COMPARISON OF RHEOLOGICAL PROPERTIES OF NEW AND USED BIOLUBRICANTS

Ján CSILLAG[1], Ana PETROVIĆ[1], Vlasta VOZÁROVÁ[1], Matúš BILČÍK[1], Monika BOŽIKOVÁ[1], Tomás HOLOTA[2]

[1]Department of Physics, Faculty of Engineering, Slovak University of Agriculture in Nitra, Slovakia
[2]Department of building equipment and technology safety, Faculty of Engineering, Slovak University of Agriculture in Nitra, Slovakia

Abstract
This paper deals with research focused on possibilities of usage of physical methods while evaluating the chosen technological characteristics of biodegradable lubricants. Biodegradable lubricants UTTO were the subject of examination and they were compared with a sample of mineral oil Ultra. We focused on density, viscosity, fluidity and pour point. Results show that the temperature is an important factor which influences thermophysical properties. Results of the thesis include the acquired dependencies of density and viscosity on temperature described by linear and exponential regression equation of Arrhenius type. Pour point of individual samples was determined by usage of the differential scanning calorimetry.

Key words: *biodegradable lubricants; density; viscosity; fluidity; thermal analysis.*

INTRODUCTION

The term ecological lubricant is not well defined in the literature. Such materials that do not have a negative impact on the environment are generally considered as organic substances. In the case of lubricants, these are biodegradable lubricants, or biomass and require rapid and particularly complete biodegradability by microorganisms. Ecological lubricants can equally replace lubricating oils and greases on mineral base. The economic benefits of organic products are largely because the operating costs are reduced when they are used. The use of ecological lubricants is the best alternative in practice (*Beleš & Zelenka, 2010). Bhusham (2001)* adds that in the future, the environmental properties of a lubricant should take precedence over performance. The aim of our paper is a comparison of ecological lubricant with mineral oil by using the physical methods. It is mainly about measuring the temperature dependencies, such as the dependence of viscosity and density on temperature and their comparison. We will compare new samples and samples which were cyclically stressed in a special test device.

MATERIALS AND METHODS

Dynamic viscosity η (Pa.s), which is the ratio of shear stress τ (Pa) and share rate γ (s^{-1}) as shown in eq. 1.

$$\eta = \frac{\tau}{\gamma} \tag{1}$$

was measured on the digital rotary viscometer Brookfield DV2TLV. Generally, the dynamic viscosity depends on several quantities or variables, such as physical-chemical structure of the sample, temperature, pressure, time, and shear rate (*Severa & Los, 2008*). Measurements of the dynamic viscosity in the temperature interval from temperature 20 °C to 100 °C, are provided. Density of oils is measured by the digital density meter Mettler Toledo DM40 in the temperature interval from 0 °C to 100 °C. The measuring principle of density is based on the electromagnetic induced oscillation of the U-shaped glass tube. The fluidity is an ability of matters to flow. The measure of fluidity is expressed by viscosity. It is defined as a reciprocal of dynamic viscosity. Lubricating oil gradually stops flowing at low temperature until it reaches the point which is referred to as the pour point. The pour point is the highest temperature at which the lubricant no longer flows under the prescribed test conditions. The result is reported in °C (*Stopka, 2014*). The changing of the liquid to the solid can be defined in two stages. The first stage starts to exclude fine hydrocarbon crystals from the oil, the second stage forms a crystal lattice by gradual cooling which prevents the movement of the liquid. This temperature is called a pour point. The value of the pour point largely depends on the chemical composition of the oils and generally increases with the size of the molecules. The pour point of most engine and gear oils ranges from -10 °C to -30 °C

(*Lahučký & Tóth, 2011*). The pour point is also the limit of oil usability. It characterizes the ability of the oil to flow at low temperatures. As *Abdullah et al. (2016)* published in his article, a large proportion of ecological lubricants are used in industrial machines that operate at low temperatures. Exploring the pour point is therefore an important information for the application of lubricants. To measure the pour point we used Mettler Toledo DSC 1. In the case of DSC calorimeters with thermal flow the power difference is measured directly, but this quantity is derived from the temperature difference between the sample and the reference substance (*Šimon, 2000*). From the difference between the temperature of the sample and the temperature of the reference cup (DSC sensor), the DSC 1 module calculates the heat flow signal and offers the possibility of differential calorimetry. The initial peak temperature is counted when the curve begins to deviate from the baseline. The onset and endset temperatures (extrapolated start and end) are the points where the tangents, guided by the inflection points of the curve, intersect with the baseline. The peak temperature is the point which is corresponded by the maximum heat flow, and the final temperature is the point at which the curve stops deviating from the baseline (*Klubal & Ostrý, 2014*). The resulting peak, or the course of the whole measurement, can be influenced by several factors that appear on the graph. The issue of undesirable DSC artefacts was addressed by *Tarasov (2012)*.

We will measure the ecological lubricant Mol Farm Bio UTTO which is also a biodegradable tractor oil. The oil is made from vegetable natural oil and special additives. The oil is designated for use in the gearbox and hydraulic circuit of agricultural and construction machines. It is used for lubrication of gearboxes, hydraulic circuits, for agricultural and construction machinery. Primary biodegradation per CEC L-33-A-93 is 90% within 21 days and test method CEC L-33-A-93 (28 days) is 91 % (*Majdan et al., 2011a*). For comparison, we had MOL Traktol NH Ultra. It is a mineral oil of the same use as UTTO, but the primary biodegradation is almost 45%. Sample was worn in special laboratory equipment, which was at the Department of Transport and Handling at Faculty of Engineering, Slovak University of Agriculture in Nitra. The laboratory equipment was constructed from the elements of the hydraulic systems of the tractors. The equipment uses a tractor gear pump type UD 25 *(Jihostroj Velešín, Czech Republic*), which is used by Zetor Forterra (*Zetor Brno, Czech Republic*). The laboratory equipment of the hydraulic system makes it possible to simulate the pressures of the tractor's hydraulic system in a significantly shorter time than during the operating of the tractor. Hydraulic pump was loaded with cyclically changing pressure from 0.1 MPa to the nominal pressure of the hydraulic pump 20 MPa during the test. It is these pressure surges that burden the tractor's hydraulic system the most (*Tkáč, Majdan & Kosiba 2014*).

RESULTS AND DISCUSSION

In Fig. 1 – Fig. 4 we monitor the temperature dependence of dynamic and kinematic viscosity, density and fluidity of biodegradable oil Mol Farm Bio UTTO.

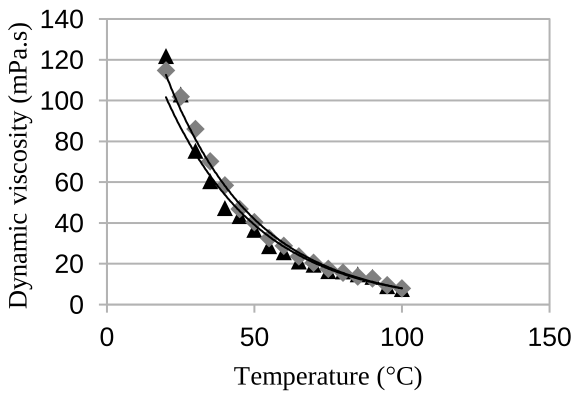

Fig. 1 Temperature dependencies of new oil UTTO ▲ and oil after 750 000 cycles ◆ of dynamic viscosity.

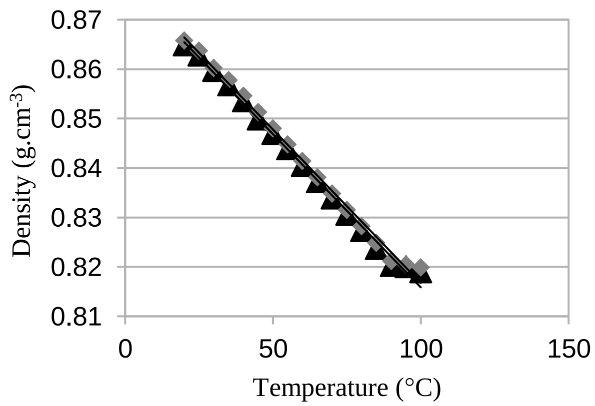

Fig. 2 Temperature dependencies of new oil UTTO ▲ and oil after 750 000 cycles ◆ of density.

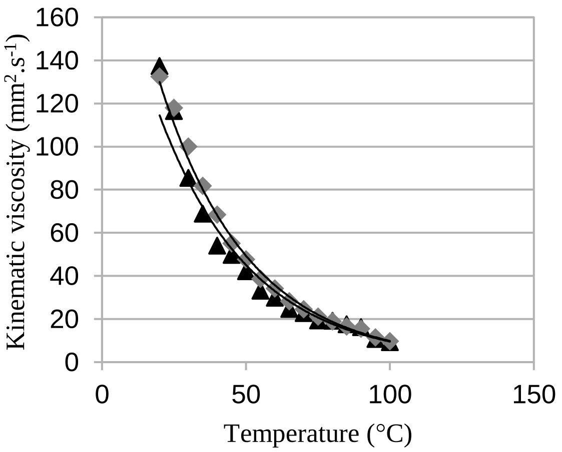

Fig. 3 Temperature dependencies of new oil UTTO ▲ and oil after 750 000 cycles ◆ of kinematic viscosity.

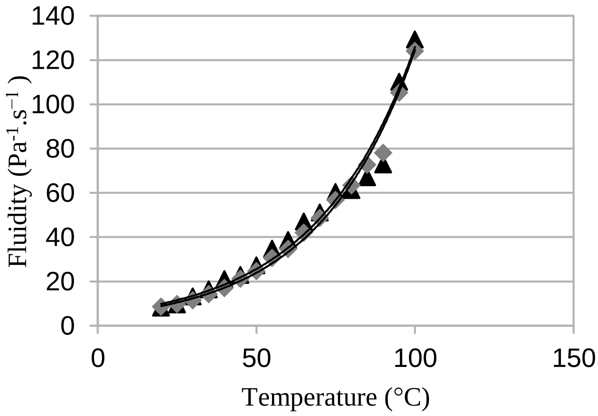

Fig. 4 Temperature dependencies of new oil UTTO ▲ and oil after 750 000 cycles ◆ of fluidity.

Listed dependences for all samples were described by the mathematical regression equation – decreasing exponential dependence of the Ahrrenius type:

$$\eta = Ae^{-Bt} \tag{2}$$

where A and B are coefficients of the regression equation.

The new sample reached the highest viscosity values at temperature up to 25 °C. With the rising temperature, the viscosity of the new sample decreased most significantly. At the temperature of 40 °C, the new sample had a dynamic viscosity value of 47.35 mPa.s and for the cyclically burdened sample the value was 58.53 mPa.s. This phenomenon was up to about 75 °C. From this temperature, the viscosity of the new sample increased again, in the comparison with the cyclically burdened sample. The determining coefficients of the exponential regression equation reach a high value, for the new sample it was R^2= 0.9786 and after 750 000 cycles it was R^2= 0.9954. From these values we can say that the given regression equations describe the obtained dependences very accurately. Measurement results of oils density are presented in the graph on the Fig. 2. It is shown that density linearly decreases with temperature of oil. *Kosiba et al. (2016)* dealth with the effect of biodegradable synthetic fluid on operation of tractor hydraulic circuit, using the same biodegradable lubricant UTTO. Density, they measured, at 15 °C was 931 kg.m^{-3} and ours was 867 kg.m^{-3}. Their sample also was subject to a measuring of kinematic viscosity at 40 °C (67.52 mm^2.s^{-1}), while our new sample had 54.15 mm^2.s^{-1}. The manufacturer reports the values of kinematic viscosity at the temperature of 40 °C equal 58.14 mm^2.s^{-1}. Our measurement revealed a value of 68.48 mm^2.s^{-1} after the cyclic stressing of the sample. Similar small differences were also at the temperature of 100 °C, where the manufacturer's kinematic viscosity value for both samples differed from our measured value by 1 mm^2.s^{-1}. From Fig. 4, we can see that the fluidity increases with the increasing temperature. The new sample reaches higher values of fluidity except for the temperature range between 80 – 90 °C. At the temperature 85 °C, the stressed sample had a fluidity of 72.85 Pa^{-1}.s^{-1} and the new sample of 67.08 Pa^{-1}.s^{-1}. The fluidity of the new sample increased again from this temperature.

Tab. 1 Defining the exothermic course of the pour point for the UTTO sample

	New Sample	Sample after 750 000 cycles
Pour point (°C)	-34.11	-33.75
Initial exothermic reaction temperature (°C)	-32.61	-31.89
Final exothermic reaction temperature (°C)	-35.97	-35.6

From the measured values from the DSC module (Tab. 1), we see that the interval of the temperature stability for the new sample ends at the value of -32,61 °C, when the exothermic reaction begins. The new UTTO sample reached the pour point at the temperature of -34.11 °C, while the *Kosiba et al. (2016)* got the -48 °C. A sample after 750 000 cycles had an exothermic peak value and a pour point at the temperature of -33.75 °C. For this sample, the end of the temperature stability interval is at the value of -31.89 °C.

In Fig. 5 – Fig. 8 we monitor the temperature dependence of dynamic and kinematic viscosity, density and fluidity of mineral oil MOL Traktor NH Ultra.

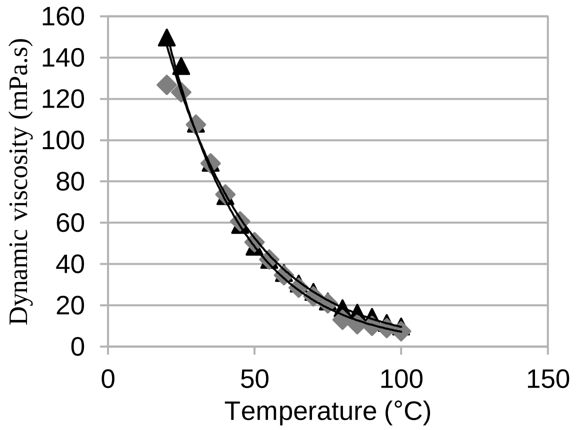

Fig. 5 Temperature dependencies of new oil Ultra ▲ and oil after 750 000 cycles ◆ of dynamic viscosity.

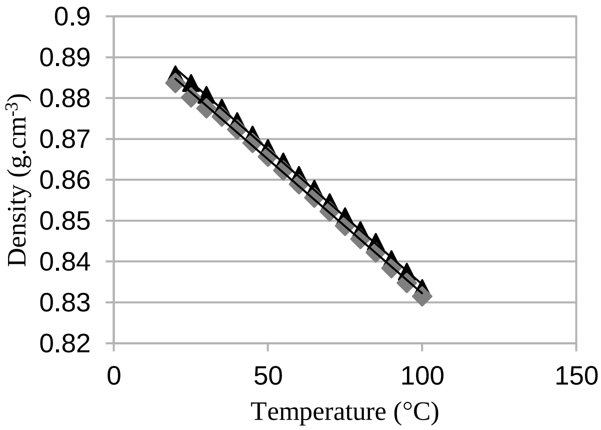

Fig. 6 Temperature dependencies of new oil Ultra ▲ and oil after 750 000 cycles ◆ of density.

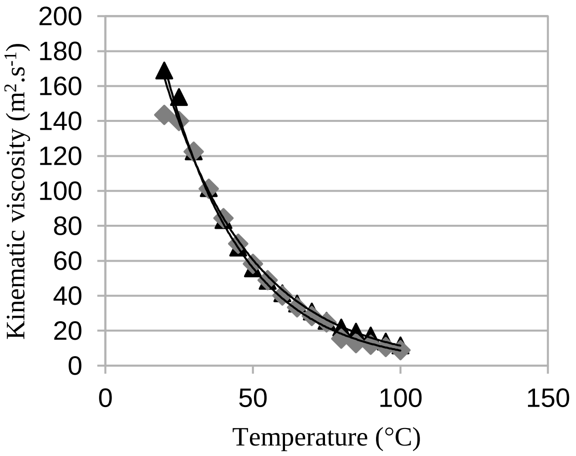

Fig. 7 Temperature dependencies of new oil Ultra ▲ and oil after 750 000 cycles ◆ of kinematic viscosity.

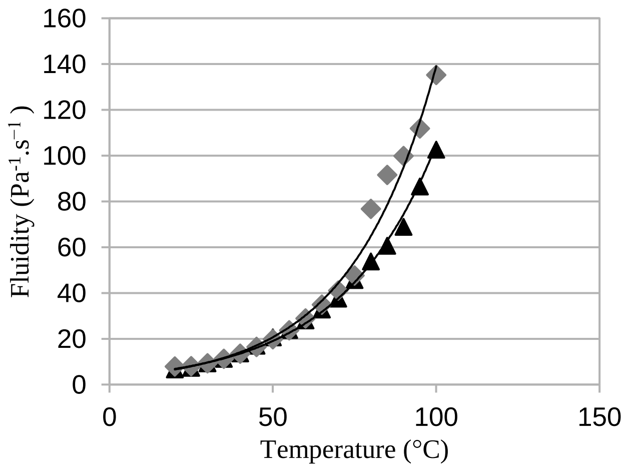

Fig. 8 Temperature dependencies of new oil Ultra ▲ and oil after 750 000 cycles ◆ of Fluidity.

For both samples we can see that with increasing temperature the dynamic viscosity exponentially decreases. In the range between 25 °C – 35 °C the new sample achieved very similar values of dynamic viscosity as the sample after the 750 000 cycles. At the temperature of 40 °C the sample after 750 000 cycles reached the viscosity value of 73.74 mPa.s while the new sample reached the value of 72.86 mPa.s. From the temperature of 55 °C we can see the increase of viscosity value again for the new sample. The sample after 750 000 cycles reached lower values of viscosity from the temperature of 80 °C. The coefficients of determination reach high values, for the new sample a value of 0.995 and for the sample after cyclic stressing the value of 0.988. The sample after 750 000 cycles had lower values of density – the new sample had a density value of 0.8755 $g.cm^{-3}$ at the temperature of 40 °C and the sample after 750 000 cycles reached the density value of 0.8723 $g.cm^{-3}$. It is shown that density linearly decreases with temperature of oil. The manufacturer lists a kinematic viscosity value of 80 $mm^2.s^{-1}$ at the temperature of 40 °C. We measured the value of 83.35 $mm^2.s^{-1}$ for the new sample, and a value of 84.53 $mm^2.s^{-1}$ for the cyclically stressed sample. The value of the new sample differs from the data given by the manufacturer by 0.8 $mm^2.s^{-1}$ at the temperature of 100 °C. With the cyclically stressed sample the kinematic viscosity dropped by 1.9 $mm^2.s^{-1}$ from the manufacturer's data. The fluidity exponentially increases with the increasing temperature and from the temperature of 80 °C, the sample after cyclic stressing has higher values than the new sample.

Tab. 2 Defining the course of the exothermic pour point for the ULTRA sample

	New Sample	Sample after 750 000 cycles
Pour point (°C)	-33.12	-36.32
Initial exothermic reaction starting temperature (°C)	-31.17	-35.17
Final exothermic reaction temperature value (°C)	-36.06	-38.19

In the Tab. 2 we can see that the temperature stability for the new sample ends at -31.17 °C and the pour point is at the value of -33.12 °C. The sample after 750 000 cycles reaches the end of the temperature stability at -35.17 °C and the pour point reaches the value of -36.32 °C. For mineral oil, the cyclically stressed samples reached lower initial peak rising values, thus the exothermic reaction in these samples had occurred at a lower temperature. This may be related with a change in the lubricant structure in cyclic stress and thus the transition from liquid to solid occurs at lower temperatures.

CONCLUSIONS

Measured temperature dependencies of density, dynamic and kinematic viscosity, and fluidity show good accordance with published results (*Hlaváč et al., 2014*; *Božiková & Hlaváč, 2014*). Presented linear and exponential dependencies of physical properties on the temperature indicate significant impact of the temperature on oils thermal properties. Both lubricants have the same use and the results presented by our measurements prove only small differences between the mineral and ecological lubricants.
Several authors state that the comparison of biodegradable and mineral oils has yielded comparable results (*Kardjilova et al., 2013, Majdan et al., 2011b, Tkáč et al.,2012*). *Beleš & Zelenka (2008)* also devoted their works to the ecological lubricants and their broad usage in practice. These lubricants help to clean the equipment from deposits and carbon. *Kačmár (2014)* emphasizes the use of ecological lubricants mainly in agriculture, forestry and environment protection.

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Corresponding author:
Ing. Ján Csillag, Ph.D., Department of Physics, Faculty of Engineering, Slovak University of Agriculture in Nitra, Slovakia, Tr. A. Hlinku 2, 949 76 Nitra, e-mail: jan.csillag@uniag.sk