vacuum distilled (<1 mmHg). Unreacted maleic anhydride and oleic acid esters were distilled at 70°C and between 160 and 190°C, respectively. ASA were then distilled between 240 and 260°C under this pressure. The purity of the distilled fractions (oleic acid esters and ASA) was evaluated by LC. The HPLC system was composed of a Spectra-Physics pump and a refractometer detector 350RI (Varian) at 35°C. A Spherisorb ODS2

column (silica-grafted C_{18}) operated at 25°C, with a 1 mL/min acetonitrile (Riedel-de Haën, St Quentin Fallavier, France) flow as the mobile phase.

IR spectroscopy. IR spectra were recorded on KBr windows using a Perkin-Elmer 1600 FTIR in the 400–4000 cm^{-1} region.

NMR spectroscopy. 1H NMR spectra were obtained in a Bruker AC200 apparatus at 200 MHz. The samples were analyzed in $CDCl_3$ 99% (Sigma).

MS. Mass spectra were obtained in a Nermag R 1010 spectrometer. After dilution in CH_2Cl_2 , the samples were chemically ionized by ammonia (NH_3).

Density. Density was determined using a 10-mL pycnometer according to ISO standard 279-1981.

Rheometry. Dynamic viscosities were measured with a Carrimed CSL100 viscometer. The operating conditions for oleic esters were as follows: cone angle, 2°; cone diameter, 6 cm; truncation, 56 μm ; strain, constant 1 N/m^2 for 1 min; temperature, 20°C. The operating conditions for ASA were as follows: cone angle, 2°; cone diameter, 4 cm; truncation, 54 μm ; strain, linear from 10 to 30 N/m^2 for 2 min; temperature, variable from 0 to 60°C.

DSC. Thermal transitions of oleic esters were recorded on a PerkinElmer Pyris1 apparatus. The temperature program was –50 to 25°C at 10°C/min. ASA compounds were studied in a Netzsch 204 apparatus. The temperature program was –120 to 25°C at 10°C/min. Melting points of these compounds were calculated from thermograms according to the tangent method.

Thermogravimetric analysis. The degradation temperatures of ASA corresponding to 10 and 50% mass loss were determined in a Setaram TG-DTG 92 apparatus. The samples were heated from 20 to 600°C at 10°C/min under air and helium.

RESULTS AND DISCUSSION

Synthesis of alkyl oleates. Five oleic acid alkyl esters, from methyl to pentyl, with reasonably high purity (>85%) were required for ASA synthesis. Methyl oleate was commercially available. Butyl oleate and pentyl oleate were successfully synthesized by the esterification technique. After distillation, no residual oleic acid accompanied the desired product. The purities of these alkyl oleates were 90 and 87%, respectively, the rest being butyl and pentyl esters of other FA as the initial source, which were of technical grade. On the contrary, the esterification technique was not successful for the synthesis

of ethyl and propyl oleates. These reactions were not complete, and significant quantities of oleic acid remained in the reaction medium. This was probably due to the low reaction temperature, limited by the boiling temperature of the water-alcohol azeotrope. Moreover, the distillation of the medium did not allow an effective separation of the ethyl and propyl oleates from oleic acid. Consequently, the synthesis of the former were finally properly achieved by acylation of the corresponding alcohol with oleoyl chloride. Purities of 84 and 89% in ethyl and propyl oleate, respectively, were reached after distillation, with no free reagents left. The rest was assumed to be ethyl or propyl esters of other FA.

Synthesis of ASA. Two isomers of ASA can be formed, since the addition reaction of maleic anhydride on oleic acid esters can occur either on carbon 9 or carbon 10 (atoms concerned with the double bond) of the unsaturated chain. The two isomers could not be separated by vacuum distillation, but the HPLC analysis of the distillate showed two peaks that were poorly resolved. They were therefore integrated as a unique peak for purity calculations based on the following area ratios: 95% for methyl oleate succinic anhydride (ASAOM), 99% for ethyl oleate succinic anhydride (ASAOE), 99% for propyl oleate succinic anhydride (ASAOPr), 88% for butyl oleate succinic anhydride (ASAOB), and 98% for pentyl oleate succinic anhydride (ASAOPE).

ASA characterization. All distilled ASA were clear yellow, oily liquids (Gardner's color index from 5 to 7). FTIR spectra of oleic ASA presented significant bands representative of the groups present (Fig. 2). The major IR peaks arising from anhydride carbonyl stretching were located at 1785 and 1863 cm^{-1} . They also showed a stretching vibration band typical of five-membered cyclic anhydrides, such as succinic

anhydride, at 917 cm^{-1} . The carbonyl stretching band of the alkyl ester appeared at 1732 cm^{-1} .

^1H NMR spectra of the samples showed the expected characteristic peaks. ASA from methyl oleate showed a peak at 5.5 ppm (*m*, 2H) belonging to the $-\text{CH}$ of the double bond. The peak at 3.6 ppm (*s*, 3H) belonged to the $-\text{CH}_3$ in the ester part. The peaks between 3.1 and 2.6 ppm (*m*, 3H) were assigned to $-\text{CH}$ belonging to the succinic link and to the anhydride moiety. The peaks at 2.2 ppm (*t*, 2H) and at 1.5 ppm (*m*, 2H), respectively, were identified as $-\text{CH}_2$ in positions α and β to the ester group and part of the unsaturated chain. The peak at 1.9 ppm (*d*, 2H) belonged to the $-\text{CH}_2$ in a position to the double bond. The peak at 1.2 ppm (*m*, 20H) was representative of the $-\text{CH}_2$ from the linear fatty chain. Finally, the peak at 0.80 ppm (*t*, 3H) could be assigned to the terminal $-\text{CH}_3$ moiety of the alkyl chain. These spectra provided confirmation of the nature of our products.

Additional confirmation of the structures was obtained from MS. The M.W. of ASA compounds were obtained from the formation of $\text{ASA}-\text{NH}_4^+$ ions for m/z 412, 426, 440, 454, and 468, which corresponded to the theoretical M.W. of ASAOM, ASAOE, ASAOPr, ASAOB, and ASAOPE. Other characteristic peaks were m/z 395, 409, 423, 437, and 451, corresponding to the formation of $\text{ASA}-\text{H}^+$ ions. For each MS spectrum, a common peak for m/z 398 was obtained, corresponding to a NH_4^+ ionized fragment in which the alkyl part of the carboxylic acid ester moiety of ASA was being removed.

Physical properties of ASA. After confirmation of the structure of ASA, several physical characteristics were evaluated. Our conclusions took into account the stereoselectivity, the length of the ester moiety, and the influence of the suc-

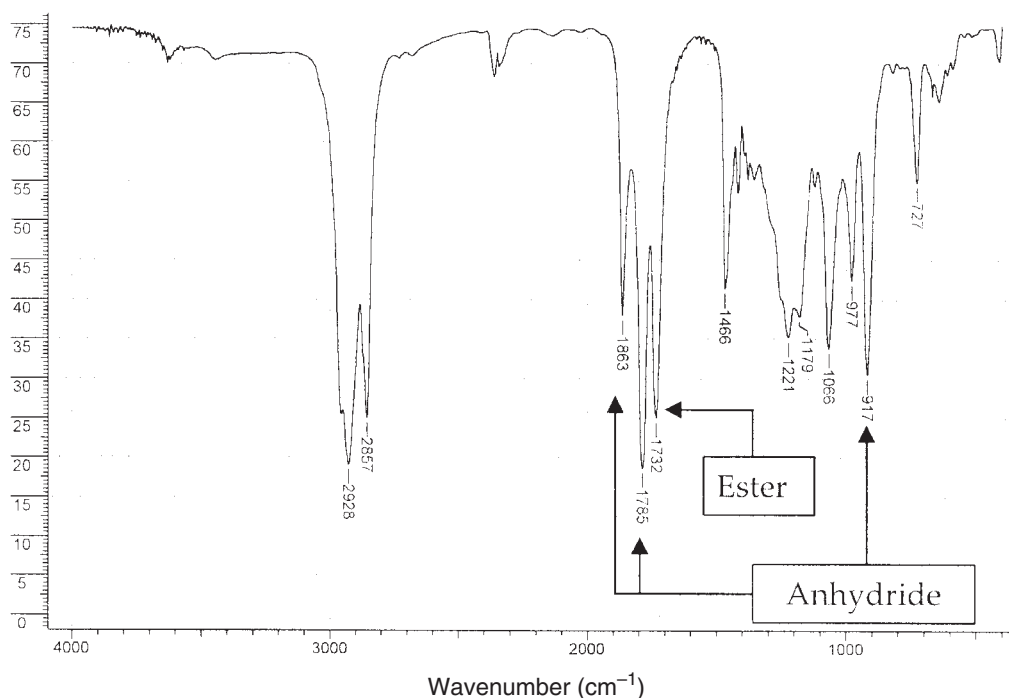


FIG. 2. FTIR spectrum of pentyl oleate succinic anhydride.

cinic moiety. With regard to the stereoselectivity, previous studies (7,15,16) have indicated that the mechanism of the ene reaction for a *cis* alkene (oleic acid) with a maleic anhydride leads to 100% *trans* adducts. This change in configuration and the presence of the ester and succinic moieties influ-

ences the intermolecular arrangement and consequently the physical properties of vegetable ASA compounds.

Viscosity. The rheological behavior of ASA was studied at 20°C (Fig. 3). The gradient was an increasing linear function of the strain. The viscosity, i.e., the slope of the preceding

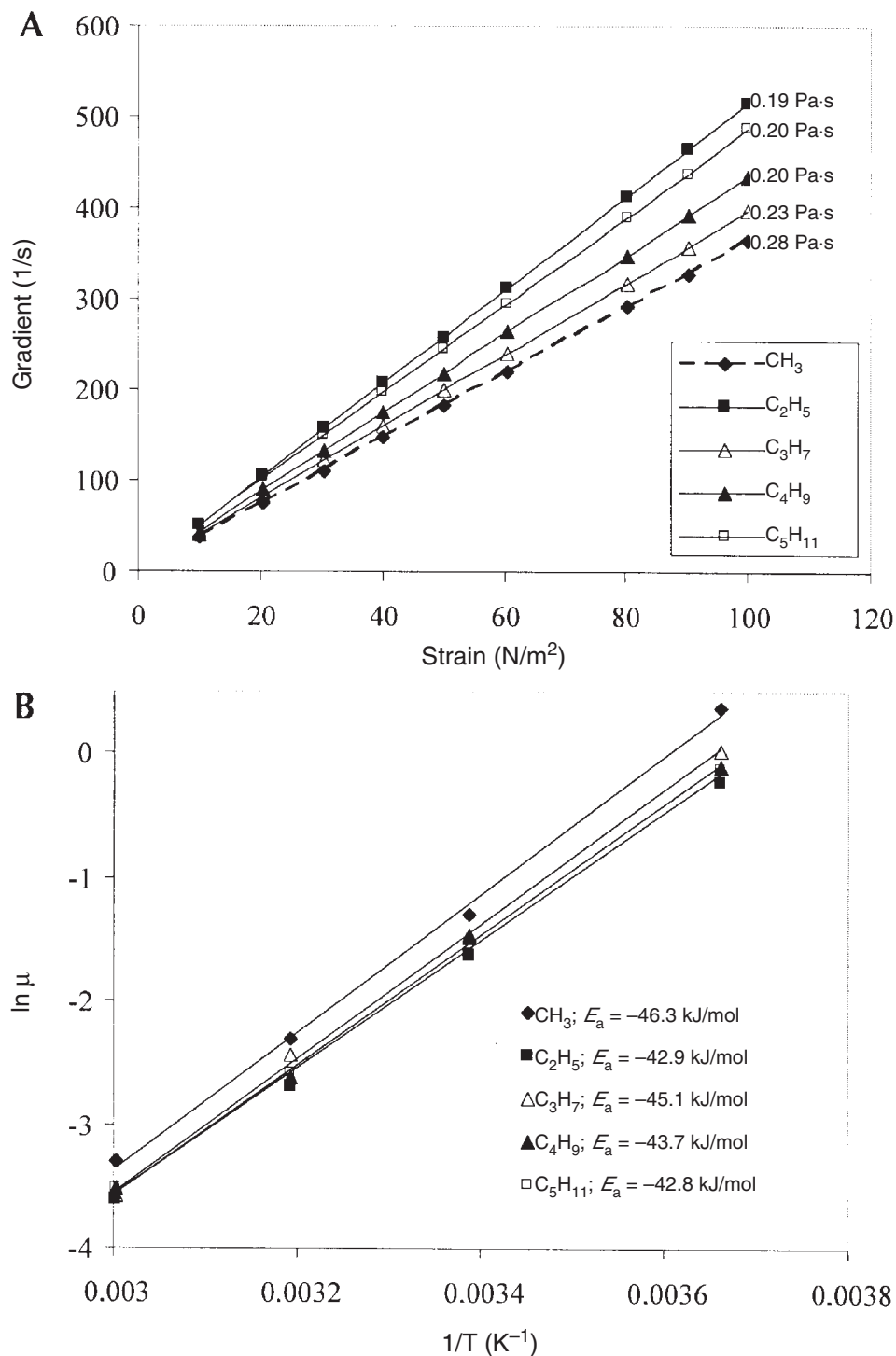


FIG. 3. Rheological behavior of ASA. (A) Gradient vs. strain applied. (B) Dynamic viscosity vs. temperature. Methyl oleate succinic anhydride (CH₃), ethyl oleate succinic anhydride (C₂H₅), propyl oleate succinic anhydride (C₃H₇), butyl oleate succinic anhydride (C₄H₉), pentyl oleate succinic anhydride (C₅H₁₁). For other abbreviation see Figure 1.

curves, was therefore constant for all strains applied. The viscosity values ranged from 0.19 to 0.28 Pa·s from methyl to pentyl. The lowest value was measured for ASAOE. We can propose no explanation for this exception to the tendency. ASA appeared to be Newtonian liquids whose viscosities were at least 30 times higher than those of the corresponding alkyl oleates, which ranged from 0.003 to 0.009 Pa·s. This was linked to both the increase in M.W. and the presence of a new function, branched to the alkenyl chain, corresponding to the grafted maleic anhydride, which created friction phenomena between the molecules. The maximal viscosity corresponded to the shortest alkyl moiety, which was also the most polar. This compound seemed to undergo the most important friction between molecules even if its M.W. was the lowest of the series. The evolution of viscosity with temperature can be mathematically expressed as $\ln \mu = a/T + b$ whatever the strain applied (Fig. 3). This behavior is also characteristic of Newtonian fluids. On the one hand, these equations can be used as predictive models for the evaluation of ASA viscosities at every temperature, which are useful values for determining fluid transport conditions. On the other hand, by analogy with the Arrhenius law, it is possible to calculate the E_a as being equal to $E_a = -a \times R$. Except for ASAOE, the E_a increases as the length of the ester moiety decreases. The less polar the molecule (longest alkyl chain), the lower friction there is between molecules, so the less energy is necessary to overcome the initial friction.

Density. Specific gravities (S.G.) of ASA and alkyl oleates were evaluated at 20°C according to a standardized method. When the length of the alkyl substituent increased, the S.G. of ASA decreased, presumably due to an increase in steric hindrance (Fig. 4). The terminal unit acted as a “spacer” between molecules. The S.G., plotted as a function of the number of carbon atoms in the alkyl moiety, followed a parabolic

relation, $S.G. = 0.0003n^2 - 0.0065n + 1.0204$, with a correlation coefficient $R^2 = 0.9796$. This type of correlation also was found for the corresponding alkyl oleates: $S.G. = 0.0007n^2 - 0.0067n + 0.8830$, with $R^2 = 0.9984$. Thus, grafting maleic anhydride onto alkyl oleates led to an important densification of the molecule. For each ester, maleinization allowed an increase of about 0.12 kg/m³. This was quite surprising since the succinic moiety also could act as a spacer between molecules. However, because the -ene reaction on alkyl oleates (*cis* compounds) leads only to *trans* ASA compounds, we can hypothesize that molecule stacking is more compact for ASA than for the oleates. Furthermore, for the vegetable ASA compounds considered, even if they possess a long hydrocarbon chain (C_{18:1} unsaturated; ester moiety ranging from CH₃ to C₅H₁₁), they have an S.G. approximately equal to that of water. Because ASA molecules consist of a long hydrophobic chain and two polar groups, we can propose that these ASA would be easily emulsified in water and used as wetting agents. Some preliminary tests have demonstrated a real improvement in emulsion stability when compared with conventional ASA not bearing an ester moiety.

DSC. The melting temperatures of alkyl oleates and ASA were evaluated by DSC (Table 1). The melting temperatures of vegetable ASA followed a parabolic relation vs. the length of the ester moiety, whose equation was: $T_m = 0.086n^2 - 2.514n - 61.48$, with $R^2 = 0.997$. The longer the ester moiety, the lower the m.p. The thermal transitions in the thermograms revealed that what we called melting was in reality a phenomenon close to glass transition, as the ASA were passing through a mesomorphic state before reaching the liquid state. This phenomenon became clearer with the longest alkyl esters. In addition, maleinization decreased the melting temperatures of alkyl oleates to about 30°C in each case. Because the -ene reaction leads only to *trans* isomer compounds, the

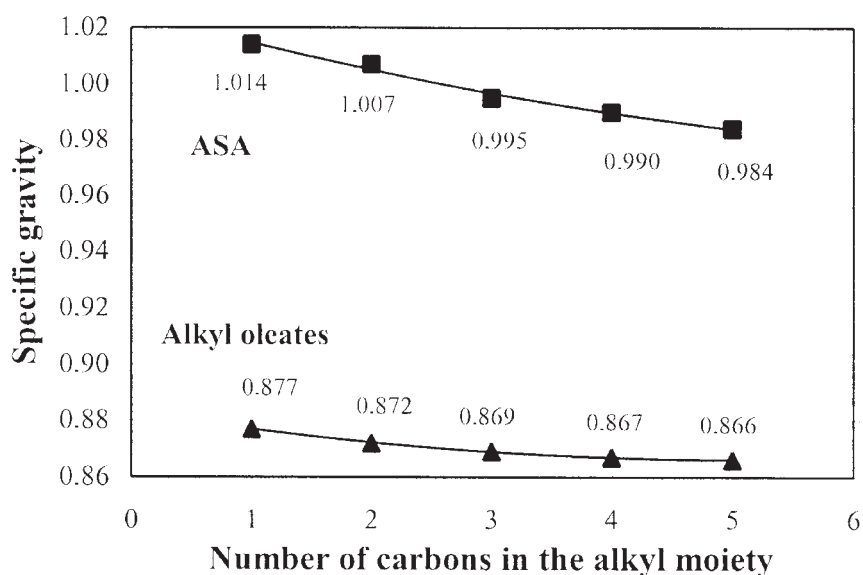


FIG. 4. Specific gravities of ASA and alkyl oleates as a function of the length of their ester moiety. For abbreviation see Figure 1.

TABLE 1
Melting Temperatures of Alkyl Oleates and Alkenyl Succinic Anhydrides (ASA)

Ester moiety	Melting temperature (°C)	
	Ester	ASA
Methyl	-18.9	-63.8
Ethyl	-24.3	-66.4
Propyl	-32.8	-68.2
Butyl	-35.5	-70.0
Pentyl	-31.9	-72.0

stacking of molecules was changed to a more compact arrangement. The molecules may be arranged in a way to minimize steric hindrance between groupings. Layers may be formed, with vertical chains with ester moieties having a head-to-tail arrangement and thus an increased mobility. Therefore, long alkyl moieties act as spacers, significantly decreasing the melting temperatures of the corresponding ASA compounds. For the succinic parts, they can be arranged here and there from the plan formed by the *trans* alkenyl chains, having minimal steric hindrance. Because of the decrease in melting temperature, the products obtained are then liquids that can be used under very low temperatures (<-50°C), which is useful in applications for biolubricants. For alkyl oleates, the melting temperatures ranged from -19 to -35°C and were best fitted by a parabolic relation: $y = 2.538x^2 - 20.496x + 6.28$ (correlation coefficient: $R^2 = 0.9853$). The alkyl oleate melting at the lowest temperature was thus the butyl one. These data were in good agreement with those available in the literature (17).

Thermogravimetric analysis. Starting degradation and degradation temperatures were defined as temperatures corresponding to a 10 and 50% weight loss. They were obtained by thermogravimetric analysis under both an air and a helium atmosphere. Under helium, the molecules started to degrade at a minimum of 315°C, whereas these degradation temperatures shifted to at least 325°C under air (Table 2). Degradation temperatures ranged from 363 to 381°C under helium and from 380 to 389°C under air, according to the length of the alkyl group. Such high degradation temperatures represent the good thermal resistance of ASA even under an ambient atmosphere. Grafting on maleic anhydride caused a 25% increase in the M.W. of the molecule. Thus, compared with esters whose degradation temperatures were about 320–340°C, the anhy-

dride moiety and the change to a *trans* configuration provided molecules more stable to high-temperature conditions of at least 40°C. We also observed that the degradation temperature increased according to the length of the ester moiety. ASA of vegetable origin can thus be used at high temperatures with little or no degradation.

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TABLE 2
Degradation and 10% Weight Loss Temperatures of ASA^a Under an Air or Helium Atmosphere vs. Length of the Alkyl Moiety

Ester moiety	10% weight loss temperature (°C)		50% weight loss temperature (°C)	
	Under helium	Under air	Under helium	Under air
Methyl	316.2	342.6	363.0	379.9
Ethyl	316.2	338.2	365.2	383.0
Propyl	336.8	326.5	376.7	379.6
Butyl	332.4	332.3	377.2	383.8
Pentyl	341.2	351.5	380.8	389.0

^aFor abbreviation see Table 1.

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