Temperature Dependence of Dynamic Viscosity and DSC Analysis of the Plantohyd samples

Teplotná závislosť dynamickej viskozity a DSC analýza vzoriek Plantohydu

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Abstract

The present work deals with physical properties – dynamic viscosity and DSC analysis of biodegradable hydraulic fluids and lubricating oils based on vegetable oils or on synthetic esters – PLANTOHYD S series (15S, 46S) and PLANTOHYD N series (40N). The brief characterization of investigated material is presented. This article presents the experimental results of measuring the main rheological characteristic – dynamic viscosity of samples of Plantohyd. Measurements were made under laboratory conditions with digital viscometer DV-3P Anton Paar. Examination of the dynamic viscosity in the temperature interval from -10 °C to 50 °C was made. The exponential dependency of viscosity on the temperature for the each sample was obtained in accordance with Arrhenius equation. DSC (Differential Scanning Calorimetry) analysis providing information on thermal effects in the sample subjected to the temperature programme was realised in the temperature range from -30 °C to 100 °C by using differential scanning calorimeter DSC 822e METTLER TOLEDO. It was determined endo/exo thermal effects and temperature interval with no thermal effects for each sample of Plantohyd.

Keywords: DSC analysis, dynamic viscosity, Plantohyd

Abstrakt

Predkladaná práca sa zaoberá fyzikálnymi vlastnosťami – dynamickou viskozitou a DSC analýzou biologicky rozložiteľných hydraulických kvapalín a lubrikačných olejov na báze rastlinných olejov alebo syntetických esterov - PLANTOHYD S série (15S, 46S) and PLANTOHYD N série (40N). V práci je prezentovaná stručná charakteristika skúmaného materiálu. V príspevku sú uvedené experimentálne výsledky merania dôležitej reologickej vlastnosti – dynamickej viskozity vzoriek Plantohydu. Merania boli vykonané v laboratórnych podmienkach pomocou digitálneho viskozimetra DV-3P Anton Paar. Bolo uskutočnené skúmanie dynamickej viskozity v teplotnom intervale od -10 °C do 50 °C. Boli získané exponenciálne závislosti dynamickej viskozity od teploty pre každú vzorku v súlade s Arrheniovou rovnicou. DSC (diferenčná kompenzačná kalorimetria) analýza poskytujúca informácie o tepelných efektoch vo vzorke podrobenej teplotnému režimu bola realizovaná v teplotnom intervale od -30 °C do 100 °C použitím DSC kalorimetra s tepelným tokom DSC 822e METTLER TOLEDO. Zistené boli endo/exo tepelné efekty a teplotný interval bez tepelných efektov pre každú skúmanú vzorku.

Kľúčové slová: DSC analýza, dynamická viskozita, Plantohyd

Detailný abstrakt

Predkladaná práca sa zaoberá fyzikálnymi vlastnosťami – dynamickou viskozitou a DSC analýzou biologicky rozložiteľných hydraulických kvapalín a lubrikačných olejov na báze rastlinných olejov alebo syntetických esterov - PLANTOHYD S série (15S, 46S) and PLANTOHYD N série (40N). Uvedené oleje sú odporúčané pre využitie v mobilných alebo stacionárnych hydraulických zariadeniach najmä v poľnohospodárstve, kde hrozí znečistenie pôdy, podzemnej vody alebo vodných zdrojov.
V príspevku sú uvedené experimentálne výsledky merania dôležitej reologickej vlastnosti – dynamickej viskozity vzoriek Plantohydu. Merania boli vykonané v laboratórnych podmienkach pomocou digitálneho viskozimetra DV-3P Anton Paar. Princíp merania využíva závislosť odporu meraného materiálu voči otáčaniu sondy. Matematický model pre výpočet viskozity predpokladá, že vzorka má jednotnú textúru, neobsahuje mechanické nečistoty a vzduchové bubliny, teplota je konštantná v celom objeme a prúdenie je laminárne. Uvedeným zariadením bolo uskutočnené meranie dynamickej viskozity v teplotnom intervale od -10 °C do 50 °C. Namerané hodnoty dynamickej viskozity pre vzorky Plantohydu 46S (563,5 mPa*s pri teplote -10 °C a 103,4 mPa*s pri teplote +50 °C) a Plantohydu 40N (600,6 mPa*s pri teplote -10 °C a 78,4 mPa*s pri teplote +50 °C) sú pomerne blízke, značne nižšie sú hodnoty dynamickej viskozity Plantohydu 15S (206,3 mPa*s pri teplote -10 °C a 62,3 mPa*s pri teplote +50 °C). V meranom teplotnom intervale boli získané exponenciálne závislosti dynamickej viskozity od teploty pre každú vzorku v súlade s Arrheniovou rovnicou. Závislosť dynamickej viskozity od teploty pre vzorku Plantohyd 15S je matematicky opísaná regresnou rovnicou: $y = 167{,}98e^{-0{,}02x}$ s najvyššou hodnotou koeficienta determinácie $R^2 = 0{,}9922$. Závislosť dynamickej viskozity od teploty pre vzorku Plantohyd 46S opisuje regresná rovnica v tvare: $y = 334{,}87e^{-0{,}028x}$, kde koeficient determinácie má hodnotu $R^2 = 0{,}9255$. Závislosť dynamickej viskozity od teploty pre vzorku Plantohyd 40N opisuje regresná rovnica: $y = 318{,}01e^{-0{,}032x}$, pričom koeficient determinácie má hodnotu $R^2 = 0{,}9145$.
Fyzikálne a chemické procesy prebiehajúce v materiáli v dôsledku zmien teploty je možné skúmať metódami termickej analýzy – metódou diferenčnej kompenzačnej kalorimetrie (DSC), termogravimetrickej analýzy (TGA) a ďalšími. DSC analýza poskytujúca informácie o tepelných efektoch vo vzorke podrobenej teplotnému režimu bola realizovaná v teplotnom intervale od -30 °C do 100 °C použitím DSC kalorimetra s tepelným tokom DSC 822^e METTLER TOLEDO. Meranie sa uskutočnilo v atmosfére dusíka (s tokom 80 ml za minútu) a rýchlosťou ohrevu 5 °C za minútu. Na DSC krivkách pre jednotlivé vzorky sú výrazné endotermické píky: pre vzorku Plantohyd 15S pri teplote -25,1139 °C, pre vzorku Plantohyd 46S pri teplote -22,6445 °C a pre vzorku Plantohyd 40N pri teplote -19,1214 °C. Tieto píky

pravdepodobne zodpovedajú fázovým premenám jednotlivých zložiek Plantohydu, ich tvar sa líši pre jednotlivé vzorky. Menej ostrý pík je pozorovaný pri Plantohyde 40N. Vzhľadom na meraný teplotný interval (od -30 °C), nie sú dobre viditeľné začiatky endotermických procesov pre jednotlivé vzorky. Získané výsledky nepotvrdzujú informácie o teplotnej stabilite Plantohydu (od -27 °C pre Plantohyd N, a od -35 °C pre Plantohyd S) udávané výrobcom. Tvar DSC kriviek v teplotnom interval od 0 °C do 100 °C je veľmi podobný a nevykazuje žiadne tepelné efekty. V závere príspevku sú porovnané získané výsledky s teóriou, resp. inými publikovanými dátami. Experimentálne výsledky potvrdzujú, že teplota je významný faktor, ktorý ovplyvňuje vlastnosti a procesy prebiehajúce v skúmanom materiáli – Plantohyd série S a N.

Kľúčové slová: DSC analýza, dynamická viskozita, Plantohyd

Introduction

Modern agricultural technology automatically controlled processes with respect of the ecological aspects require use of new approaches, sophistic methods and environmentally friendly materials. To this kind of materials can be count renewable and biodegradable materials such as many types of bio-oils, bio-fuels or wide spectrum bio-based and biodegradable materials for different (not only) technical proposes.

Several authors deal with current topic of bio-oils, bio-fuels or biodegradable hydraulic fluids to keep environmental safety namely in agricultural technology. Tkáč et al. (2008) suggested devices for tests of biodegradable hydraulic fluids destined for tractors. Other authors (Majdan et al., 2010, Majdan et al., 2011) described the methods for smart inspection of biodegradable transmission oil of tractor and they provided comparison of biodegradable hydraulic fluid with mineral oil on the basis of selected parameters. Test of biodegradable transmission and hydraulic fluid designed for agricultural tractors and study of ecological fluid properties under operational conditions of tractors were introduced in the works (Tkáč et al., 2012a, Tkáč et al., 2012b).

Physical properties such as viscosity and temperature interval of thermal stability are very important factors of bio-lubricants or bio-fuels which influence the possibilities of their use in agricultural machinery. Thermophysical and rheological properties of bio-oil, bio-diesel and bio-ethanol were investigated by Božiková and Hlaváč (2013a, 2013b).

Materials and Methods

PLANTO oils are high performance lubricants based on harvestable raw materials, such as rapeseed and sunflowers, with a combination of downstream esters and specially selected additives (Fuchs Europe Schmierstoffe GMBH, Product information).

According to product information the main advantages of PLANTOHYD are:

- Rapidly biodegradable (greater 90 % within 14 days),
- Excellent viscosity-temperature dependence,

- Applicable at wide temperatures interval.

The PLANTOHYD N series of oils are based on vegetable oils, the PLANTOHYD S series are based on synthetic esters. Both, Plantohyd N and S series, represent an environmentally friendly alternative to mineral oil-based hydraulic oils.

Plantohyd products are fully compatible with all materials usually found in hydraulic systems. The base fluids used in these products are non-toxic. The fluids are free of heavy metals and chlorinated compounds. Plantohyd hydraulic lubricants are suitable for all mobile and stationary hydraulic equipment in vehicles and industry. Their use is recommended especially when there is a danger of leakage of hydraulic and lubricating oils in soil, groundwater or surface water.

Theoretical basis: Materials, where internal friction is generated, can be characterized by viscosity. Dynamic viscosity η (Pa*s) is defined as a constant between tangential tension τ and gradient of layer velocity ($grad\ v$):

$$\tau = \eta\ grad\ v \qquad (1)$$

Dependency of dynamic viscosity on temperature can be described by Arrhenius equation

$$\eta = \eta_0 e^{-\left(\frac{E_A}{RT}\right)} \qquad (2)$$

where η_0 is reference value of dynamic viscosity, E_A is activation energy, R is gas constant and T is temperature. According this equation, viscosity exponentially decreases with temperature.

Dynamic viscosity and others rheologic properties were measured by many authors. Severa et al. (2010) examined influences of storing and temperature on viscosity of egg fluids. Severa and Los (2008), Hlaváč (2010) were looking for influence of temperature on dynamic viscosity of milk during storage. Thermophysical and rheologic dependencies of acidophilus milk were investigated by Božiková and Hlaváč (2010). Measurement of energy values and rheological properties of bioethanol and bio-lubricants were published by Kardjilova et al. (2012, 2013).

Physical and chemical processes running in the material due to temperature changes can be investigated by method of thermal analysis. They are the analytical techniques that measure physical and chemical properties of the sample as a function of the temperature or time (Laidler, 1987, Haines, 1995). The sample is subjected the temperature program and the dependence measured value (heat, mass, volume, specific heat etc.) on the time and temperature are determined. It is provided mainly by using following methods of thermal analyses:

- differential thermal analysis (DTA) or differential scanning calorimetry (DSC) – provides information on thermal effects which are characterized by an enthalpy change and by temperature range,
- thermogravimetric analysis (TGA) – measures the mass (change of the mass), provides information on the content of components.

Interpretation of the obtained TGA, DSC curves provides information about processes running in the materials, changes of physical and chemical properties and conditions of it, e.g. phase transitions, drying, oxidation stability, thermal stability, chemical reaction, denaturation, compositional analysis, purity, etc.

Many authors deal with methods of thermal analysis, namely differential thermal analysis, differential scanning calorimetry and thermogravimetry (e.g. Šimon, 2000). The same author Šimon et al. (2000) studied oxidation of rapeseed and sunflower oils by differential scanning calorimetry. Also different kind of materials can be investigated by DSC methods; Trník et al. (2012) dealt with study of building material properties – concrete with metakaolin addition.

Condition of measurement: Measurement of Plantohyd samples (Plantohyd 15S, 46S, 40N) dynamic viscosity was performed by digital rotational viscometer Anton Paar (DV-3P). Principle of measuring by this viscometer is based on dependency of sample resistance against the probe rotation. The combination of spindles and speed allows an optimal choice for measuring viscosity. Mathematical model for calculation of viscosity suppose: measurements are conducted in laminar flow, sample has a uniform texture and it is free of mechanical impurities and air bubbles and temperature is constant throughout the volume of the sample.

Differential scanning calorimeter DSC 822e (METTLER TOLEDO) was used for study of thermal stability of Plantohyd. Measurements were performed on samples of Plantohyd 15S, Plantohyd 46S and Plantohyd 40N under nitrogen atmosphere (flow rate 80 ml per minute) in the temperature range from -30 °C to 100 °C with heating rate 5 °C per minute. Mass of the samples was:

- Plantohyd 15S: 39,8720 mg
- Plantohyd 46S: 45,2780 mg
- Plantohyd 40N: 37,3320 mg.

The samples were embedded in standard aluminium pans where an empty pan was used as a reference.

Results and Discussion

Temperature dependencies of Plantohyd viscosity and regression equations with value of determination coefficient R^2 for each sample are on the Fig. 1-3. Progress of obtained dependencies can be described by decreasing exponential function:

$$\eta = Ae^{-B\left(\frac{t}{t_0}\right)} \qquad (3)$$

where t is temperature, t_0 = 1 °C; A, B are constants dependent on kind of material, and on ways of processing or storing. The exponential dependency for the each sample was obtained in accordance with Arrhenius equation (2).

Experimental values of dynamic viscosity for Plantohyd 46S and 40N are close; significantly lower values of dynamic viscosity are for Plantohyd 15S:

- Plantohyd 15S: 206,3 mPa*s at the temperature -10 °C to 62,3 mPa*s at +50 °C,
- Plantohyd 46S: 563,5 mPa*s at the temperature -10 °C to 103,4 mPa*s at +50 °C,
- Plantohyd 40N: 600,6 mPa*s at the temperature -10 °C to 78,4 mPa*s at +50 °C.

Experimental results of differential scanning calorimetry – DSC curves for samples of Plantohyd is on the Fig. 4 (exothermal peaks are oriented up). There is observed significant endothermal peak for each sample on the DSC curves:

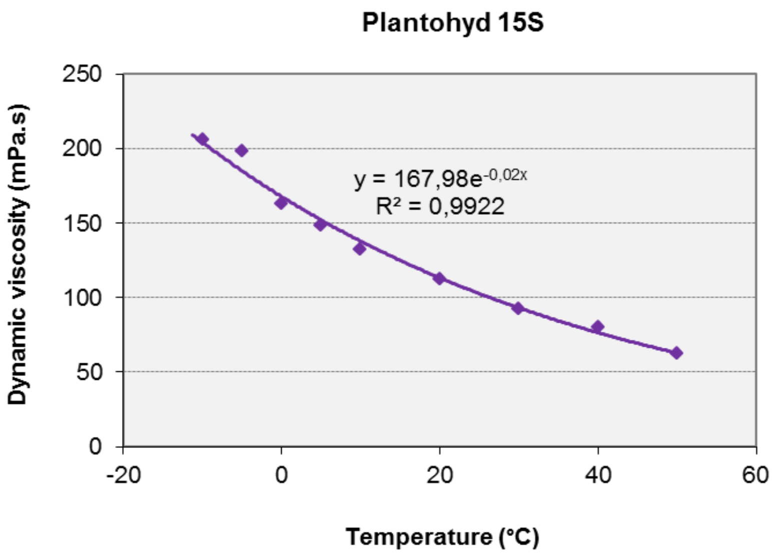

Fig. 1 Dynamic viscosity as a function of temperature for sample of Plantohyd 15S (Regression equation: $y = 167{,}98e^{-0{,}02x}$; Determination coefficient: $R^2 = 0{,}9922$)

Obr. 1 Závislosť dynamickej viskozity od teploty pre vzorku Plantohyd 15S (Regresná rovnica: $y = 167{,}98e^{-0{,}02x}$; Koeficient determinácie: $R^2 = 0{,}9922$)

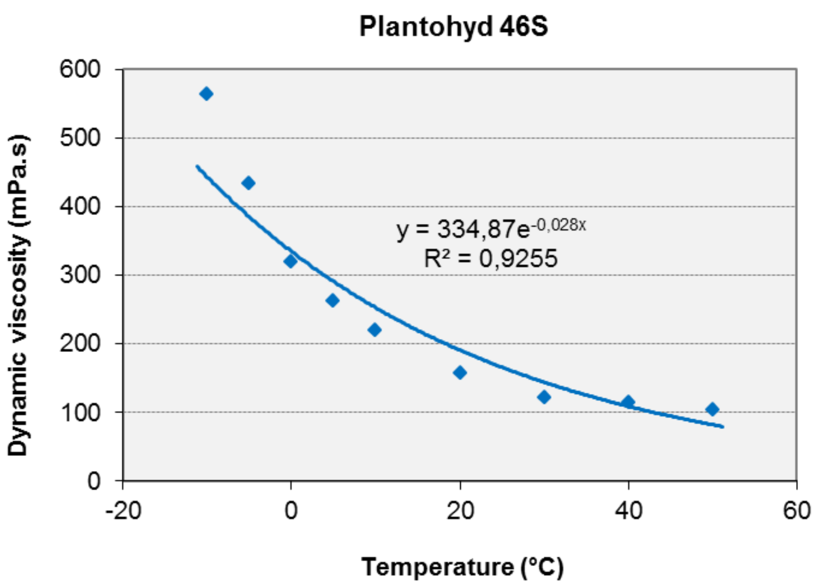

Fig. 2 Dynamic viscosity as a function of temperature for sample of Plantohyd 46S (Regression equation: $y = 334{,}87e^{-0{,}028x}$; Determination coefficient: $R^2 = 0{,}9255$)

Obr. 2 Závislosť dynamickej viskozity od teploty pre vzorku Plantohyd 46S (Regresná rovnica: $y = 334{,}87e^{-0{,}028x}$; Koeficient determinácie: $R^2 = 0{,}9255$)

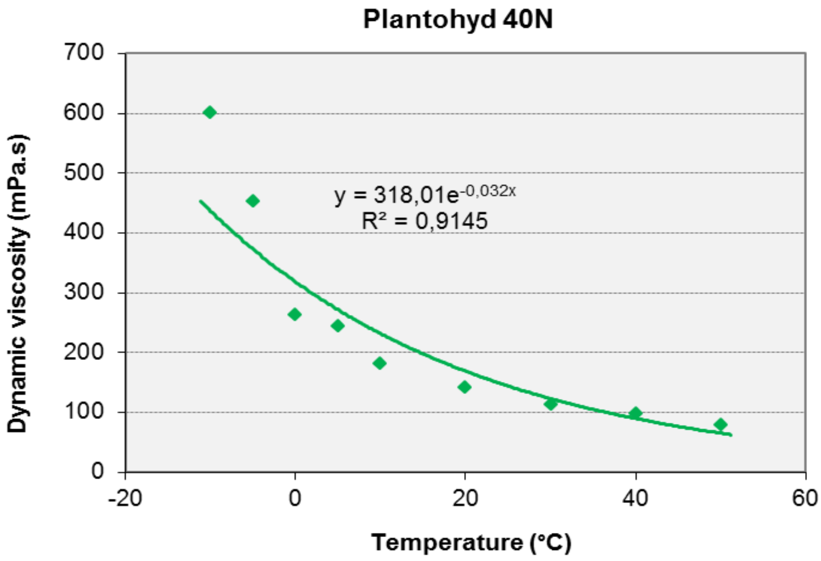

Fig. 3 Dynamic viscosity as a function of temperature for sample of Plantohyd 40N (Regression equation: $y = 318{,}01e^{-0{,}032x}$; Determination coefficient: $R^2 = 0{,}9145$)

Obr. 3 Závislosť dynamickej viskozity od teploty pre vzorku Plantohyd 40N (Regresná rovnica: $y = 318{,}01e^{-0{,}032x}$; Koeficient determinácie: $R^2 = 0{,}9145$)

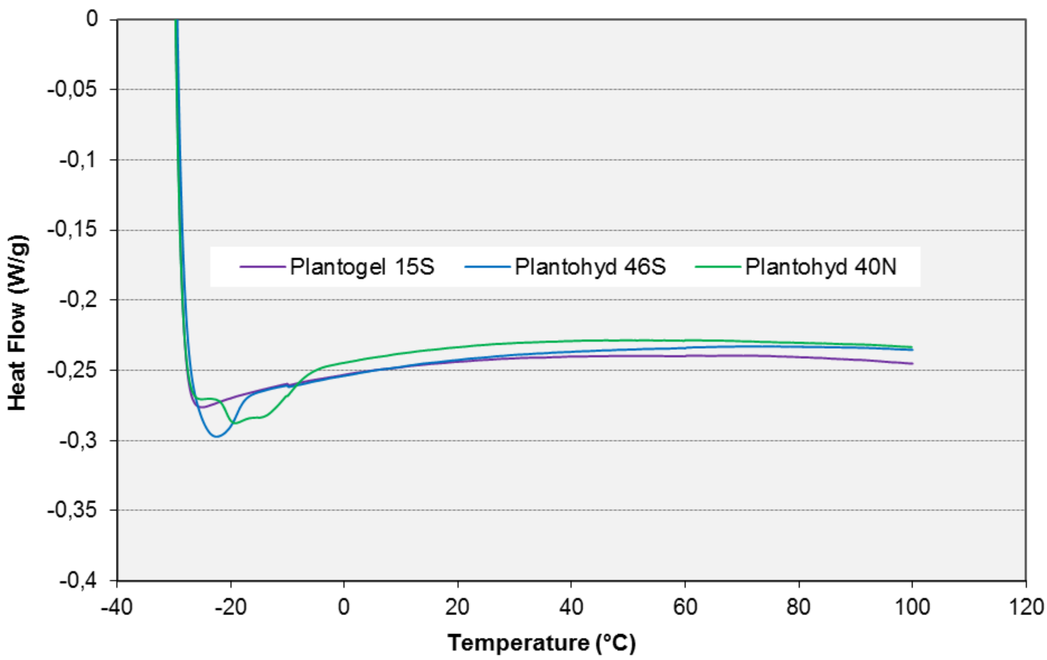

Fig. 4 DSC curves of Plantohyd 15S, Plantohyd 46S and Plantohyd 40N

Obr. 4 DSC krivky vzoriek Plantohydu 15S, Plantohydu 46S a Plantohydu 40N

- Plantohyd 15S at the temperature -25,1139 °C,
- Plantohyd 46S at the temperature -22,6445 °C,
- Plantohyd 40N at the temperature -19,1214 °C.

These endothermal peaks are caused by phase transition of Plantohyd components. They have different shape for individual kind of Plantohyd. Less sharp shape of the peak is observed at Plantohyd 40 N. Because of the measurement interval from -30 °C, beginning of endothermal processes for individual sample is not good recognizable. It is visible on the Fig. 4, that in the temperature range from 0 °C to 100 °C thermal effects are not observed and shape of DSC curves is very similar for individual samples.

Conclusion

In generally, presented temperature dependency of dynamic viscosity are in accordance with theory and published data. All obtained regression equations are Arrhenius type, with different values of coefficients A, B for each sample. Measured values of viscosity for Plantohyd presented in this paper have higher number than experimental data obtained in the same laboratory (Kardjilova et al, 2013). Differences can be caused by time of storing, which is important factor affecting viscosity of biological materials (Hlaváč, 2010, Božiková - Hlaváč, 2010).

As for DSC study of Plantohyd, our results did not confirm production information concerning temperatures interval of thermal stability (from -27 °C for Plantohyd N, and from -35 °C for Plantohyd S, respectively). There are observed significant endothermal peak for each sample on the DSC curves: for Plantohyd 15S at the temperature -25,1139 °C, for Plantohyd 46S at the temperature -22,6445 °C and for Plantohyd 40N at the temperature -19,1214 °C. However it is necessary to realise next experiments in the temperature interval with the focus on the phase transition.

Experimental results showed that temperature is one of the essential factors which influence material properties and processes running in the investigated material – Plantohyd S and N series.

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