BULETINUL Universităţii Petrol – Gaze din Ploieşti	Vol. LVIII No.4/2006	37-44	Seria Tehnică

Rheological Behavior of Multi-Grade Oils

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Abstract

Rheological measurements of 3; 6; 10 and 12% INFINEUM SV 260 solutions in SAE 10W mineral oil show non-Newtonian behavior in the temperature range 313-370 K and shear rates ranging between 3 and 1312 s^{-1}: they follow the Bingham model at low concentrations, low shear rates and high temperatures and the Herschel-Bulkley model at high concentration, high shear rates and low temperatures. The slopes of the lines representing the variation of log viscosity with the reciprocal of temperature increase slightly with concentration between 3 and 10% for INFINEUM SV 260 solutions and decreases for 12%.

Key words: *rheological behavior of concentrated polymer solutions, viscosity improvers, multi-grade oils*

Introduction

Viscosity is a measure of the “shear strength” of a thin layer of oil [1] or, in other words, of the property the oil has to develop and maintain a certain amount of shearing stress dependent on flow, and than to offer continued resistance to flow.

The temperature the oil is exposed to in vehicles ranges from cold ambient temperatures in the winter before the vehicle is started up to hot operating temperatures when fully warmed up in summer. As the viscosity of oils decreases logarithmically with increasing temperature, such a difference is too large to be covered by any single-grade mineral oil.

The changes in viscosity with increasing temperature can be reduced using lubricating oil additives, called also viscosity index improvers or modifiers. Such additives are special polymers that, added to low viscosity oils, improve their viscosity/temperature characteristics [2]. They effectively thicken the oil at all temperatures, but the increase of viscosity is more pronounced at high temperatures. The lubricating effect is extended across a wider temperature range and the oil becomes thus a multi-grade one. Its viscosity still decreases logarithmically with temperature, but the slope representing the change is lessened. This slope is dependent on the nature and amount of additive to the base oil.

The object of this paper is to determine the rheological behavior of some concentrated solutions of copolymer INFINEUM SV 260 produced by Infieum UK Limited respectively and recommended as viscosity improvers for multi-grade mineral oils at shear rates ranging between 3 and 1,312 s^{-1} and temperatures between 40 and 100 °C, to estimate their efficiency as lubricating additives for the low viscosity mineral oil SAE 10W.

Experimental Part

The following copolymers were used as viscosity improvers: hydrogenated poly(isoprene-co-styrene) (Infieum UK LIMITED) – trade name INFINEUM SV 260 .The low viscosity oil SAE 10W (INCERP, Romania) was used as mineral oil.

The characteristics of the copolymer and of the mineral oil SAE 10W were given in a previous paper [3].

Dissolution of polymers was realized at room temperature with gentle shaking now and then. Solutions having the concentrations 3; 6; 10 and 12 g/dL were prepared.

The rheological behavior of solutions was determined using a Haake VT 550 Viscotester developing shear rates ranging between 3 and 1,312 s^{-1} and measuring viscosities from 10^4 to 10^6 mPa·s when the HV_1 viscosity sensor is used. The temperature ranged between 40 °C and 100 °C and the measurements were made from 10 to 10 °C. The accuracy of the temperature was $\pm$ 0.1 °C.

Results and Discussion

The viscosity is the most significant physical property of a lubricant. The way it varies with temperature, shear rate and pressure determines its performances in an engine [4].

Viscosity modifiers are oil-soluble organic polymers having molecular weights ranging between 10^4 and 10^6 g/mole, able to provide the oil adequate hydrodynamic lubrication at high temperatures and good starting/pumping performance at low temperatures [5].

The volumes of macromolecular coils are increased in solutions in good solvents compared with that in bulk state. The measure to which the polymer increases solution viscosity is determined by the volume of the swollen macromolecular coils that depends – in its turn – on the interaction between the polymer and solvent. Polymer solutions presenting usually upper critical solution temperature phase diagrams, the solvent becomes better as temperature increases. Consequently, the higher the temperature, the higher the polymer solubility, the larger the volumes of coils, and the higher the thickening effect.

In addition to its nature and concentration, the performance of a polymer as a viscosity improver depends also on its resistance to mechanical shear (shear stability) and its chemical and heat stability [6]. The loss due to shear is reflected in a loss in lubricating viscosity [2].

For a given polymer type, the shear stability decreases with an increase in molecular weight, while the thickening effect increases with an increase in molecular weight. Consequently, a balance between the thickening efficiency and shear stability is important when selecting a polymer as a viscosity improver.

The behavior of an oil film trapped between two moving surfaces is quantified by the dynamic viscosity, which relates the shear stress and the shear rate.

For some applications – like the cranking resistance at start up – high shear rate performances are important, while for others – like the pumpability of the crankcase oil – low shear rate performances are required [7]. The understanding of the viscosity performances of the viscosity modifier polymer solutions over a range of shear rates is thus critical in determining the true effectiveness of a particular additive.

While the rheological behavior of some viscosity improver polymers at low and high shear rates ($10^4 \ldots 10^6$ s^{-1}) was investigated [5, 8], that at intermediate ones was not and the necessity of such a study becomes obvious.

The base oils usually exhibit Newtonian behavior. When a polymer is introduced into an oil, the viscosity of solutions is increased dramatically even at pretty low concentrations. Diluted solutions have usually Newtonian behavior, while the semi-diluted and concentrated ones behave as non-Newtonian fluids.

The rheograms obtained for the 3; 6; 10 and 12% INFINEUM SV 260 solutions for shear rates ranging between 3 and 1312 s^{-1} were analyzed according to the models that describe the deviations from the Newtonian behavior [9]:

Bingham:

$$\tau = \tau_o + \eta\dot{\gamma}\ , \tag{1}$$

Casson:

$$\tau^{1/2} = \tau_o^{1/2} + \eta^{1/2}\dot{\gamma}^{1/2}\ , \tag{2}$$

Ostwald-de Waele:

$$\tau = k\dot{\gamma}^n\ , \tag{3}$$

and Herschel-Bulkley:

$$\tau = \tau_o + k\dot{\gamma}^n\ , \tag{4}$$

where τ is the shear stress, τ_o – yield stress, η – viscosity, $\dot{\gamma}$ – shear rate, *n* – flow index and *k* – index of consistency.

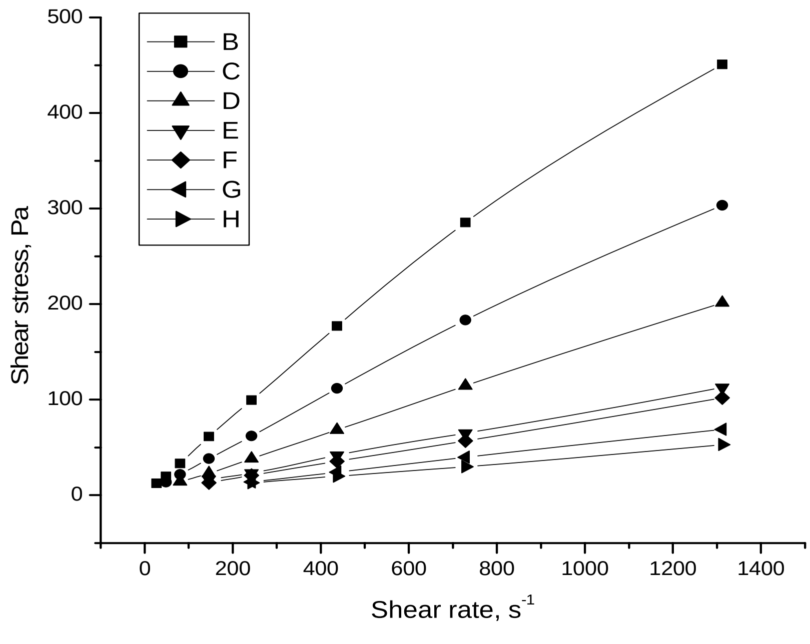

Fig. 1. Rheograms of 3% INFINEUM SV 260 solution at: ■ 313; • – 323; ▲ – 333; ▼ – 343; ♦ - 353; ◄ – 363 and ► – 370 K

The rheograms of 3% INFINEUM SV 260 solution at the specified temperatures and shear rates are shown in Figure 1.

The Figure 1 shows that 3% INFINEUM SV 260 solution behaves as a slight pseudoplastic fluid that follow the Herschel-Bulkley equation with a flow index very close to unity (0.97) at

313 and 323 K and as a Bingham fluid at higher temperatures. Thinning of solution (decreasing of viscosity) takes place at a shear rate of about 450 s^{-1} at 313 K and of 730 s^{-1} at 323 K. Thus, the higher the temperature, the higher the shear rate at which the decreasing of viscosity starts.

The decreasing of solution viscosity with increasing shear rate can be explained by the lining up of polymer molecules in the direction of the shear force at the above mentioned shear rates, which reduce the thickening effect they have when randomly distributed [8]. The higher the temperature, the higher the shear force necessary to line up the molecules, which explains the increasing of shear rate for thinning with increasing temperature. Reducing the shear rate the viscosity returns to its previous value, and the rheograms obtained with increasing and decreasing of shear rates superpose, that is the effect of shear rate is reversible (no time-dependent effect is observed).

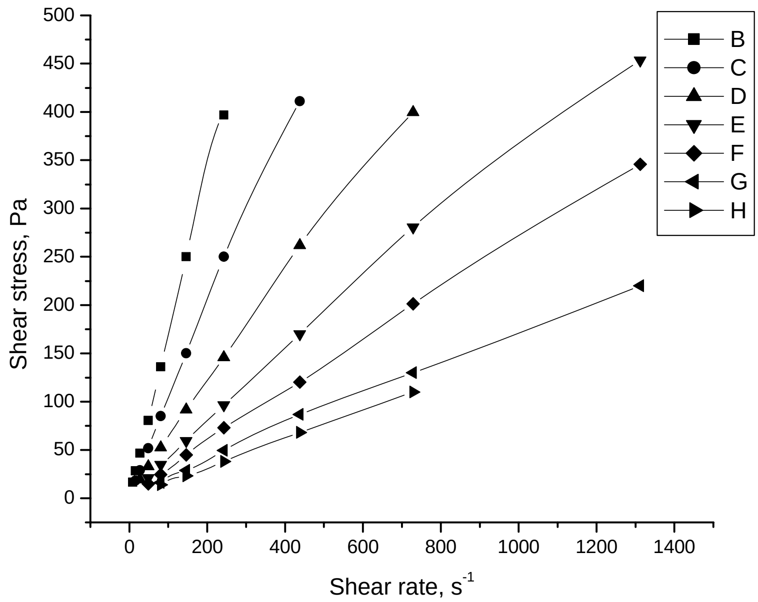

Fig. 2. Rheograms of 6% INFINEUM SV 260 solution at: ■ 313; • – 323; ▲ – 333; ▼ – 343; ♦ – 353; ◄ – 363 and ► – 370 K

Increase of solution concentration at 6% increases the temperature range on which the behavior is pseudoplastic, as can be seen from Figure 2: it behaves as a Bingham fluid only at 370 K. The flow index has the same value as for the previous solution. The conclusion regarding the dependence of shear rate at which the decreasing of viscosity starts on temperature remains valid.

If solution concentration is 10% viscosity increases very much and the shear rates range on which the measurements are possible reduces drastically: it varies between 3 and 243 s^{-1}, as can be seen in Figure 3.

At this concentration, decreasing of viscosity with increasing shear rate (pseudoplastic behavior) can be observed at 16.2 s^{-1} for 313 K. At 323 K it is not be observed because of the very narrow shear rate range on which the measurements were made (3-27 s^{-1}, the same as for the previous temperature). The values of shear rate for thinning for the other temperatures are: 48.6 s^{-1} for 333 and 343 K, 81 s^{-1} for 353 K. The solution behaves as a Bingham fluid at 363 K because of the low shear rate range on which the measurements are possible.

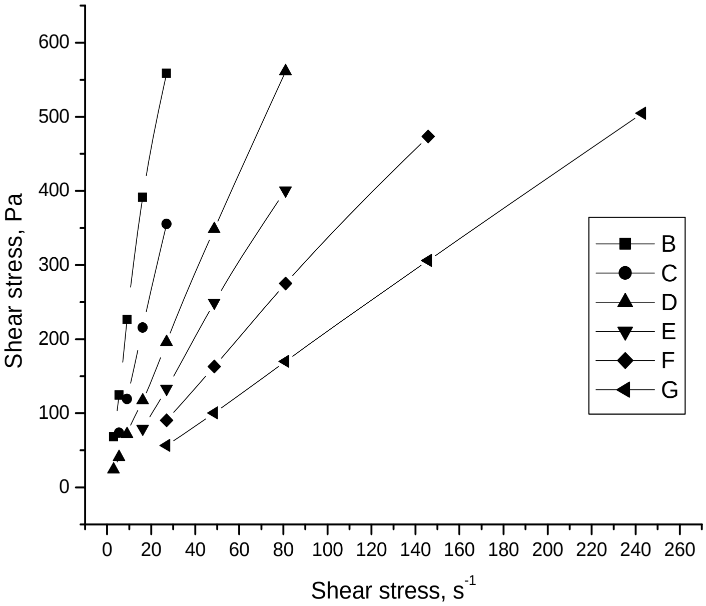

Fig. 3. Rheograms of 10% INFINEUM SV 260 solution at: ■ 313; ● – 323; ▲ – 333; ▼ – 343; ♦ - 353 and ◄ – 363 K

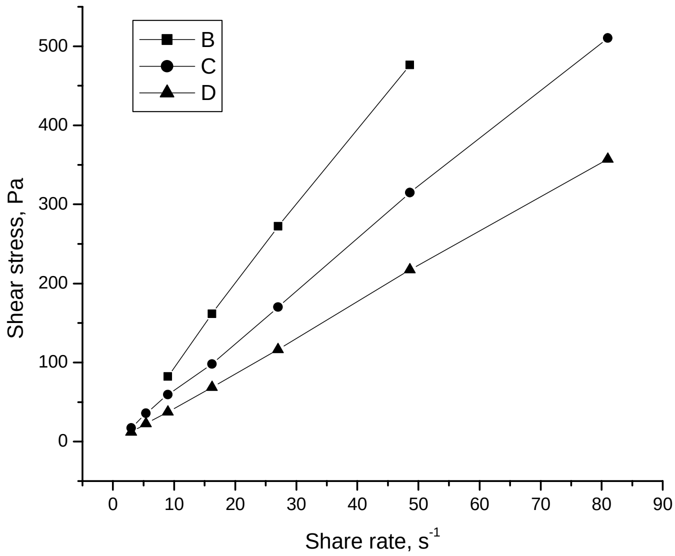

Fig. 4. Rheograms of 12% INFINEUM SV 260 solution at: ■ – 343; ● – 353 and ▲ – 363 K

Increasing of concentration at 12% reduces both the temperature and shear rate ranges for measurement, as Figure 4 shows, and decreasing of viscosity is obtained for lower shear rates: 48.6 s^{-1} for 343 K and 81 s^{-1} for 353 and 363 K.

Its flow index at 313 and 323 K is a little bit lower compared with that of the INFINEUM 260 solution having the same concentration (0.93), which indicates a more pronounced pseudoplastic behavior.

As it is well known, viscosity decreases when temperature increases, following the Vogel's equation [10]:

$$\eta_o = k \exp\left(\frac{\theta_1}{\theta_2 + T}\right), \tag{5}$$

where η_o is the zero shear rate viscosity (mPa·s), T – oil temperature (°C), and k (mPa·s), θ_1 (°C), and θ_2 (°C) are constant for a given lubricant.

The dependence of viscosity on shear rate respects the Cross' equation [7, 11]:

$$\frac{\eta_o - \eta}{\eta - \eta_\infty} = (K\dot{\gamma})^m, \tag{6}$$

where η is the lubricant dynamic viscosity (mPa·s), η_∞ – its fully shear thinned dynamic viscosity (mPa·s), $\dot{\gamma}$ – the shear rate (s^{-1}), K – a constant which has the units of time, and m – a shear index which is dimensionless. The degree of shear thinning is dictated by the value of m: when it approaches zero the liquid is Newtonian, while the most shear thinning liquids have a value of m approaching unity.

The complete description of shear rate dependence of viscosity requires the temperature dependence of the parameters in equation (6).

The temperature variation of η_o is given by equation (5); that of η_∞ is assumed to be the same. Thus, the ratio:

$$\eta_\infty / \eta_o = r, \tag{7}$$

where r is a constant independent of temperature, whose value is lubricant dependent. The obtaining of η_∞ being difficult, it is considered the same as that of the base oil.

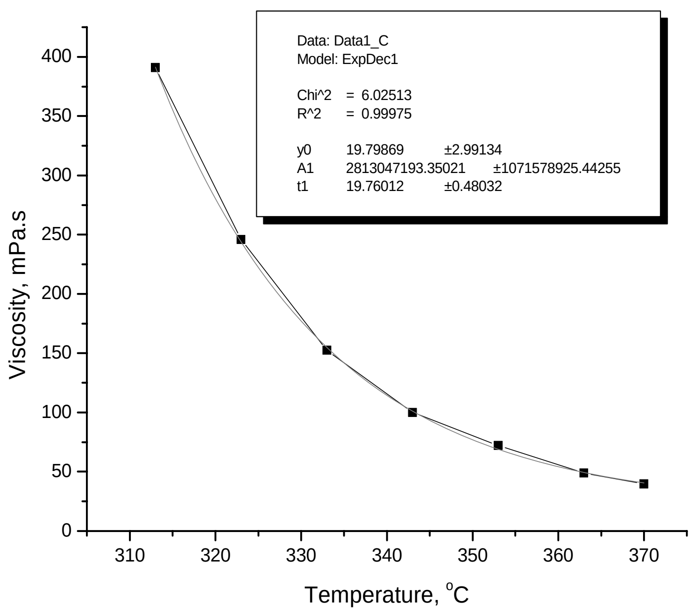

Fig. 5. Dependence of viscosity of 3% INFINEUM SV 260 solution on temperature

The dynamic viscosity of most materials, including polymer solutions and polymer melts well above their glass transition temperatures, decreases with temperature in accordance to Andrade equation [12]:

$$\eta = A \cdot 10^{B/T}, \tag{8}$$

where *A* and *B* are constants characteristic of the polymer and *T* is the absolute temperature.

The dependence of dynamic viscosity of 3% INFINEUM SV 260 solution on temperature follows, indeed, a first order exponential decay shown in Figure 5.

Plots of log viscosity versus $1/T$ for all the INFINEUM SV 260 solutions are given in Figure 6. It was found that log η as a function of $1/T$ was a straight line for all the tested solutions for temperatures ranging between 40 and 100 °C, which are well above their glass transition temperatures.

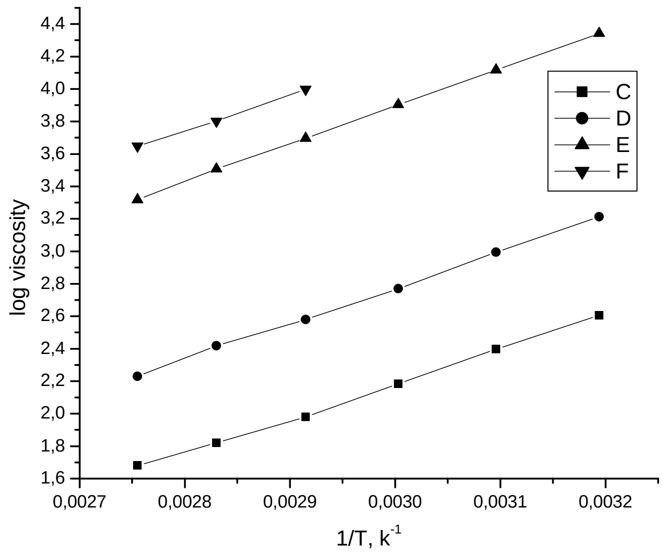

Fig. 6. Plots of log viscosity as a function of $1/T$ for INFINEUM SV 260 solutions: *C* – 3%; *D* – 6%; *E* – 10%; *F* – 12%

The constants A and B were also determined for the above solutions and listed in Table 1.

Table 1. Constants *a* and *b* in the Andrade equation for INFINEUM SV 260 solutions

Concentration, %	INFINEUM SV 260	
	log *A*	*B*
3	–4.07609	2087.67
6	–3.90898	2230.75
10	–3.07262	2322.20
12	–2.38099	2187.08

As can be seen, the value of A increases with increasing concentration for the both copolymers. The same think happens with the value of *B*, excepting the most concentrated solution, for which a decrease was obtained. Thus, the lowest slope was obtained for 3% INFINEUM SV 260 solution, followed by 12%, and the highest one for 10% solution. This means that the copolymer is better viscosity improver at low and high concentrations. INFINEUM SV 260 solutions, but all the values are lower than the corresponding ones given by the named copolymer, while the *B* constant of 10% solution is lower than that of 6%. The lowest *B* value was obtained for 12% solution, followed by 3%, whilst 6% solution had the highest value. This means that the viscosities of these solutions are less dependent on temperature for all the concentration. In addition, the viscosities of 10 and 12% solutions are pretty close at all the temperatures, but the viscosity of the most concentrated solution depends less on temperature.

Conclusions

Rheological behavior of 3; 6; 10 and 12% INFINEUM SV 260 solutions in SAE 10W mineral oil shows that they follow the Bingham model at low concentrations, low shear rates and high temperatures and the Herschel-Bulkley model at high concentration, high shear rates and low temperatures.

INFINEUM SV 260 solution in SAE 10W are more viscous corresponding the Herschel-Bulkley model over the whole studied ranges of concentrations, shear rates and temperatures.

The slopes of the straight lines representing the dependences of log viscosity on 1/T increase slightly with increasing concentration within the concentration range 3-10% for INFINEUM SV 260 solutions, but decreases for 12%; the lowest slope was obtained for 3% solution, followed by 12%, and the highest one for 10% solution.

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Comportarea reologică a uleiurilor multigrade

Rezumat

În acest articol sunt prezentate cele mai importante aspecte ale comportării reologice ale unor uleiuri aditivate. Comportarea reologică a soluţiilor a fost determinată cu viscozimetrul Haake VT 550 pentru viteze de forfecare cuprinse între 3 şi 1312 s^{-1} *şi viscozităţi* 10^4 *la* 10^6 *mPa·s. Intervalul de temperatură la care s-au făcut determinările este cuprins între 40 şi 100 °C. Măsurătorile reologice ale soluţiilor de 3; 6; 10 şi 12% INFINEUM SV 260 în uleiul mineral SAE 10W arată comportarea nenewtoniană între temperaturile (313…370) K şi la viteze de forfecare cuprinse între 3 şi 1312* s^{-1}*: modelul Bingham la concentraţii mici, viteze de forfecare mici şi temperaturi ridicate şi modelul Herschel-Bulkley la concentraţii mari, viteze de forfecare mari şi temperaturi scăzute.*