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Basestock Oils for Lubricants from Mixtures of Corn Oil and Synthetic Diesters

Loredana Pop · Cosmina Puşcaş · Geza Bandur · Gabriela Vlase · Remus Nuţiu

Abstract Environmentally friendly vegetable oils and their derivatives represent alternatives to mineral-based lubricants. Vegetable oils have high biodegradability and low production costs. Their poor thermo-oxidative stability and poor low temperature properties are disadvantages in their use as lubricant basestocks. In our study we used corn oil and diester mixtures, which become lubricants when additives are introduced. These mixtures of corn oil and di-2-ethylhexyl-adipate (DOA) and di-2-ethylhexyl-sebacate (DOS) offer a wide range of kinematic viscosities, pour points lower than −39 °C and flash points over 218 °C. The diameters of wear scars measured under four-ball testing (40 daN) are less than 0.90 mm and the copper strip corrosion test result is 1a. The differential scanning calorimetry study and thermogravimetric study under nitrogen atmosphere and in synthetic air are reported. From these studies a higher thermal stability was observed for corn oil than for diester oils. The thermo-oxidative instability occurred at temperatures higher than 350 °C. The low production cost of corn oil and its mixtures with diesters makes them an attractive alternative to mineral oil lubricants.

Keywords Lubricants · Vegetable oils · Synthetic esters

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Introduction

It is well known that approximately 85% of fluids used as lubricants are mineral oils [1]. Because of their low biodegradability (lower than 30%), mineral oils are not environmentally friendly. The petroleum resources are limited. So, a legitimate question appears: what will be the source of raw materials for lubricants in the future? We consider that vegetable and synthetic oils and their mixtures may represent such a source.

In order to avoid pollution of the environment, it is necessary to use biodegradable lubricants [2, 3]. The biodegradable oils are esteric and vegetable oils. Esteric oils have a biodegradability of over 90%, and vegetable oils over 95% [2, 4]. While the source of synthetic esteric oils is limited, vegetable oils could be produced in vast amounts [5–7] being a renewable source.

The use of vegetable oils as lubricants offers a wide range of advantages such as: high biodegradability [8], low pollution of the environment, compatibility with additives [9], low production cost [10], wide production possibilities [11], low toxicity, high flash points, low volatility and high viscosity indices [12]. As drawbacks for their use as lubricants [12–14] we mention relatively high freezing points [2] and their low thermo-oxidative stability [15].

Vegetable oils are also a source of fatty acids for polyol esters [16, 17]. These polyol-esters are also base oils for environmentally friendly lubricants.

Synthetic esteric oils offer the advantage of high biodegradability, medium viscosity indices, high thermal-oxidative stability, low pour points, compatibility with additives, low volatility and high flash points. Among their disadvantages are high production costs and limited raw materials for production [18].

In our previous work [9, 18–20] we studied the mixtures of three vegetable oils (sunflower, soybean and rapeseed oils) with diesters (DOA and DOS). These oils mixtures provide a wide range of viscosities for the manufacture of industrial lubricants. To follow up our studies we used in this work the corn oil because it is a renewable source and it has high tribological properties. We also used di-2-ethylhexyl-adipate (DOA) and di-2-ethylhexyl-sebacate (DOS) because they are more industrial accessible than other diesters. The aim of this study was to present the physico-chemical and tribological properties as well as their thermal and thermo-oxidative stability of corn oil and its mixtures with diesters.

Experimental

New base-stock oils obtained from mixtures of a synthetic diester, DOA, DOS and corn oil were studied. In our studies we used food commercial corn oil, type "Bunica" from Romania, with an iodine value of 126 g I_2/100 g oil and fatty acid composition: 11% palmitic acid, 2% stearic acid, 28% oleic acid, 58% linoleic acid, 1% linolenic acid. This composition was determinated by transesterification of triglycerides with methanol, followed by gas-chromatography of methyl esters of fatty acids. The DOA used had 98.5% purity and DOS had 98.7% purity, made by "Solventul" Plant Work from Timisoara, Romania.

The crude oils (diesters and vegetable oils) studied were purified by washing with a solution of 5% NaOH and water. After vacuum volatilization at 10 mm Hg, for 2 h, they were treated with 2% activated Al_2O_3 and filtered, obtaining the base-stock oils. The oil mixtures were prepared at room temperature, with vigorous stirring. They contain 25/75, 50/50 and 75/25 mass% corn oil/diester.

Physico-chemical and rheological properties were determined using ASTM methods specified in Tables 1 and 2. The four-ball machine used was made by the Army Research Institute from Bucharest, Romania, according to the ASTM D4172 method.

Density determinations were made at 20 °C in agreement with ASTM D1298-IP 160 using a Hydrometer P204 (87H) provided by Analis Comp., Namur, Belgium.

The volatility was determined in agreement with ASTM D6184 in an electrical stove using glass pans of 4 cm diameter.

Flash point determinations were conducted in agreement with ASTM D92 using a Cleveland open-cup flash point tester, provided by Analis Comp., Namur, Belgium.

Pour point determinations were made in agreement with ASTM D97 using an automated pour point tester (MPC series), Tanaka, Japan.

The kinematic viscosities were measured at 40 and 100 °C (ASTM D445) with an Ubbelohde viscosimeter P101 and P102 supplied by Analis Comp., Namur, Belgium.

The copper corrosion determinations were made in agreement with ASTM D130 using electrolytic copper plates of the dimensions 76/12/2 mm. For comparison we used the ASTM copper strip corrosion standards supplied by Stanhope-Seta, Surrey, UK.

Abbé refractometer used was A. Krüss Optronic GmbH Germany, type 1997.

The differential scanning calorimetry (DSC) and thermogravimetric (TG)/derivate thermogravimetric (DTG) tests were recorded on Netzsch equipment (DSC 204 Phoenix, system Controller TASC 414/3A), in a nitrogen

Table 1 Physico-chemical and rheological properties of corn oil and di-2-ethylhexyl adipate mixtures

Characteristic	Corn oil	Basestock corn oil/DOA			DOA	Test method
		25/75	50/50	75/25		
Density (g/cm^3)	0.916	0.923	0.920	0.918	0.929	ASTM D1298
Refractive index, n_D^{20}	1.475	1.457	1.463	1.470	1.448	Abbé refract
Colour	6	7	8	8	4	Iodine scale
Volatility, 120 °C (%)	0.21	1.89	1.84	1.02	1.85	ASTM D6184
Acid value, (mg KOH/g)	0.31	0.24	0.26	0.28	0.22	Alcoholic KOH sol. titration
Flash point (°C)	280	218	228	250	207	ASTM D92
Kinematic viscosity, 40 °C (mm^2/s)	32.41	10.87	16.21	22.90	7.85	ASTM D445
Kinematic viscosity, 100 °C (mm^2/s)	8.06	3.18	4.26	5.80	2.37	ASTM D445
Viscosity index	237.5	158.49	181.89	215.49	124	ASTM D2270
Pour point (°C)	−26	−39	−35	−28	≤50	ASTM D97
Copper strip corrosion test, 3h, 100 °C	1a	1a	1a	1a	1a	ASTM D130
Four ball wear test, 40 daN, 1 h (mm)	0.72	0.84	0.78	0.74	0.91	ASTM D4172

Table 2 Physico-chemical and rheological properties of corn oil and di-2-ethylhexyl sebacate mixtures

Characteristic	Corn oil	Basestock corn oil/DOS			DOS	Test method
		25/75	50/50	75/25		
Density (g/cm^3)	0.916	0.911	0.913	0.914	0.907	ASTM D1298
Refractive index, n_D^{20}	1.475	1.459	1.465	1.471	1.454	Abbé refract
Colour	6	7	8	8	5	Iodine scale
Volatility, 120 °C (%)	0.21	1.79	1.87	1.52	1.8	ASTM D6184
Acid value (mg KOH/g)	0.31	0.28	0.27	0.30	0.26	Alcoholic KOH sol. titration
Flash point (°C)	280	226	240	266	225	ASTM D92
Kinematic viscosity, 40 °C (mm^2/s)	32.41	14.3	18.87	25.07	11.4	ASTM D445
Kinematic viscosity, 100 °C (mm^2/s)	8.06	3.91	4.92	6.29	3.2	ASTM D445
Viscosity index	237.5	181.93	203.8	219.19	154	ASTM D2270
Pour point (°C)	−26	−42	−35	−30	−50	ASTM D97
Copper strip corrosion test, 3 h, 100 °C	1a	1a	1a	1a	1b	ASTM D130
Four ball wear test, 40 daN, 1 h (mm)	0.72	0.85	0.86	0.87	0.905	ASTM D4172

atmosphere with 5 °C/min heating rate. The TG and DTG test in synthetic air atmosphere were recorded with a Diamond TG/DTA Perkin–Elmer-2006 instrument, with 5 °C/min heating rate.

The DSC calibration was performed using the standard kit DSC 200 and the program included in the installation kit of the apparatus. The software used was Netzsch-TA4. The sample pan was sealed and then perforated, in order to avoid expansion. We used approximately 10-mg samples, in an aluminum pan. The nitrogen flow was 15 mL/min. There were three determinations for each sample.

The calibration of Perkin–Elmer TG/DTG apparatus was carried out using PIRIS 8.0 software and Perkin–Elmer calibration standards (Pb, Zn, In, Sn, Al, Au, Sb). The quantity of sample used was 8–10 mg, in an open aluminum pan. Synthetic air (20% O_2 spectroscopic purity and 80% N_2) was delivered by Linde Gas supplier, is a compressed air and has a 5.0 purity (99.999% purity). The air flow was 100 mL/min. The software used for data processing was PIRIS 8.0.

Rheological determinations were performed with a pycnometer, calibrated by the Romanian State Metrological Institution form Bucharest.

Results and Discussion

Tables 1 and 2 describe the main physico-chemical and tribotechnical properties of corn oil and DOA and DOS, respectively. All mixtures have flash points above 225 °C and pour points below −26 °C. Because the values for densities and refractive indices present linear increase from diester to corn oil we may conclude that these are physical mixtures. We also notice that kinematic viscosities present values between 2.37 and 8.06 mm^2/s at 100 °C and

between 7.85 and 32.4 mm^2/s at 40 °C. The viscosity indices of the mixtures are better than those of diesters base oils, from 124 to 237. Tables 1 and 2 also show that the volatilities of the mixtures are lower than 1.9%, the wear scar diameter on the four ball machine (40 daN/1 h) is lower than 0,84 mm and the copper corrosion is very low, having a 1a mark.

For a better understanding, we present for comparison the physical characteristics of a light spindle mineral oil [5]:

- density = 0.9 g/cm^3,
- kinematic viscosity at 40 °C = 10.1 mm^2/s,
- kinematic viscosity at 100 °C = 2.48 mm^2/s,
- viscosity index = 52,
- flash point = 160 °C,
- pour point = −10 °C.

So all the properties of diesters and vegetable oils mixtures have better values than those of a mineral oil.

Thermal and Thermo-Oxidative Studies

In Fig. 1 the DSC curve and in Fig. 2 the TG/DTG curves for corn oil are reported. In Figs. 3 and 4 the TG/DTG curves for corn oil/DOA and corn oil/DOS mixtures are also reported. In the DSC curve of corn oil (Fig. 1), recorded in a nitrogen atmosphere, an endothermic peak at −30.3 °C was recorded corresponding to the melting point of the oil. We can also observe an exothermic process at 188.1 °C (where double bond C=C is probably implicated) and a thermal decomposition process at 392.2 °C. The TG/DTG curves of corn oil (Fig. 2) show that 0.61% mass is lost prior to 200 °C. The major decomposition process,
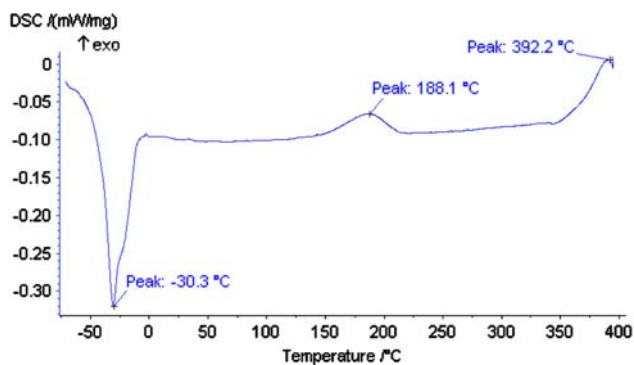
Fig. 1 DSC curve of corn oil in nitrogen atmosphere

with 51.91%, begins at 369.7 °C. The higher decomposition rate, of 89.41% mass loss, is recorded at 400 °C and the total mass loss is registered at 500 °C. The DSC and TG/DTG curves for DOA and DOS were described in our previous works [19].

In Figs. 3 and 4 the TG/DTG curves of corn oil/DOA and corn oil/DOS mixtures in nitrogen atmosphere are recorded. These figures show the temperatures of major decomposition in two stages corresponding to corn oil and diester. First decomposition process corresponds to diester and the second to the corn oil. It also proves that the mixture of these two oils is a physical one.

In Figs. 5, 6 and 7, the TG and DTG curves of corn oil, 50% corn oil–50% DOA and 50% corn oil–50% DOS mixtures in synthetic air recorded are presented. From the TG/DTG curves of corn oil (Fig. 5) we notice that no major decomposition takes place up to 350 °C, compared to the curves recorded in a nitrogen atmosphere. Over this temperature the decomposition process takes place in a different manner. At 435 °C a new minimum is recorded

in the DTG curve, which is probably associated with the double bonds oxidation process.

In the TG/DTG curves of the oil mixture 50% corn oil–50% DOA in synthetic air (Fig. 6) the two decomposition processes specific to the two oil types are shown. The first major decomposition is recorded at 260 °C and corresponds to DOA, and the second one, at 335 °C corresponds to corn oil. The graphic also shows some minor decomposition processes at 400 °C which probably are due to the double bonds oxidation. The total decomposition is registered at approximately 500 °C.

The TG/DTG curves for 50% corn oil–50% DOS mixture in synthetic air present the first major decomposition process at 275 °C and the second, not so pronounced, at 345 °C. Figure 7 also shows some minor decomposition processes at 410–415 °C and the total decomposition is registered at 500 °C.

From the TG/DTG curves recorded in nitrogen atmosphere and synthetic air we notice that in both cases the first decomposition process takes place at close temperatures (limited by the apparatus precision). For the thermograms recorded in synthetic air this first decomposition is major. The second decomposition in synthetic air is recorded at a lower temperature (about 30 °C) than the one recorded in nitrogen atmosphere.

In a previous paper we proved, using TG determinations, that synthetic oils have higher thermal stability than mineral oils [21]. Mixtures of corn oil and diesters constitute a new source of basestock oils for lubricants. The iodine value (unsaturated compounds) of the mixtures decreases, assuring an increase of their thermo-oxidative stability.

Corn oil represents a raw material for lubricants. The mixtures of corn oil and diesters create a source of basestock

Fig. 2 TG and DTG curves of corn oil in nitrogen atmosphere
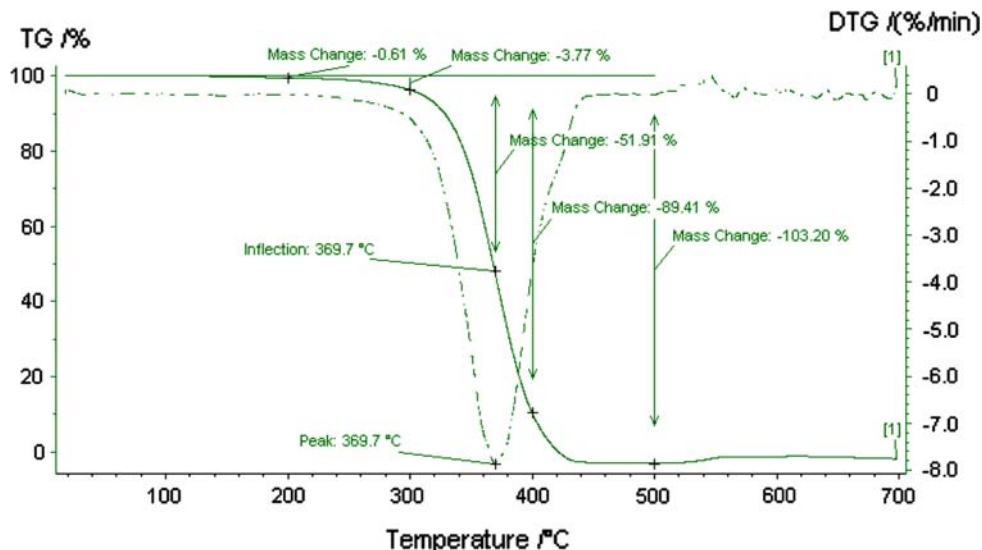
Fig. 3 TG and DTG curves of corn oil (50%)–DOA (50%) mixture in nitrogen atmosphere
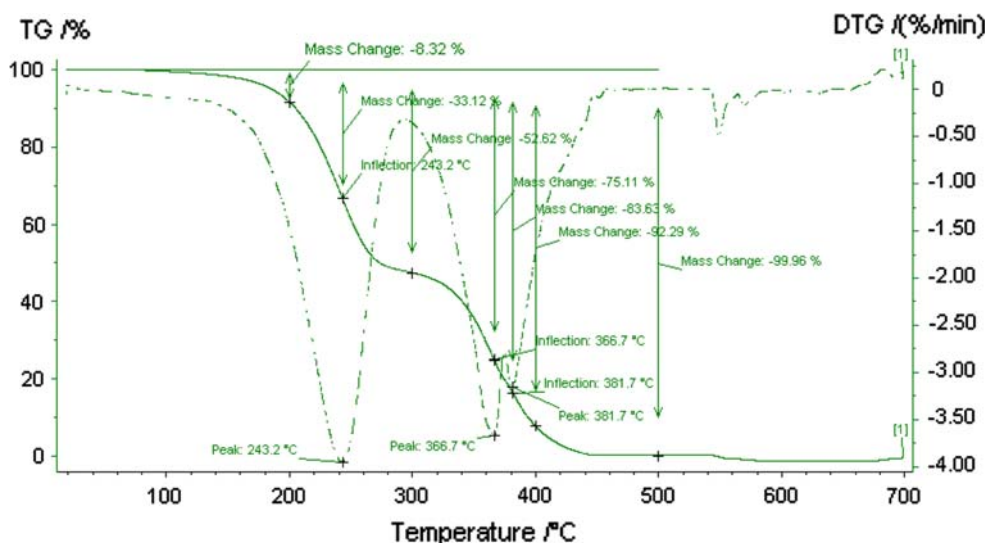

Fig. 4 TG and DTG curves of corn oil (50%)–DOS (50%) mixture in nitrogen atmosphere
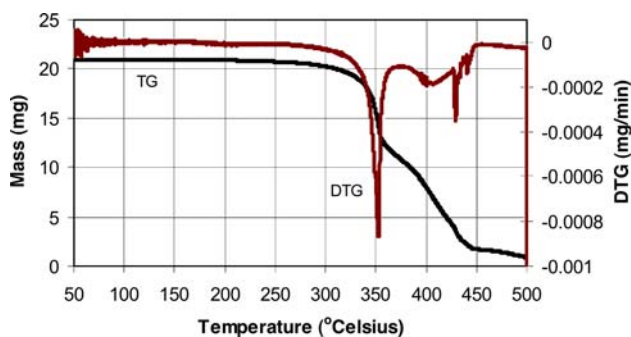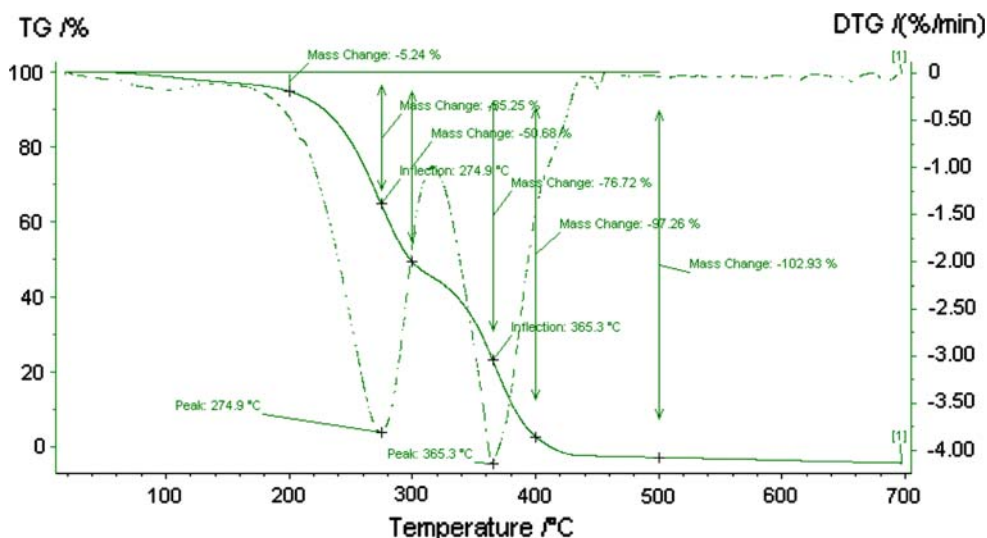

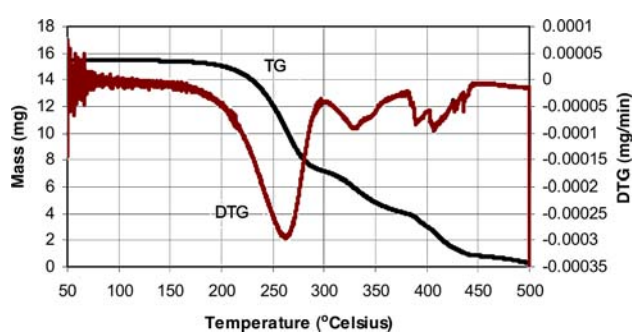Fig. 5 TG and DTG curves for corn oil, in synthetic air

Fig. 6 TG/DTG curves for 50% corn oil–50% DOA mixture, in synthetic air

for lubricants. The viscosity indices of mixtures with over 25% corn oil are between 158 and 237, while the pour points are lower than −39 °C and flash points are over 218 °C.

Thermal and thermo-oxidative studies reveal that the thermal stability of corn oil is better than that of diesters, and thermo-oxidative stability is only influenced by
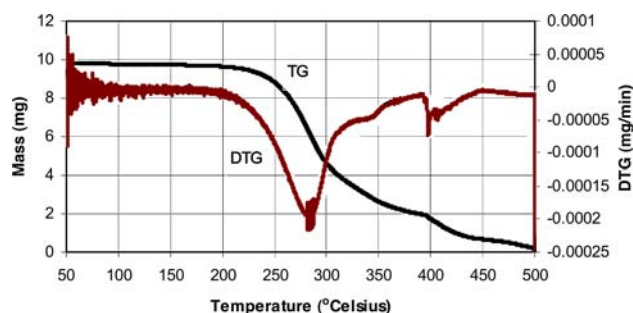
Fig. 7 TG/DTG curves for 50% corn oil–50% DOS mixture, in synthetic air

temperatures over 400 °C. The mixtures of corn and diester oils are physical homogeneous mixtures.

Through their characteristics the mixtures of corn oil and diesters prove to be superior to mineral oils, as presented in the "Results" section. They can be used as lubricants for engines and machines demanding the viscosity values corresponding to those of these mixtures.

References

1. Bartz WJ (2006) Ecotribology: environmentally acceptable tribological practices. Tribol Int 39(8):728–733
2. Novotny-Farkas F, Kotal P, Bohme W (2001) Condition monitoring of biodegradable lubricants. In: 2nd World Tribology Congress, Abstract of Papers, Vienna, p 313–316
3. Boyde S (2001) Optimising the environmental performance of lubricants. In: 2nd World Tribology Congress, Abstract of Papers, Vienna, p 246–250
4. Kodali DR, Nivens S (2001) Biodegradable high performance lubricants derived from natural oils. In: 2nd World Tribology Congress, Abstract of Papers, Vienna, p 235−235
5. Ullmann J (1990) Ullmann's encyclopedia of industrial chemistry, 5th edn (completely revised). 15A, VCH Verlagsgesellschaft mbH, Weinheim, Germany, p 423−518
6. Walsh JW (2002) Determination of triglyceride composition of vegetable oils using HPLC and evaporative light scattering detection. In: IFT Annual meeting and Food Expo, Session 306, Anaheim, California
7. Havet L, Blouet J, Valloire FR, Brasseur E, Slomka D (2001) Tribological characteristics of some environmentally friendly lubricants. Wear 248(12):140–146
8. Battersby NS (2000) The biodegradability and microbial toxicity testing of lubricants—some recommendations. Chemosphere 41:1011–1027
9. Puşcaş CL, Bandur G, Modra D, Nuţiu R (2005) Consideration about using vegetable oils in lubricants. In: World Tribology Congress III, September 12−16, Washington DC, USA, p T-17
10. Krzan B, Vizintin J (2003) Tribological properties of environmentally adapted universal tractor transmission oil based on vegetable oil. Tribol Int 36:827–833
11. Guzman D (2002) Vegetable oil in lubricants and additives slated for strong growth. Chemical Market Reporter, June 10, 1−2
12. Santos JCO, Santos IMG, Conceiço MM, Trindade MFS, Souza AG, Prasad S, Fernandes Jr. VJ, Araújo AS, (2004), Thermoanalytical, kinetic and rheological parameters of commercial edible vegetable oils. J Therm Anal Calorim 75:419–428
13. Buzás I, Simon J, Holló J (1977) Effect of the experimental conditions on the thermooxidative behaviour of vegetable oils. J Therm Anal Calorim 12:397–405
14. Dweck J, Sampaio MSC (2004) Analysis of the thermal decomposition of commercial vegetable oils in air by simultaneous TG/DTA. J Therm Anal Calorim 75:385–391
15. Fox NJ, Tyrer B, Stachowiak GW (2004) Boundary lubrication performance of free fatty acids in sunflower oil. Tribol Lett 16(4):275–281
16. Schuchart U, Sercheli R, Vargas RM (1998) Transesterification of vegetable oil: a review. J Braz Chem Soc 9(1):199–210
17. Gryglewicz S, Piechocki W, Gryglewicz G (2003) Preparation of polyol esters on vegetable and animal fats. Bioresour Technol 87:35–39
18. Andraşescu C, Modra D, Nuţiu R (2003) Tribological and rheological properties of some lubricant oils obtained from mixtures of vegetable and synthetic oils Ann West Univ Timişoara Ser Chem 12(3):1467–1473
19. Puşcaş CL, Bandur G, Modra D, Nuţiu R (2006) Mixtures of vegetable oils and di-2-ethylhexyl-sebacate as lubricants. J Syn Lubr 23:185–196
20. Puşcaş C, Modra D, Bandur G, Nutiu R (2006) Uleiuri de bază pentru lubrifianţi obţinute din amestecuri de uleiuri vegetale şi di-2-etil-hexil-adipat. Mater plast 43(2):138–145
21. Nutiu R, Farcas M, Gros I, Maties M (1987) Low viscosity synthetic lubricating oils base don diesters. In: Tribotehnica '87, The 5th Conference on Friction, Lubrication and Wear, Bucuresti, 24−26 Sept, p 177