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Thermostability and physicochemical properties of two macauba oils and their derivatives related to their use as a lubricant base

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Abstract
Nowadays, the search for enforcement actions that are aligned with the concept of sustainable development is noted in various areas of knowledge. In lubricants, there is an increase in the number of researchers applying vegetable oils in many areas of lubrication. Nevertheless, the exploitation of the potential of several Brazilian oils has not been explored. The macauba tree is abundant in many regions of Brazil and has good oil productivity per hectare when compared to soybean, for example. This study evaluates the ability of macauba seed oils, extracted from pulp and almond, and some chemically modified products derived from them, as lubricants. The chemical modifications were carried out mainly in order to improve the thermostability of the extracted oils. Physicochemical tests required to commercial lubricant oils were applied to the extracted oils and their derivatives, such as kinematic viscosity, viscosity index and total acidity number. The results were compared to the mineral and synthetic bases conventionally used. From this comparison, it was possible to identify the positive and negative physical and chemical characteristics of these products in relation to basic oils derived from petroleum.

Keywords Biolubricants · Base oil · Vegetable oil · Thermal analysis · Macauba oil

Introduction

There is now a huge worldwide effort to reduce the dependence on petroleum products, due to the reduction of oil reserves and the negative impacts on the environment of its derivatives. Brazil has been contributing to this worldwide effort by using biofuels, such as biodiesel and ethanol. However, this has not been the case for the market of lubricating oils, where the use of basic oils derived from petroleum is still prevailing [1–3].

The scenario above can be modified using vegetable oils as basic lubricating oils and lubricating additives. Biolubricants can be defined as lubricants having in their composition vegetable oils *in natura* or modified, and with high biodegradability and low ecotoxicity. The percentage of oleaginous can be integral or partial, varying according to the type of application of the product [4–6].

There is a trend of increasing demand for biolubricants due to environmental demands and population awareness of their benefits. Several studies already indicate the gains of the use of vegetal bases in comparison with minerals considering the smallest impact on the environment.

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Vegetable bases generally have superior lubricity, biodegradability and volatility when compared to mineral oils. However, vegetable oils have less oxidative stability and they degrade when used as lubricants, generating insoluble compounds, which increases the viscosity and acidity of the product [7–9].

Macauba (*Acrocomia aculeata*) is a palm tree of the genus *Acrocomia*, and it is characterized by a wide geographic distribution, extending from Mexico to Argentina, with greater abundance in Costa Rica, Paraguay and Brazil. The productivity of macauba is 15 tons per hectare, reaching the value of 4 tons per hectare of oil, while the same amount of soybean is around 1 ton per hectare of oil extracted [10–12]. Table 1 shows the composition of the oils of the almond and the pulp of macauba tree. The values were provided by the oils suppliers, and they were obtained by gas chromatography analysis.

The need for a detailed study on the viability of the application of vegetable oils as lubricating bases and the abundance and productivity of macauba tree has encouraged this research. Therefore, this work aims to study the physicochemical properties of oils extracted from the pulp and almond of macauba seeds and to obtain diols and diesters of these oils to improve the thermostability without disturbing other physicochemical properties, which are essential in a lubricant evaluation.

Experimental

Materials

In this work, we used macauba pulp oils from the Central do Cerrado company and the macauba almond oil from Mundo dos Óleos company. The mineral oils medium neutral paraffinic (PNM) and hydrogenated naphthenic (NH) were donated by Petróleo Brasileiro S.A., the synthetic oil Etro was donated by Petronas Lubrificantes Brasil S.A, and the additive LZ 7652^{a} was donated by the company Lubrizol do Brasil Aditivos S.A.

Table 1 Fatty acid composition of macauba oils

Composition (fatty acids)	Macauba almond/%	Macauba pulp/%
Caprylic C8:0	5	–
Caproic C10:0	2	–
Lauric C12:0	13	–
Myristic C14:0	10	–
Palmitic C16:0	12	17
Palmitoleic C16:1	2	3
Stearic C18:0	6	2
Oleic C18:1	42	57
Linoleic C18:2	3	17
Linolenic C18:3	–	2
Other	5	2

The reagents for chemical reactions and physicochemical tests were: formic acid (85%, Dynamic), hydrogen peroxide (30%, Vetec), acetic anhydride (97%, Vetec), methylamine (Vetec), sodium acetate (Vetec), ethyl acetate (99%), triethylamine (97%, Sigma-Aldrich), dimethylaminopyridine (5%, Sigma-Aldrich), dichloromethane (Vetec), sodium sulfate (Vetec), sodium bicarbonate (Vetec), hydrochloric acid (Dynamics), sodium hydroxide (Vetec), phenolphthalein (Merck) and potassium biphthalate (Vetec). In addition to the reagents, a rotary evaporator Laborota 4000 and an analytical balance Precisa XT 220 were employed.

Calculations of the molar mass and the unsaturation index of the macauba oils

The reaction stoichiometry, the molar mass and the number of moles of unsaturation in the triglyceride of the macauba almond oil and pulp were calculated by means of their ^{1}H NMR spectra, according to Miyake et al. (1997), using the integration of the peaks related to the integrations of the carbons that compose the oleaginous ones [13].

Diol synthesis

The methodology of Okieimen et al. (2005) was used to obtain the diol in which an equimolar amount of formic acid and double bonds of the oils were mixed under stirring at room temperature, followed by addition of an excess peroxide (4 equivalents). Then, the temperature of the medium reaction was raised to 80 °C and the reaction mixture was kept under stirring for 14 h. The isolation step was carried out by extracting the organic material from the aqueous phase using ethyl acetate. The collected organic phases were washed with water (3*x*) and dried over sodium sulfate, followed by solvent evaporation using a rotary evaporator [14].

Diester synthesis

The diester was obtained by reacting the diol with an equimolar amount of acetic anhydride in the presence of 4-dimethylaminopyridine (DMAP, 0.1 equivalents) and triethylamine (1 equivalent) at room temperature and stirring for 30 min, using dichloromethane as solvent. The collected organic phases were washed with water (3*x*) and dried over sodium sulfate, followed by solvent evaporation using a rotary evaporator.

Characterization of the modified vegetable oils

Vegetable oils derivatives were characterized by infrared, ^{1}H and ^{13}C NMR spectroscopic techniques [15, 16].

Fourier transform infrared spectroscopy

The infrared spectra (from 400 to 4000 cm^{-1}) of the samples were obtained on a PerkinElmer Spectrum One spectrophotometer—coupled to the Universal ATR Sampling Accessory. The samples were in liquid form and were measured in ATR with a resolution of 4 cm^{-1} and 16 scans.

Nuclear magnetic resonance (NMR)

The ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR spectra were obtained using a Bruker Ascend 600—Console III HD spectrometer, referenced to TMS (SiMe$_4$, $\delta = 0.0$ ppm) and deuterated chloroform (CDCl$_3$, $\delta = 77.0$ ppm), respectively. The ^{1}H spectra were obtained with pulses of 1.0 s and 16 scans, while the ^{13}C spectra were run with 1024 scans. The data obtained were treated with Master C program.

Thermostability and other physicochemical analysis

Thermostability

The thermostability of the vegetable oils was investigated using thermogravimetry (TG)/derivative thermogravimetry (DTG) curves obtained in a thermogravimetric analyzer, model DTG—60H/Shimadzu. For this, masses between 5.0 and 10.0 mg of each sample were weighed and then heated in a platinum crucible, from room temperature to 600 °C, at 10 °C min^{-1}, under an oxidizing atmosphere with synthetic air (30 mL min^{-1}) and under an inert atmosphere with nitrogen (30 mL min^{-1}). TG curves were used to determine the percentage of mass loss. The decomposition temperature (T_d) of the oil corresponds to the temperature of the maximum decomposition per degradation step, and it is directly related to thermostability. Graphically, T_d is the temperature associated with the minimum points in DTG.

Kinematic viscosity

The procedures indicated by ASTM D445 were used for this test. The time, in seconds, is determined by a fixed volume of liquid to flow by gravity through the capillary of a calibrated viscometer, at a controlled temperature. The kinematic viscosity is the product of the flow time measured by the viscometer constant. The equipment used for this test was the automatic viscometer CAV 2200—CANON. The measurements were taken at temperatures of 40 and 100 °C for all vegetable, mineral and synthetic oils [17].

Viscosity index (IV)

From the results of the kinematic viscosity at 40 and 100 °C and the equations described in standard ASTM 2270, the values of the viscosity index of the oils studied were calculated [18].

Total acidity number (TAN)

The procedures indicated by ASTM D974 were used for this test; the total acid number can be understood as the amount of potassium hydroxide, in milligram, required to neutralize one gram of sample, by titration [19].

Results and discussion

Characterization of the obtained products

FTIR

The FTIR spectra of the oils of the almond and pulp are very similar (Fig. 1), with some small differences: The stretch of the double bond around 3000 cm^{-1} for the oil of the macauba pulp is almost absent for almond oil; at about 850 cm^{-1}, a small band relative to off-plane deformation of the sp^2 carbons is observed for the pulp oil.

After diol formation, the appearance of an intense band around 3300 cm^{-1} relative to the OH stretch demonstrates

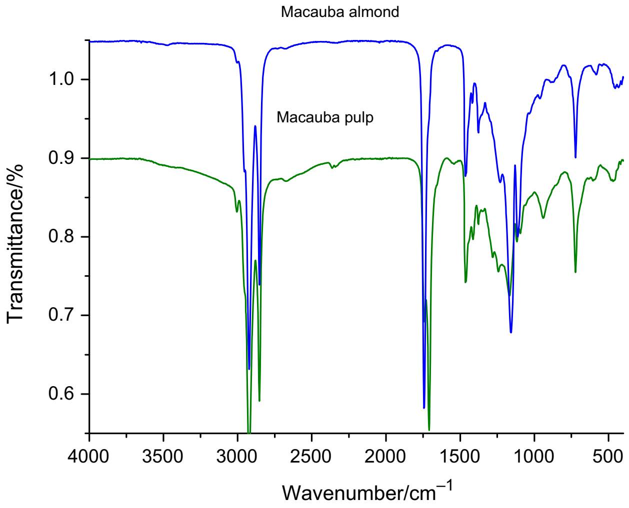

Fig. 1 FTIR spectra of the macauba oils (almond and pulp)

the existence of the hydroxyl group. There is also an increase in the intensity of asymmetric deformation C–O, around 1150 cm^{-1}, compared to the spectra of vegetable oils. In addition, it is observed that the decrease in the band around 3000 cm^{-1}, relative to the stretch of the double bond. (Fig. 2).

Compared to the spectra of the diols, one can see, in the spectra of the diesters, the disappearance of the OH stretch band around 3300 cm^{-1} and an increase in band intensity concerning carbonyl stretching, near 1750 cm^{-1} (Fig. 3).

To support the observations made with the FTIR, NMR analyses were performed.

^{1}H and ^{13}C NMR

The ^{1}H and ^{13}C NMR spectra of the macauba oils and their derivatives (diols and diesters) are shown in the supplemental material. The main difference between ^{1}H and ^{13}C NMR spectra of the pulp and the almond oils is the presence of the bis-allylic hydrogens in the first (at 2.8 ppm) and in the second (at 135 ppm) due to the presence of linoleic and linolenic esters in the pulp oil.

For the diols formed, the following was observed in the ^{1}H NMR spectra: the appearance of a new peak near 3.0 ppm relative to the O–H bond; the decrease in intensity of the peaks relative to the olefinic hydrogens and the increase in the intensity of the hydrogen peaks of aliphatic carbons (CH_3 and CH_2). In the ^{13}C NMR spectra, the appearance of a peak around 70 ppm relative to carbinolic carbon and vanishing of peaks close to 135 ppm related to the sp^2 carbons confirmed the formation of the diol.

For the diesters formed, worthy of note is the decrease in the signals of the olefinic hydrogens that are located around 5.2 ppm. This is followed by an increase in the signal of the methylene hydrogens of glycerol and an appearance of a signal at about 2.0 ppm, related to the methyl singlet. In the ^{13}C NMR spectra, the appearance of new peaks relative to the carbonyl ester groups between 172 and 173 ppm and the disappearance of the peaks relative to the sp^2 carbons close to 135 ppm were observed.

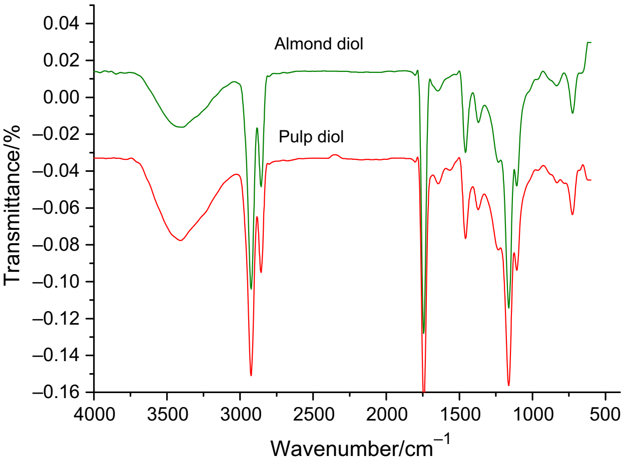

Fig. 2 FTIR spectra of the diols of the macauba oils

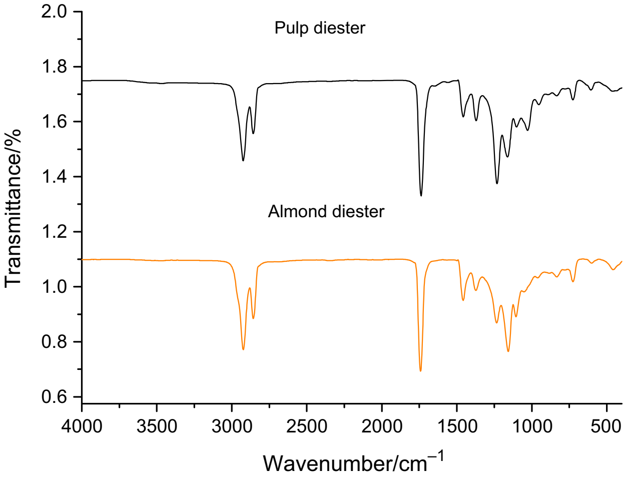

Fig. 3 FTIR spectra of the diester of the macauba oils

Thermal analysis

Oxidative atmosphere

Much of the applications of lubricating oils occur at elevated temperatures and oxidizing atmosphere, such as lubrication of automotive engines, cutting machines, bearings. The thermal analysis gives us important information about the behavior of oils at high temperatures and how and when their degradation occurs under oxidizing atmosphere [20].

According to Eychenne et al. [21], the thermal decomposition of a vegetable oil can occur in two or three stages and it is related to the degree of unsaturation of oilseeds. In the first step, the alkyl radicals react with oxygen, forming peroxides and hydroperoxides. These reactions occur at the site of the π bonds of the molecules. The second stage will have the greatest mass loss because the degradation of the carbonic chains will occur. The third stage occurs at temperatures above 720 K, and it is linked to the polycondensation and carbonization of the formed compounds. Since the formation of peroxides and hydroperoxides occurs relatively at low temperatures, the thermostability in the oxidizing atmosphere is expected to occur at lower temperatures, according to the inert atmosphere (nitrogen).

Table 2 shows information about each degradation stage of the oils: T_d, initial (T_{onset}) and final (T_{end}) temperatures and mass losses (total and by stages).

The results evidenced the high thermostability of the oil of the almond, based on T_d results, which can be explained

Table 2 TG/DTG measurements in oxidizing atmosphere

Product	T_d1/K [T_{onset}–T_{end}]	T_d2/K [T_{onset}–T_{end}]	T_d3/K [T_{onset}–T_{end}]	T_d4/K [T_{onset}–T_{end}]	Total mass loss/% [mass loss by stage]
Almond	607 [590–635]	681 [678–737]	801 [790–815]		98 [78–17–3]
Almond diol	619 [599–627]	683 [671–697]	835 [829–872]		99 [70–23-6]
Almond diester	621 [605–631]	679 [671–721]			97 [71–26]
Pulp	510 [498–556]	694 [670–694]	625 [618–644]	796 [717–796]	99 [40-25–24–10]
Pulp diol	630 [629–683]	759 [752–797]	799 [790–811]		98 [78–13–7]
Pulp diester	619 [615–735]	696 [694–729]			96 [79–17]
PNM	623 [530–668]				92 [92]
Etro	597 [508–661]	–	–		100 [90]
NH	570 [435–625]	–	–		90 [90]

by the high content of saturated fatty acids in its composition. One can see an increase in the thermostability of the diol and diester in relation to the oil of the almond. For all these, it is possible to observe a higher thermostability in relation to the Etro and NH oils and similar to that of the PNM oil. Considering the T_{onset}, they are even more stable than PNM.

In relation to pulp oil, the lower oxidative stability of the macauba pulp can be observed in comparison with the other oils. This fact can be related to the degree of unsaturation contained in this oil. It is worth noting that their diol and diester presented values similar to the best commercially analyzed basic oil (PNM). These two oils derived from the pulp showed an increase in T_d higher than 100 °C, compared to the vegetable oil *in natura*. The values obtained for the diols and diesters were close; this fact may be related to ester hydrolysis under oxidative conditions, which leads to the reduction of the ester to diol formation with the formation of acetic acid and water, consequently, a thermal behavior similar to the diol.

According to Politi et al. [9], the thermal degradation of mineral and synthetic oils occurs in one step, in a small temperature range and with well-defined DTG peaks. This is due to the homogeneity of the oils composition. For the oils conventionally used as lubricating bases, the best results were obtained for the paraffinic oil, followed by the Etro and naphthenic oils.

It can be noticed by the TG analysis (Fig. 4) that the vegetable oil of the macauba almond and its derivatives (diol and diester) have similar thermostability compared to the PNM oil and it is superior to the Etro and NH oils.

DTG curves obtained for the almond oils in this study are shown in Fig. 5. It can be observed that the degradation of the almond and diol occurs in three stages, in a similar way. These stages can be attributed to the formation of oxygenated compounds, the degradation of the carbon chains and, later, the carbonization and polycondensation of the formed compounds. It is worth mentioning that alcohols in oxidative environments can lead to compounds with higher oxidation states, such as aldehydes, ketones and carboxylic acids. For the diester, only two stages were noted, which are related to the degradation of the carbon chains and the carbonization of the formed compounds.

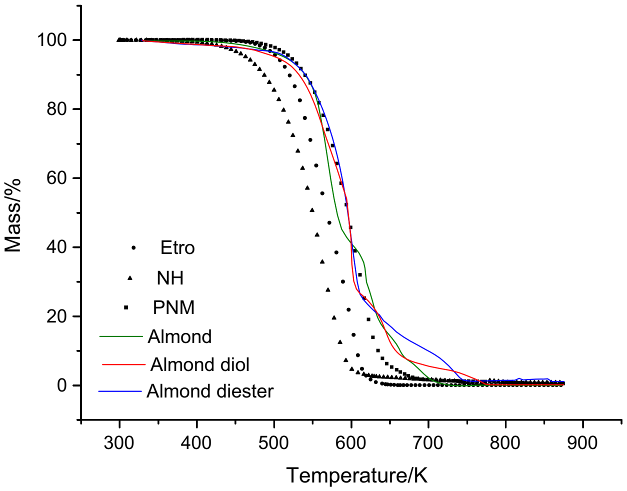

Fig. 4 TG curves of commercial lubricants, almond oil and derivatives

According to Fig. 6, a lower thermostability of the macauba pulp oil in relation to the mineral and synthetic oils and also in relation to the macauba almond oil can be noticed. This lower stability may be attributed to the higher degree of unsaturation in the macauba pulp oil (3.5 per molecule of triglyceride) compared to the macauba almond oil (0.7 per molecule of triglyceride). It should be pointed out, notwithstanding, that the diol and diester obtained from the pulp have a greater increase in their thermostability, presenting better results than the conventionally used basic oils.

Figure 7 shows the DTG curves of macauba pulp oil and its derivatives where four stages of degradation are

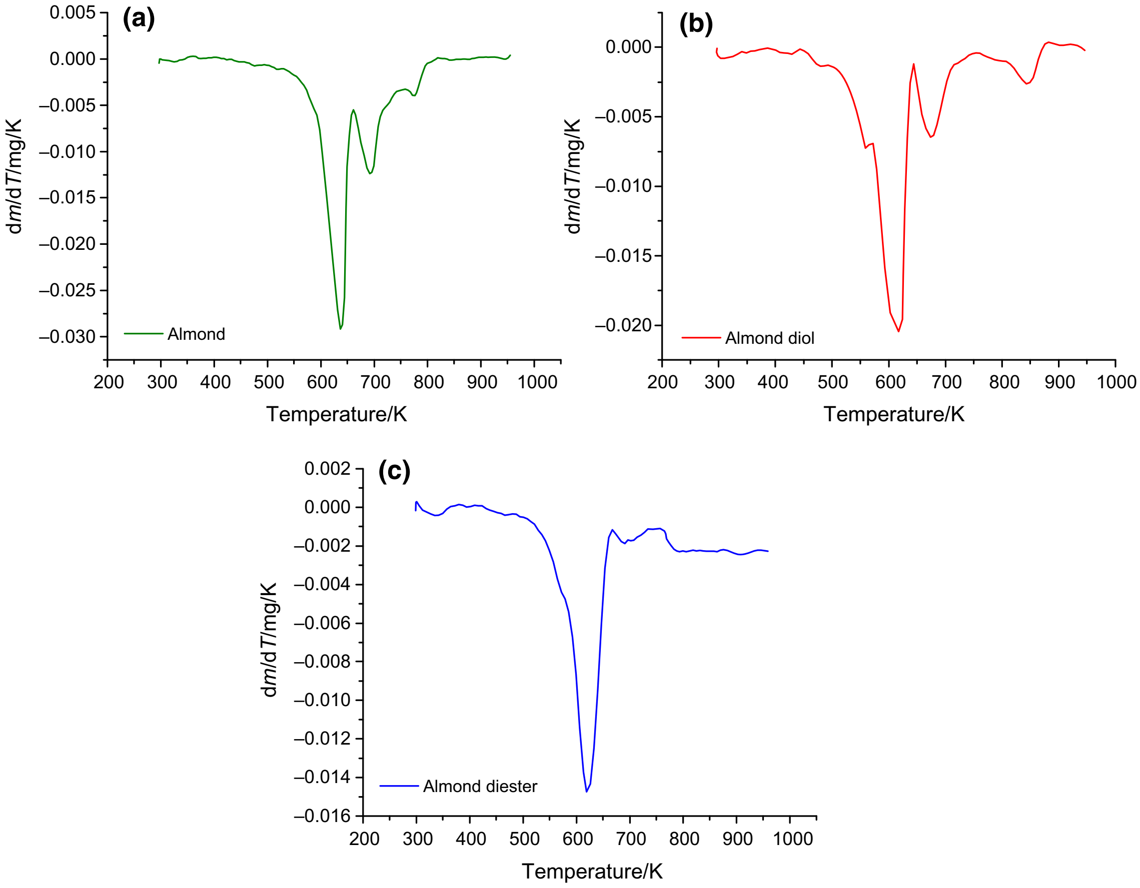

Fig. 5 DTG curves of macauba almond oil and its derivatives. **a** Macauba almond oil, **b** diol from macauba almond oil, **c** diester from macauba almond oil

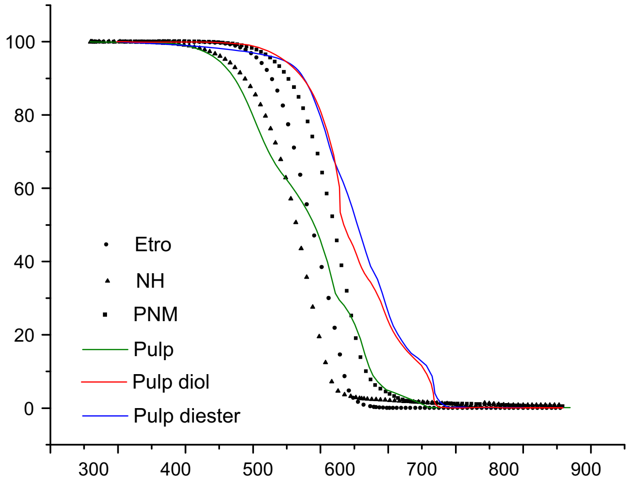

Fig. 6 TG curves of the derivatives of the macauba pulp oil

observed. The first is related to the formation of peroxides and hydroperoxides. The second and third correspond to the degradation of the chains of the oxygenated compounds and of the carbon chains, respectively. The fourth refers to polycondensation and carbonization of the compounds formed. For the diol formed, we observed only three stages. Their degradations are similar to those of the macauba pulp oil except for the stage related to the formation of peroxides and hydroperoxides. For the diester, we observed two stages, related to carbon chain degradation and the polycondensation and carbonization of the compounds formed.

Inert atmosphere

Some applications of lubricating oils occur in practically inert atmosphere, such as step-type transmission boxes and refrigeration compressors, among others. In order to verify the behavior of the vegetable oils and their derivatives under these conditions, thermal analysis tests were carried out under inert atmosphere—N_2 [20].

According to Eychenne et al. [21], in an atmosphere with the absence of oxygen, the number of double bonds does not affect preponderantly, but rather the length of the carbon chains.

Table 3 shows T_{d}, T_{onset} and T_{end} by stages of degradation of the oils and mass losses.

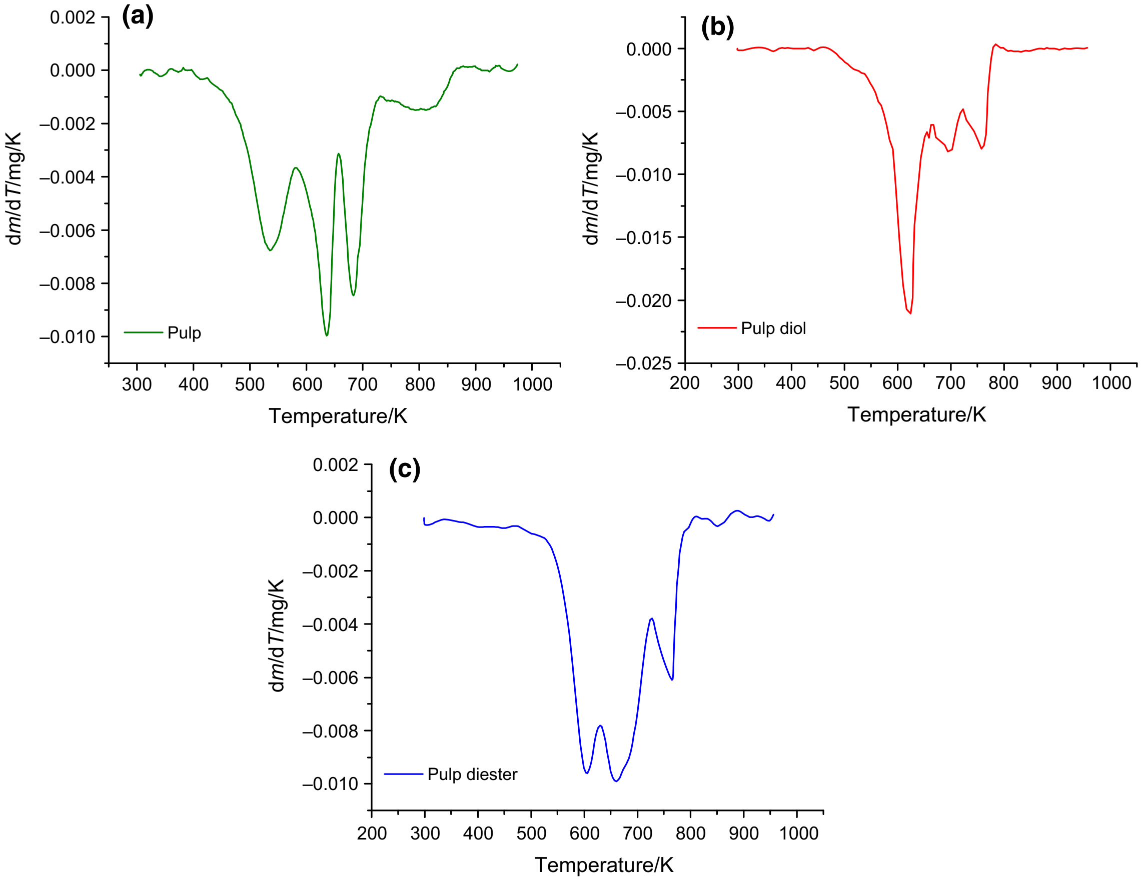

Fig. 7 DTG curves of macauba pulp oil and its derivatives: **a** macauba pulp oil, **b** diol from macauba pulp oil, **c** diester from macauba pulp oil

Table 3 TG/DTG measurements in inert atmosphere

Products	$T_{\mathrm{d}}1$/K [T_{onset}–T_{end}]	$T_{\mathrm{d}}2$/K [T_{onset}–T_{end}]	$T_{\mathrm{d}}3$/K [T_{onset}–T_{end}]	Total mass loss/% [mass loss by stage]
Almond	617 [535–652]	755 [720–803]		98 [73–15]
Almond diol	621 [611–655]	711 [660–721]		97 [88–9]
Almond diester	651 [617–686]			96 [96]
Pulp	536 [500–561]	672 [646–680]	720 [683–730]	97 [33–49–15]
Pulp diol	635 [485–655]	694 [680–715]	780 [717–787]	96 [61–26–9]
Pulp diester	685 [637–692]	742 [721–762]		99 [81–18]

In relation to the almond and its derivatives, a highest increase in the thermostability for the diester in comparison with the diol is noticed. This fact may be related to the increase in the carbon chain of the diester. For the pulp and its derivatives, a great increase in the thermostability was observed and, as the same as for the almond, it was higher for the diester than for the diol.

The thermal behavior of the macauba almond oil was similar to the diol thermal behavior obtained in an inert atmosphere according to Fig. 8. The diester had a major increase in thermostability, which may be related to the longer chain length of this modified vegetable oil.

As shown in Fig. 9, the thermal degradations of the almond oil and of the diol occur in two stages, related to the degradation of the carbon chains and polycondensation and carbonization of the chains, whereas for the diester, only one step was observed.

The macauba pulp oil (Fig. 10) presented the lowest thermostability in an inert atmosphere, which shows that even occurring in a single step the degradation of the π bonds occurs at lower temperatures than those of the σ

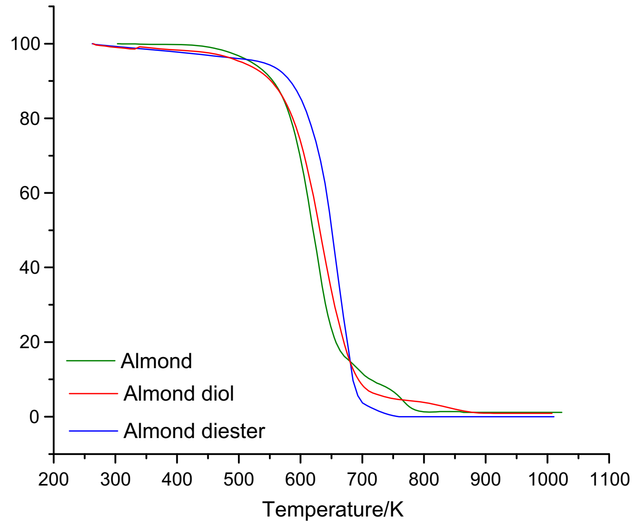

Fig. 8 TG curves of macauba almond oil derivatives

bonds, decreasing the thermostability of the oil. The diol had a very small increment in its T_d and the pulp diester showed the greater thermostability under inert atmosphere, which can be explained by the increase in the carbon chain in the formation of this compound. Unlike in oxidizing atmosphere in which several reactions occur, the thermostability in inert atmosphere is related to the breakdown of the bonds of the carbonic chains.

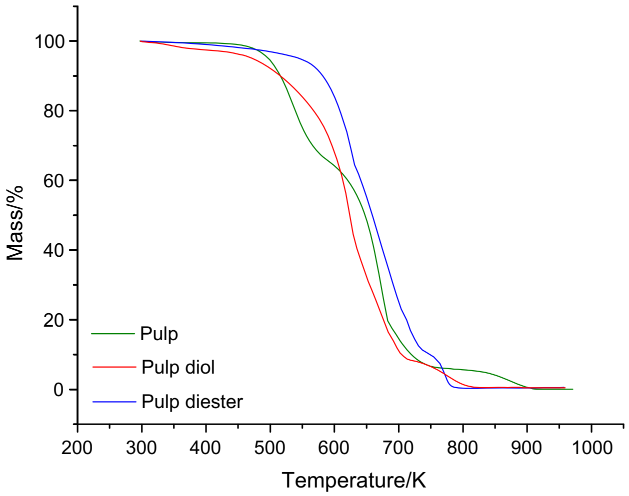

Fig. 10 TG curves of the macauba pulp oil and its derivatives

The degradation of the macauba pulp oil and its derivatives under inert atmosphere occur in three steps (Fig. 11). For the pulp, the three separate and distinct

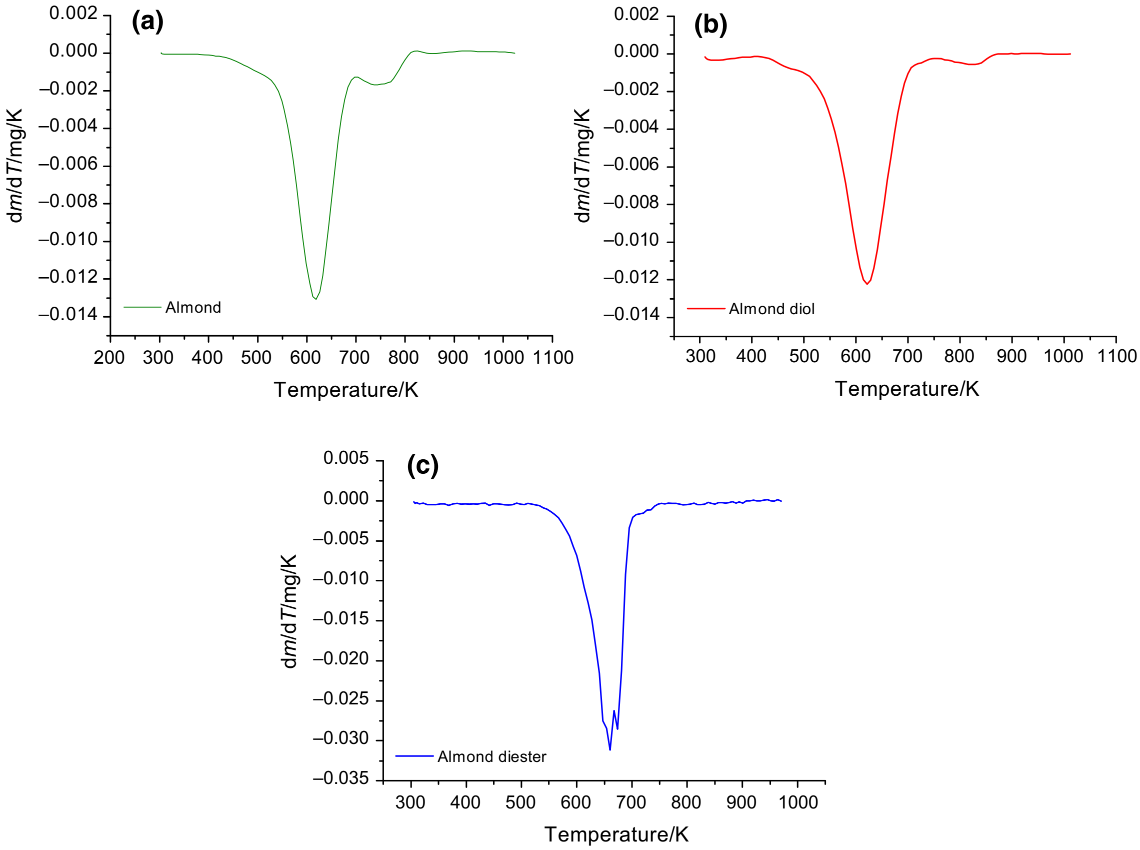

Fig. 9 DTG curves of the macauba almond oil and its derivatives: **a** macauba almond oil, **b** diol from macauba almond oil, **c** diester from macauba almond oil

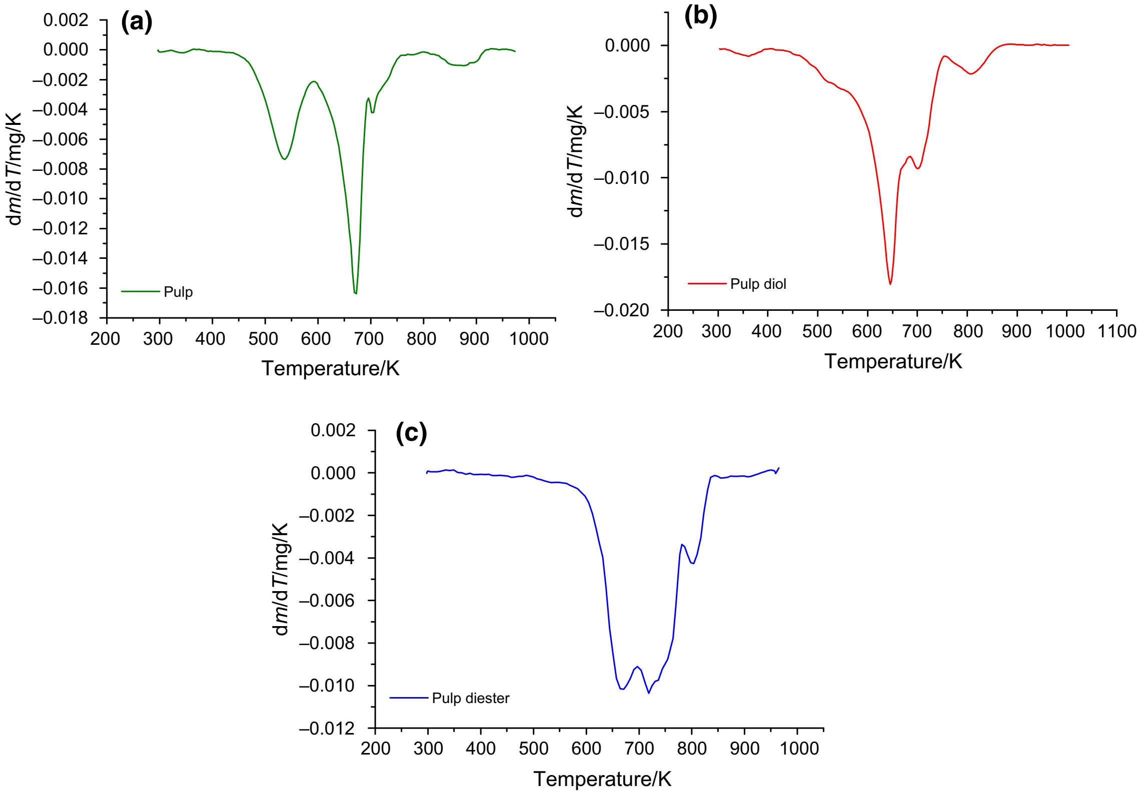

Fig. 11 DTG curves of the macauba pulp oil derivatives: **a** macauba pulp oil, **b** diol from macauba pulp oil, **c** diester from macauba pulp oil

stages may indicate degradation of π bonds, σ bonds and carbonizations, respectively. For its derivatives (diol and diester), two very close peaks and a third at a much higher temperature were seen, which indicates the degradation of the bonds and its carbonization, respectively.

Other physicochemical results

As shown in Table 4, the diols and the diesters have higher kinematic viscosities than their precursors—pulp and almond oils, especially the diol. These observations can be justified due to the higher polarity of the derivatives and, possibly, because of the formation of hydrogen bonds in the diol, which should increase the intermolecular interaction between the carbon chains.

According to Table 5, the viscosity indexes of the vegetable oils are higher than those of the synthetic bases and paraffinic or naphthenic minerals. This is an essential property for a good lubricating oil since the temperature variation in several areas of the lubrication is high (for instance, a car engine heats from room temperature to 200 °C in a few minutes). It is possible to explain this high viscosity index of vegetable oils due to their linear carbon chains, which facilitates the van der Waals interactions. In addition, it is worth mentioning that the viscosity index has become even higher for the diols and diesters, which

Table 4 Kinematic viscosities of macauba oils and their derivatives

Product	Viscosity 40/mm^2 s^{-1}	Viscosity 100/mm^2 s^{-1}
Pulp	40.48	7.97
Pulp diester	54.05	12.30
Pulp diol	223.20	36.40
Almond	28.33	6.45
Almond diester	32.36	8.94
Almond diol	150.60	32.45

Table 5 Viscosity indexes of mineral and vegetable oils

Product	VI
Pulp	174
Pulp diol	214
Pulp diester	233
Almond	201
Almond diol	259
Almond diester	277
PNM	97
Etro	131
NH	3

Table 6 Total acidity number of *in natura* and modified vegetable oils

Product	TAN/mg g^{-1}
Pulp	7.38
Pulp diol	0.73
Pulp diester	0.77
Almond	1.42
Almond diol	0.49
Almond diester	0.48

increases the potential of using these products as lubricating bases.

In relation to the total acidity number, a significant decrease was observed for all four products obtained, in relation to macauba oils (Table 6). It should be noted that a high acidity can lead the lubricating oil to promote rust in metal parts.

Conclusions

We have been able to demonstrate the applicability of macauba oils and their derivatives in three important aspects for lubrication: thermostability, viscosity index and total acidity number. The thermal analysis of macauba vegetable oils and their modified derivatives (diols and diesters) demonstrated how thermal decomposition takes place under inert or oxidizing atmosphere and how the degree of unsaturation and the increase in the polarity of the triglycerides increased their thermostabilities. The diols and diesters produced from macauba almond and pulp oils showed thermostability under oxidizing atmosphere close to the mineral bases commercially used. The most expressive results were observed for the diester produced from almond macauba, a diol of the pulp macauba that surpassed the results of base oils derived from petroleum. It is clear that for the oxidizing atmosphere, the number of π bonds is determinant for the stability of the compounds, due to the formation of peroxides and hydroperoxides at low temperature. It was also possible to note the similarity in the behavior of the diesters and diols in the oxidizing atmosphere, which may be related to ester hydrolysis. Furthermore, it can also be noted that the introduction of oxygen groups (diols and diesters) increased the stability of the modified oils.

Under inert atmosphere, the gain in relation to the thermostability was higher for the diester. As the double bonds are not the predominant fact for stability under this atmosphere, it is possible to infer that the gain was due to the increase in the carbon chain. It is worth mentioning that even with higher chain fatty acids, the macauba pulp oil showed lower thermostability values under both inert and oxidizing atmospheres, which leads to the instability of vegetable oils with a higher degree of unsaturation, regardless of the atmosphere.

This study also evidences the applicability of macauba vegetable oils, due to their high viscosity indexes, superior to those of mineral and synthetic bases. In relation to the diols and diesters, the viscosity indexes were even higher, probably due to the greater polarity of the compounds and consequently the greater interaction of the carbon chains. This makes possible the increase in the working temperature range. In addition, the decrease in the TAN value after the chemical reactions increases the applicability of these oils.

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