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RHEOLOGICAL BEHAVIOR OF SOME OILS ADDITIVATED WITH MIXED PYROMELLITIC ESTERS

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ABSTRACT. The paper presents the rheological behavior study of castor oil additivated by different types of mixed pyromellitic esters. The influence of pyromellitic esters' structure and concentration was determined, as well as that of temperature, on the rheological behavior, by setting the dependence between the shear stress τ and the shear rate $\dot{\gamma}$. The analysis of dependence $\tau = f(\dot{\gamma})$ demonstrates that the solutions studied present Newtonian behavior.

Keywords: *dynamic viscosity, flow activation energy, lubricating, oil additives*

INTRODUCTION

Along with the need to protect the environment, using vegetable oil-based lubricants has become an important alternative in tribology.

Generally, a lubricant has two major components, base oil and different auxiliary materials which have the property to improve the characteristics of oil used. The basic materials suitable for producing ecological lubricants are vegetable oils because of their high biodegradability, regeneration capacity, low toxicity and wide variety of sources [1, 2]. Unlike mineral oil-based lubricants those based on vegetable oils are rapidly and completely biodegradable, without having a negative effect on the ecosystem. However, their thermal and hydrolytic stability are comparatively lower than that of synthetic oils and need to be improved through a number of measures [3-5].

The main functions of a lubricant is to reduce friction and wear, to dissipate heat, to disperse deposits, to inhibit corrosion and rusting, and the main properties of a base oil is a relatively constant viscosity, low solidification temperature, low deposit formation, low volatility, good thermal -oxidative and hydrolytic stability, and to be biodegradable [6].

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The vegetable oils used for this purpose can be both edible category (sunflower, soybean, coconut, peanut, palm, rapeseed) and inedible (castor oil) [7, 8]. Lubricating properties of castor oil were studied and were reported to be similar or better than those of vegetable oils commonly used [4, 9].

In this paper as a base vegetable oil was used the castor oil, and as auxiliary materials (which are able to improve the characteristics of oil used) the paraffin oil and a pair of pyromellitic esters whose synthesis and characterization have been published [10, 11].

The main characteristics of the pyromellitic esters (P1 and P2) are found in Table 1. The two esters differ in the molar ratio between the radicals' 2-phenoxy ethyl and 2 - ethyl hexyl derived from the alcohols used for the esterification of pyromellitic anhydride (2:2 for P1 and 3:1 for P2).

Table 1. The properties of the pyromellitic esters used

Ester	Molecular formula	Molecular weight, kg.kmol^{-1}	Density at 20˚C, kg.m^{-3}	Refractive index at 20˚C	Saponification index, mg KOH/g
P1	$C_{42}H_{54}O_{10}$	718	1103	1.5258	311.42
P2	$C_{42}H_{46}O_{11}$	726	1176	1.5523	309.34

The composition of the samples with esters content is presented in Table 2. In all cases, the castor oil content is 93 wt %. As standard (sample A0) it was used the castor oil with boiling point 313ºC and density $910\,kg \cdot m^{-3}$ (at 20ºC). At the same temperature, the density of paraffin oil was $790\,kg \cdot m^{-3}$.

Table 2. The composition of the analyzed samples

Symbol	Composition, wt %		Symbol	Composition, wt %	
	P1	Paraffin oil		P2	Paraffin oil
A1	2	5	**B1**	2	5
A2	3.5	3.5	**B2**	3.5	3.5
A3	5	2	**B3**	5	2
A4	7	0	**B4**	7	0

The samples preparation was done by dispersing the pyromellitic ester under intense stirring in oils mixture at room temperature (~25˚C). The rheological characterization of the samples was carried out using rotational viscometer Rheotest-2, under thermostatic conditions, at temperature values between 50÷80˚C, close to the operating conditions of lubricated parts. It was followed the establishment of rheological relations $\tau = f(\dot{\gamma})$, as well as the calculation of the flow activation energy E_a [12, 13].

RESULTS AND DISCUSSION

Viscosity is one of the main properties of the oil used and its value should vary as little as possible in operation, at all engine-operating conditions. Oils additivation with different types of synthetic esters is done in order to improve lubricating properties of the base vegetable oil. This additivation should not negatively influence rheological characteristics of the oil. Thus, it was followed the rheological behavior of castor oil additivated with pyromellitic esters, at different concentrations.

The influence of ester type used as an additive, on rheological behavior of castor oil was studied for different concentrations of additive, at three temperature values. In Figure 1, $\tau = f(\dot{\gamma})$ dependence is shown for esters concentration of 3.5 wt. %.

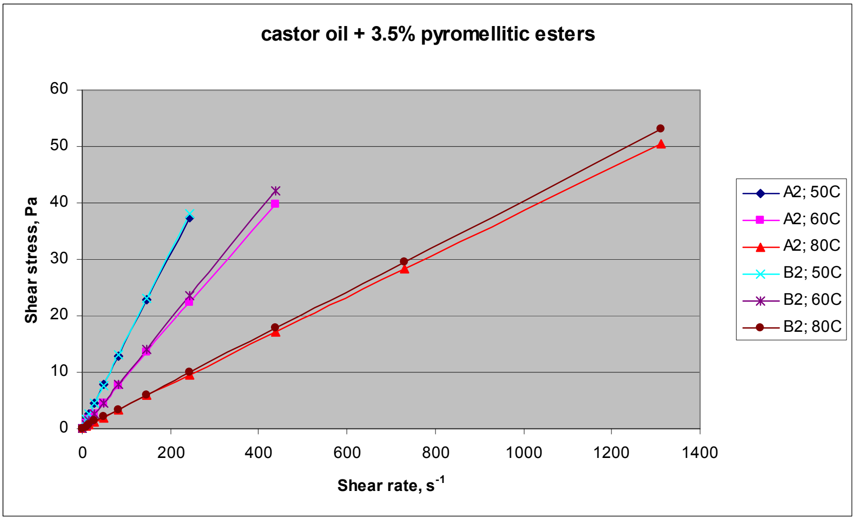

Figure 1. The dependence $\tau = f(\dot{\gamma})$ for samples A2 and B2, at different temperatures

The rheological equations corresponding to these dependencies are shown in Table 3.

Table 3. Rheological equations for samples A2 and B2

Temperature, ˚C	Equation $\tau = \eta \cdot \dot{\gamma}$		Viscosity increasing*, %
	A2	B2	
50	$\tau = 0.1540 \cdot \dot{\gamma}$	$\tau = 0.1567 \cdot \dot{\gamma}$	1.75
60	$\tau = 0.0908 \cdot \dot{\gamma}$	$\tau = 0.0965 \cdot \dot{\gamma}$	6.30
80	$\tau = 0.0385 \cdot \dot{\gamma}$	$\tau = 0.0404 \cdot \dot{\gamma}$	4.94

** Sample B2 compared with sample A2*

It is noted that for these pyromellitic esters, changing the molar ratio of alcohols' used for esterification does not change significantly the oil viscosity and no modifies its Newtonian behavior. The temperature increasing leads to the decrease of samples' viscosity but without the change of the Newtonian behavior.

Also, it was studied the influence of additive concentration on the rheological behavior of castor oil. For pyromellitic ester P1, at a temperature of 60˚C, $\tau = f(\dot{\gamma})$ dependence is shown in Figure 2.

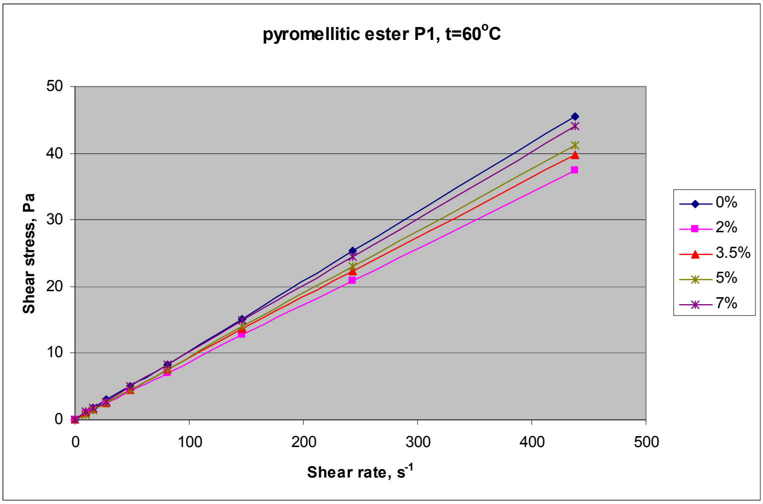

Figure 2. Dependence $\tau = f(\dot{\gamma})$ for samples A0-A4

From the slope of the obtained straight lines it is observed that the addition of pyromellitic ester leads to the decrease of samples viscosity in comparison with the viscosity of oil without additives. The viscosity decrease is relatively small; the most pronounced decrease corresponds to the minimum additive content (2%), followed by its increase with the ester content increasing, but without reaches the corresponding value of pure oil. A similar situation occurs too when the oil is additivated with P2 pyromellitic ester. The obtained viscosity values are presented in Table 4.

Table 4. Dynamic viscosities of the analyzed samples

Symbol	**Viscosity, mPa.s**		**Symbol**	**Viscosity, mPa.s**	
	50ºC	**80ºC**		**50ºC**	**80ºC**
A0	171.4	43.5	**-**	-	-
A1	150.3	36.5	**B1**	150.5	39.5
A2	154.0	38.5	**B2**	156.7	40.4
A3	161.1	40.4	**B3**	161.1	42.1
A4	169.6	42.9	**B4**	164.6	43.5

The exponential decrease of the samples viscosity with the temperature is described by an Arrhenius-type equation:

$$\eta = A \cdot \exp(E_a / R \cdot T) \tag{1}$$

where E_a - the flow activation energy, $J \cdot mol^{-1}$; R - the gas constant, $J \cdot mol^{-1} \cdot K^{-1}$; T - absolute temperature, K; A - the material constant *Pa·s*.

Through the measurements achievement at different temperatures it was possible to establish the dependence $\ln \eta = f(1/T)$ and to calculate the values of flow activation energy E_a. Particular expressions of equation (1) for the samples A0-A4 and B1-B4 are given in Tables 5a and 5b.

Table 5a. Arrhenius-type equations for samples A0-A4

Content of P1 ester, wt%	$\eta = A \cdot \exp(E_a / R \cdot T)$	E_a, $kJ \cdot mol^{-1}$
0	$\eta = 1.70 \cdot 10^{-5} \cdot \exp(5212/T)$	43.3
2	$\eta = 0.95 \cdot 10^{-5} \cdot \exp(5347/T)$	44.4
3.5	$\eta = 1.30 \cdot 10^{-5} \cdot \exp(5256/T)$	43.7
5	$\eta = 1.45 \cdot 10^{-5} \cdot \exp(5240/T)$	43.5
7	$\eta = 1.65 \cdot 10^{-5} \cdot \exp(5212/T)$	43.3

Table 5b. Arrhenius-type equations for samples B1-B4

Content of P2 ester, wt%	$\eta = A \cdot \exp(E_a / R \cdot T)$	E_a, $kJ \cdot mol^{-1}$
2	$\eta = 2.25 \cdot 10^{-5} \cdot \exp(5074/T)$	42.2
3.5	$\eta = 1.80 \cdot 10^{-5} \cdot \exp(5161/T)$	42.9
5	$\eta = 2.25 \cdot 10^{-5} \cdot \exp(5096/T)$	42.3
7	$\eta = 2.70 \cdot 10^{-5} \cdot \exp(5043/T)$	41.9

It is noted that for the same type of ester, the variation of the flow activation energy with the additive concentration is insignificant. Also, it is observed that the slight increase in molecular mass for pyromellitic ester P2 compared with P1 ester leads, on the one hand, to an increase in the constant A, but also to a decrease of flow activation energy on average 3%.

Using particular expressions of $\eta = f(1/T)$ dependence, the values of dynamic viscosity of the samples were determined in the temperature range 20÷100˚C. Thus, for samples A0, A2 and A4, the viscosity evolution is shown in Figure 3.

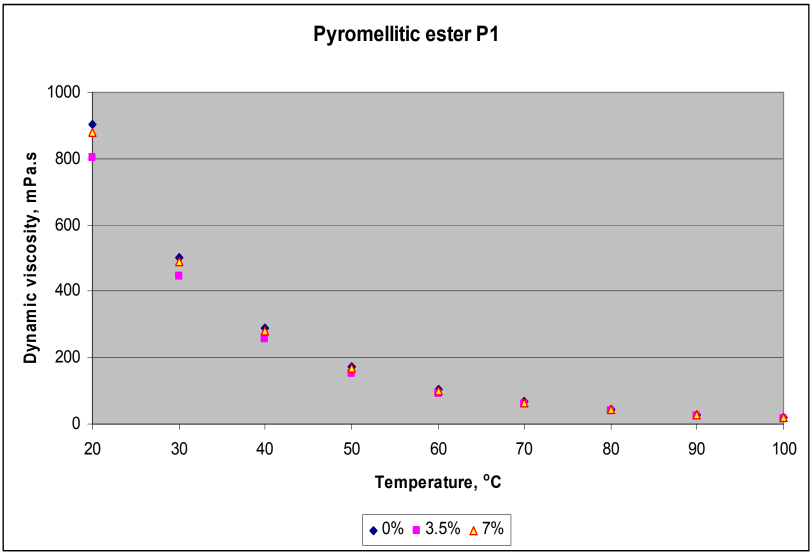

Figure 3. Dynamic viscosity vs. temperature for samples A0, A2 and A4

It is found that with increasing temperature, the values of samples' dynamic viscosity are closer, regardless of the percentage of additive used.

Since lubrication is used, usually, in rotating systems (bearings, gears etc), the dynamic characteristics (speed, dynamic pressure, shear stress) will be expressed in terms of Taylor-Reynolds criterion (Ta_{Re}) specific to this type of motion. This criterion is also used to characterize fluids flow in annulus under the effect of rotational motion.

The values of Ta_{Re} criterion were calculated with relation (2), taking into account the radii of the inner and outer cylinder (r_i and r_o), the inner cylinder revolution n and the fluid properties (viscosity η and density ρ) [14]:

$$Ta_{\mathrm{Re}} = \frac{2 \cdot \pi \cdot n \cdot r_i \cdot (r_o - r_i) \cdot \rho}{\eta} \qquad (2)$$

Increasing the hydrodynamic regime, characterized by dimensionless criterion Ta_{Re}, leads to a pronounced decrease of the ratio between shear stress τ (experimentally determined) and dynamic pressure P_{dyn} calculated with the maximum speed.

By analogy with the fluids flow through straight pipes, the dynamic pressure of the fluid in motion in ring-shaped spaces is calculated with:

$$P_{dyn} = \frac{\rho \cdot w_{\max}^2}{2} \tag{3}$$

$$w_{\max} = \pi \cdot d_i \cdot n \tag{4}$$

where $w_{\max}$ is the speed of fluid laminar layer placed next to the moving wall (inner cylinder), d_i - the inner diameter of the ring-shaped space, n - the inner cylinder revolution.

For the samples A0, A2 and A4, at constant temperature, the variation of $\tau / P_{dyn} = f(Ta_{\mathrm{Re}})$ ratio is shown in Figure 4. How change of temperature affects the same dependence, for sample A2, is shown in Figure 5.

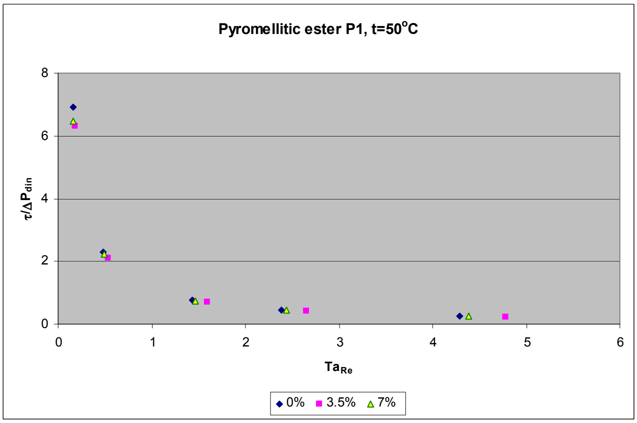

Figure 4. $\tau / P_{dyn} = f(Ta_{\mathrm{Re}})$ dependence for samples A0, A2 and A4

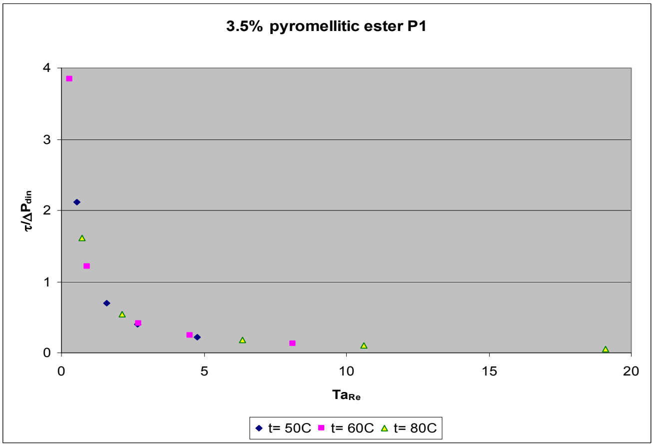

Figure 5. The temperature influence on $\tau / P_{dyn} = f(Ta_{\mathrm{Re}})$ dependence (sample A2)

One can notice that the graphical representation places the results after a parabolic curve with overlapping points, without significant changes depending on the additive concentration or temperature. The profile of both dependencies shows an accentuated decrease with the increasing of hydrodynamic flow regime.

By analogy with the circular motion of the fluid in stirring processes [15, 16], the ratio τ/P_{dyn} is correlated with Ta_{Re} criterion by a relationship of type:

$$\tau/P_{dyn} = C \cdot Ta_{\mathrm{Re}}^{m} \tag{5}$$

or, particularized by logarithmic representation:

$$\ln(\tau/P_{dyn}) = \ln C + m \cdot \ln(Ta_{\mathrm{Re}}) \tag{5a}$$

The particular forms of relationship (5a) determined for sample A2, at different temperatures, are shown in Table 6a. To a temperature of 50˚C, for samples A0, A2 and A4, the particular forms of relation (5a) are shown in Table 6b.

Table 6a. Particular forms of equation (5a) for sample A2

Temperature, ˚C	$\ln(\tau/P_{dyn}) = \ln C + m \cdot \ln(Ta_{\mathrm{Re}})$	C
50	$\ln(\tau/P_{dyn}) = 0.0957 - 1.0135 \cdot \ln(Ta_{\mathrm{Re}})$	1.100
60	$\ln(\tau/P_{dyn}) = 0.1103 - 1.0166 \cdot \ln(Ta_{\mathrm{Re}})$	1.117
80	$\ln(\tau/P_{dyn}) = 0.1417 - 1.0128 \cdot \ln(Ta_{\mathrm{Re}})$	1.152

Table 6b. Particular forms of equation (5a) for samples A0, A2 and A4, at 50˚C

Symbol	$\ln(\tau/P_{dyn}) = \ln C + m \cdot \ln(Ta_{\mathrm{Re}})$	C
A0	$\ln(\tau/P_{dyn}) = 0.0850 - 1.0055 \cdot \ln(Ta_{\mathrm{Re}})$	1.089
A2	$\ln(\tau/P_{dyn}) = 0.0957 - 1.0135 \cdot \ln(Ta_{\mathrm{Re}})$	1.100
A4	$\ln(\tau/P_{dyn}) = 0.0727 - 0.9945 \cdot \ln(Ta_{\mathrm{Re}})$	1.075

Considering the shear stress τ equivalent to the friction pressure drop, it can be assumed that the ratio of the two quantities is equal to the friction coefficient λ corresponding to laminar flow regime ($\lambda = 64 \cdot \mathrm{Re}^{-1}$).

This assumption is confirmed from two directions: on the one hand, the Ta_{Re} values lower than 60, which is the critical value that separates the laminar regime of the turbulent, for fluids flow in annulus [17-20]. On the other hand, from equations presented in Tables 6a and 6b, it is observed that the values of m coefficient are very close to the value -1, similar to the Reynolds' exponent from the expression of friction coefficient.

CONCLUSIONS

It was studied the rheological behavior of castor oil additivated with mixed pyromellitic esters, monitoring the influence of theirs type and concentration, as well as that of temperature.

For each analyzed sample (pure castor oil, respectively, additivated in different proportions), it was obtained a linear dependence between shear stress τ and the shear rate $\dot{\gamma}$, without yield point τ_0, which shows Newtonian behavior.

Additivation does not significantly change the value of the dynamic viscosity of castor oil but has favorable effects in terms of its lubricating properties.

The rheological equations corresponding to the dependence $\tau = f(\dot{\gamma})$ were determined and, from the slope of the obtained straight lines, was calculated their dynamic viscosity. Also, from the temperature influence, were calculated the flow activation energies and it was established the dependence between the rheological parameters and Taylor-Reynolds criterion (Ta_{Re}), specific to rotational motion.

EXPERIMENTAL SECTION

Determinations were made using the rotational viscometer Rheotest-2 with the system vat-drum S/S_1. For each analyzed sample, the shear stress measurement was performed both to increasing and decreasing values of the shear rate.

The samples were analyzed after one day of preparation.

REFERENCES

1. L. Rhee, *NLGI Spokesman*, **1996**, *60(5)*, 28.
2. R.L. Goyan, R.E. Melley, P.A. Wissner, W.C. Ong, *Lubrication Engineering*, **1998**, *54(7)*, 10.
3. I. Lesiga, M. Picek, K. Nahal, *Journal of Synthetic Lubrication,* **1997**, *13(4)*, 347.
4. S.Asadauskas, J.M. Perez, J. Duda, *Lubrication Engineering*, **1997**, *53(12)*, 35.

5. R. Becker, A. Knots, *Lubrication Science*, **1996**, *8*, 295.
6. S.Z. Erhan, “Vegetables oils as lubricants, hydraulic fluids and inks- Bailey’s Industrial Oil and Fat Products”, 6th ed., John Wiley & Sons Inc., New Jersey, **2005**.
7. O.N. Anand, C.V.Kumar, *Journal of Synthetic Lubrication*, **2006**, *23(2)*, 91.
8. P.V. Joseph, D. Saxena, D.K.Sharma, *Journal of Synthetic Lubrication*, **2007**, *24(4)*, 181.
9. Y. Gerbig, S.I.Ahmed, F.A. Gerbig, H. Haefke, *Journal of Synthetic Lubrication*, **2004**, *21(3)*, 177.
10. L.E. Mirci, “Esteri micşti pe bază de anhidridă piromelitică şi procedeu de obţinere a acestora”, Brevet RO 111760, **1996**.
11. L.E. Mirci, S. Ţerescu (Boran), G. Istrătucă, *Rev. Mat. Plast.*, **1999**, *36(1)*, 13.
12. A. Tămaş, M. Vincze, *Studia UBB Chemia,* **2011**, *56(2)*, 85.
13. A. Tămaş, M. Vincze, *Studia UBB Chemia,* **2011**, *56(3)*, 247.
14. N. Bors, "Contribuţii la studiul influenţei unor substanţe chimice asupra îmbunătăţirii curgerii lichidelor", Teză de doctorat, Universitatea "Politehnica" Timişoara, **2010**.
15. A.G. Kasatkin, "Procese şi aparate principale în tehnologia chimică", ed. a II-a, Ed. Tehnică, Bucureşti, **1963**.
16. K.F. Pavlov, P.G. Romankov, A.A. Noskov, "Procese şi aparate în ingineria chimică - Exerciţii şi probleme", Ed. Tehnică, Bucureşti, **1981**.
17. N. Borş, A. Tămaş, Z. Gropşian, *Chem.Bull."Politehnica" Univ. (Timişoara)*, **2008**, *53(67)*, 1-2, 16.
18. N. Borş, A. Tămaş, *Scient. Bull. "Politehnica" Univ. of Timişoara*, Transactions on Mechanics, **2010**, *1*, 81.
19. A. Tămaş, N. Borş, R. Minea, *Bull. of Petroleum-Gas Univ. of Ploieşti,* Technical Series, **2008**, *LX, 4B,* 105.
20. N. Borş, A. Tămaş, Z. Gropşian, *Studia UBB Chemia*, **2009**, LIV, *4(1)*, 55.