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Influence of Oxidation on the Rheological Parameters of Vegetable Oils

Ioana Stanciu

1 University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry, 4-12 Elisabeta Blvd, 030018, Bucharest, Romania.

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ABSTRACT

This article presents the study of the influence of the oxidation of vegetable oils on the rheological parameters. The viscosity of oxidized vegetable oils in relation to non-oxidized ones increases for soybean oil and then corn oil. For oxidized and non-oxidized olive and rapeseed oils, there are no increases as in the previous case.

Keywords: Behavior, Oils, Non-oxidized, Vegetable, Shear rate.

Introduction

In the strict sense, the term "lubricating material" refers to the products used to lubricate sliding or rolling tribosystems. However, products similar to them in terms of composition, production processes and properties, but intended for other purposes, are also considered lubricating materials. In Germany's statistical studies, the notion of "lubricating materials" includes products that are obtained in particular on the basis of mineral oils, partially or totally of synthetic oils intended for use as lubricating materials, media for the transmission of force and heat, some dielectric materials and technological liquids.

The conditions regarding the quality of lubricating materials and related products are regulated by international (ISO) and national standards or by generally accepted specifications, edited by major manufacturers and users, but also by international organizations¹⁻³. For example, the conditions regarding the quality of oils for engines and cars, of transmission oils are regulated by the minimum conditions according to the classification of SAE (Society of Automotive Engineers), API (American Petroleum Institute), MIL (US Ministry of Defense) and CCMC (Committee of Constructors of Automobiles of the European Union). The minimum conditions for insulation and hydraulic oils are regulated by IEC (International Electric Commission) or CIGRE (International Conference on Large Power Plants) specifications.

Lubricants and products that contain mineral oils and are in contact with food products must comply with the conditions, instructions for food products, in particular the conditions of the Federal Administration for the control of the quality of food and pharmaceutical products (FDA), but also

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the conditions of the European Union, through the acquis the community.

Apart from this, the specifications of the producing and user companies must be taken into account.

Analyzes and tests of lubricating materials are based on test methods standardized by the International Organization for Standardization (ISO), European Committee for Standardization (CEN)1, American Society for Testing and Materials (ASTM)2, which are often similar or with small differences between them². When analyzes and tests of lubricants are requested, it is good to specify exactly what standard or norms must be achieved.

Although the term lubricant often suggests oils or thick greases, these being the most used lubrication materials; the notion of lubricant is much broader, being represented by a wide variety of substances in all states of aggregation.

The behavior of the lubricant in a tribosystem is very important and therefore special attention is paid to its study and testing in various conditions.

The working conditions of modern machines and equipment have determined intense research to find suitable lubricants, capable of working at high speeds and pressures, but also at very high or very low temperatures.

Numerous methods of improving the lubricating properties of existing oils and greases have appeared in this way, while also creating new lubricants.

Efforts have been made to obtain antifriction materials or surface coatings capable of partially or even completely taking over the functions of lubricants in very special working conditions⁴⁻⁸. Bearings made of plastic materials, where the use of a lubricant is no longer necessary, coatings with phosphates or sulfated layers that considerably improve lubrication in the case of particularly heavy functional conditions, bearings made of porous materials to create lubricant reserves, etc. The functions of a lubricant are:

The lubrication function

It aims to separate the surfaces with relative movements in order to avoid wear or at least to keep the wear within admissible limits for the operation of the system; the lubrication function imposes on the oils that are among the most used lubricants, optimal values for viscosity, viscosity index and an appropriate behavior in terms of unctuousness, the property of adhesion of the lubricant to the respective metal surface and the formation of an adsorbed molecular film, difficult to detach from the contact surface.

The cooling function

It is of particular importance, taking into account the fact that part of the heat produced in contact is evacuated with the help of the lubricant (solid greases and solid lubricants, for example, have poor heat evacuation qualities).

The chemical protection function

It is achieved by isolating the surfaces to which the lubricant film adheres, against the action of aggressive agents; corrosion wear is thus mitigated, through the appearance of chemical compounds and protective layers.

The sealing function

It is achieved by the very presence of oil between the friction surfaces, avoiding the penetration of foreign particles into the contact area (however, a reverse trend is also possible, the oil can attract metal particles into the contact area and thereby intensifies the wear of abrasion).

The lubricant cannot be considered an auxiliary element in a tribosystem, but indispensable for the trouble-free operation of the friction areas [9]. The criteria for classifying lubricants are diverse. A first criterion would be the state of aggregation. From this point of view there are:

Gaseous lubricants: In some applications, air or other gases (helium, carbon dioxide, hydrogen, nitrogen, etc.) which also constitute the surrounding environment of the tribosystem, contribute, under certain conditions of load and speed, to the separation of bodies in contact; steam can also be included in this group.

- Liquid lubricants: Include oils of any nature, water or other non-conventional fluids (glycerin, alcohol, etc.), but also emulsions as biphasic liquids and synovial fluid (as a pseudo-plastic lubricant), etc.
- **Semi-solid or viscous-plastic lubricants such as greases:** In general, the lubricants in this group are composed of a liquid lubricant and thickening agents that can be of a very diverse nature, from metallic soaps of calcium, lead, lithium, sodium, aluminum, to polymers.
- **Solid lubricants:** this group includes lamellar substances, such as graphite and molybdenum disulfide, polymers such as polytetrafluoroethylene, some metal alloys; the latter could be analyzed here because, before being introduced into the required contact, they are solid, but during operation they soften or fluidize, behaving like a grease that is very resistant to temperature or to certain environmental conditions. This group can also include some oxides (PbO₃, SiO₂, Cr_2O_3 , etc.) and ceramic-based materials, but used in very narrow applications (casting glass in molds, etc.).

Another classification criterion is the nature of the lubricant, which can be: mineral, synthetic, vegetable or animal.

Biodegradable lubricants based on vegetable oils are of particular interest due to mainly economic advantages compared to biodegradable lubricants based on polyglycols or synthetic ester oils.

The relatively inexhaustible source as well as the non-toxicity and rapid biodegradability of vegetable oils are their main advantages. Until the 19th century, the basic components used in the manufacture of lubricants were vegetable oils and animal fats. They were compatible with the environment and biodegradable. Materials like water, vegetable oils, animal oils were used successfully 4-15.

Material and methods

To determine the variation of viscosity with temperature and shear rate, the Rheotest2 installation was used.

The oils (soybean, corn, olive and rapeseed obtained by procedures of mechanical processing were oxidized using a the installation composed of: 1-air pump, 2-air flow meter, 3-air filter, 4-test tube with oil sample, 5-thermostatic bathroom. at temperatures of 120°C and 130°C, for 5 h and 10 h, respectively. The dynamic viscosity of the oxidized oil was determined for the temperature range 30 $^{\circ}$ C ÷ 90 $^{\circ}$ C and the shear speed 3.3 s⁻¹ ÷ 80 s-1. At both temperatures and periods 5 h and 10 h oxidation, respectively test temperatures, the dynamic viscosity decreases with the increase in the shear rate $16-23$.

Results and discussion

Figures 1 and 2 represent the dependence of the dynamic viscosity of oxidized vegetable oils at a temperature of 120 $^{\rm o}$ C and shear speeds 3.3 s⁻¹ and 80 s-1.

Fig. 1. Dynamic viscosity of oxidized vegetable oils at a temperature of 120°C, tested at a shear rate of 3.3 s⁻¹ and a **temperature of 30°C (a), respectively a temperature of 90°C (b)**

Fig. 2. Dynamic viscosity of oxidized vegetable oils at a temperature of 120°C, tested at a shear rate of 80 s⁻¹ and a **temperature of 30°C (a), respectively a temperature of 90°C (b)**

In order to highlight the dynamic viscosity variations, the olive and rapeseed oils were oxidized at a temperature of 130°C and the values obtained for the dynamic viscosity are analyzed further.

120 unoxidized oxidised 5h Dynamic viscosity, mPa.s 90 xidised 10h 60 30 $\boldsymbol{0}$ canola oil olive oil (a)

The dynamic viscosity values of olive and rapeseed oils, oxidized for 5 h, do not register important increases compared to those of non-oxidized oils (Figure 3 and 4).

Fig. 4. Dynamic viscosity for oxidized oils at 130°C, tested at shear speed of 80 s-1, temperature of 30°C (a) and 90°C (b)

Significant differences for the dynamic viscosity values of the analyzed oils are observed when the oxidation time increases, from 5 h to 10 hours. After the oxidation period of 10 h, the olive oil tested at the shear rate of 3.3 s^{-1} and the test temperature of 30°C, has an increase in dynamic viscosity of 52.51% compared to the non-oxidized olive oil. The oxidized rapeseed oil, tested under the same conditions, shows an increase in dynamic viscosity of 77.4%. Corresponding to the shear rate of 3.3 s-1 and the test temperature of 90°C, the olive oil has a dynamic viscosity increase of 22.36% compared to the unoxidized olive oil, while the oxidized and tested rapeseed oil under the same conditions, they record an increase in dynamic viscosity of 44.62%.

At a shear rate of 80 $s⁻¹$ and a temperature of 30°C, olive oil has an increase in dynamic viscosity of 62.71%, compared to non-oxidized oil. Rapeseed oil registers an increase in dynamic viscosity of 87%. For the shear speed of 80 s⁻¹ and the temperature of 90°C, the increase in dynamic viscosity is 24.53% for olive oil and 36.1% for rapeseed oil, compared to non-oxidized oils.¹⁶⁻¹⁸.

Conclusion

Analyzing the percentage decrease in dynamic viscosity with temperature of non-oxidized vegetable oils, it can be observed:

- In the case of a shear speed of 30 $s⁻¹$, soybean oil has the best viscosity stability dynamics with temperature.
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For the speed of 80 $s⁻¹$, corn oil has the best stability of dynamic viscosity with temperature.

From the data obtained, it can be concluded that rapeseed oil and, in particular, olive oil have high oxidation stability. Corn oil and soybean oil have a dynamic viscosity with poor oxidation stability, the oxidation process for the latter oils starting at lower temperatures than in the case of rapeseed and olive oils. These biodegradable oils show comparable performances even better than mineral oils used for the same applications.

Conflict of interest

The author declare that we have no conflict of interest.

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