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Rheological study of Shear Degradation of High Molecular Weight Drag Reducer Polymers

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ABSTRACT

Polymer drag reducers (DRA) lose their visco-elastic properties when exposed to high shear rates. Shear rates of 3395, 6790 and 13 581sec^{-1}are imposed on two polymers with high molecular weight in order of (10-50) 10^6. The average molecular weight of polymer DRA1 is about 3-5 times higher than DRA2. The degree of degradation is estimated by the relative ratio of the calculated average molecular weight from intrinsic viscosity. The tests are run at two temperatures, 20 and 40^{o}C. At the tested temperature of 40^{o}C the low shear rate imposed on the polymer DRA1 no effect can be detected while DRA2 deviated from Newtonian when the shear rate of the measured shear viscosity exceeded about 1500 sec^{-1}.

INTRODUCTION

Polymer drag reducers (DRA) for hydrocarbons are long chain polymers with high molecular weight having an average between 10 to50 *10^6. DRA are used to increase the capacity of transporting hydrocarbon pipelines by reducing turbulent intensity. In pipelines, the DRA are exposed to high shear rates. Since they are long chain polymers, they are susceptible to degradation. In this paper the shear degradation of two polymers with different molecular weight are studied. The two polymers are designated DRA1 and DRA2, where DRA1 has an average molecular weight of approximately 2-fiver times higher than DRA2 but almost same chemistry. A comparison between the degradation of these two polymers are made based on their relative average molecular weight before and after being exposed to shear rates of 3395, 6790 and 13581 sec^{-1}.

The average molecular weight of the polymer is estimated from molecular weight -the intrinsic viscosity relationship.

Intrinsic viscosity [η] of a polymer solution is generally determined by measuring relative viscosities at series of different concentrations. Rudin[8] has proposed determination of intrinsic viscosity from a single point. In most cases, [η] can be evaluated conveniently using the graphic representations of Huggins[1] and Kraemer[2]. These techniques and other graphic solutions sometimes fail to provide accurate estimates of [η]. This is because they imply a linear, two-parameter approximation to an actual power-series relation between relative viscosity and concentrations[3]. Nonlinear least squares fitting of the actual curvilinear relation is a universal method for estimating [η] from relative viscosity data at a series of concentrations[4]. The nonlinear equation is solved and the intrinsic viscosity is then determined. The intrinsic viscosity is related to the molecular weight using the general equation by Mark-Houwink.

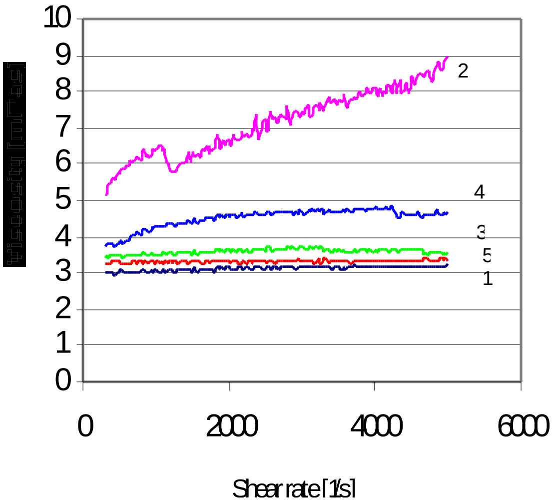

Fig.1 Viscosity of 1000 ppmw DRA1 exposed to different shear rates at 20C 1) DO, 2) 0 sec^{-1}, 3) 7690 sec^{-1}, 4) 3395 sec^{-1}, 5) 13582 sec^{-1}.

RESULTS AND DISCUSSION

When DRA are shear degraded their visco-elastic behaviour change, hence their performance in reducing the drag in pipelines declines. In this work polymers are exposed to shear rates of 3395, 6790 and 13581sec^{-1} for the same period of time (68 minutes). The used shear degradation set-up is described else where[10].

The rheological behaviour of the sheared and un-sheared polymers is studied by scanning the polymer viscosity at shear rates from 300 to 5000sec^{-1}. Indeed the effect is apparent where the sheared polymer at high shear rate showed a Newtonian behaviour. The measured viscosities are 3.18, 3.38 and 3.54 mPa.s at shear rate of the measured shear viscosity of 4980sec^{-1} and 20°C, for diesel oil and DRA1 exposed to shear of 13582 and 7690 sec^{-1}, respectively as shown in Fig.1.

When DRA1 polymer is exposed to shears at 40°C, again a Newtonian behaviour of the polymer is detected when the applied shear rates on the polymer are 6790 and 13582 sec^{-1} while almost no difference in the measured shear viscosity when the polymer is exposed to degradation shear rate of 3395sec^{-1} as shown in Fig.2. When the test is, then carried out on the polymer DRA2 at 40°C, similar observation to the one with DRA1 is shown in Fig.3. The exposed polymer to shear degradation of 6791 and 13581sec^{-1}, Newtonian fluid behaviour is observed. However, the exposed polymer to shear degradation of 3395sec^{-1} deviated from Newtonian fluid behaviour after the scanning shear of the shear viscosity measurements has exceeded 1500 sec^{-1}.

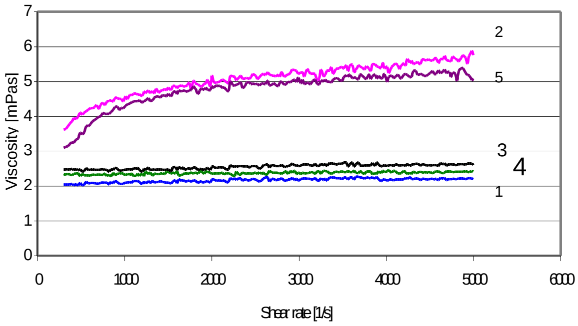

Figure 2 Viscosity of 1000 ppmw DRA1 exposed to different shear rates at 40C, 1) DO, 2) 0 sec^{-1}, 3) 6790 sec^{-1}, 4) 13582 sec^{-1} and 5) 3395 sec^{-1}

In order to determine the degree of the degradation of the sheared polymers, the molecular weight ratio of the sheared to the unsheared polymer is estimated from Mark-Houwink-Sakurada's general relation that relates the intrinsic viscosity to the molecular weight as follow:

$$[h] = K`\bar{M}_{w}^{a} \qquad (1)$$

Where, [η] is the intrinsic viscosity (dl g^{-1}), $\bar{M}_w$ is the average molecular weight of the polymer, K` and the exponent (a) are constants determined by the intercept and the slope of a plot between the intrinsic viscosity [η] and molecular weight in different solvents. The constants K` and exponent (a) are assumed to be constant for fixed temperature, polymer type and solvent. This is not strictly true, however, in this case we are after a trend.

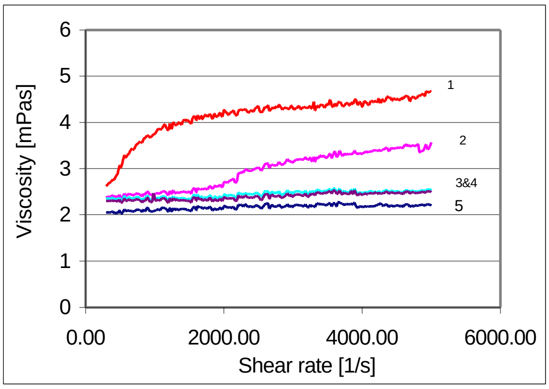

Figure 3 Viscosity of 1000 ppmw DRA2, exposed to different shear rates at 40C 1) 0 sec-1, 2) 3395 sec-1, 3) 6791 sec-1, 4) 13581 sec-1, 5) DO

Flory[5] derived the relationship between the intrinsic viscosity and the molecular weight taken into account the radius of gyration of the polymer, which is included in the constant K and arrived at the following equation

$$[h] = KM^{\frac{1}{2}}a^{3} \qquad (2)$$

Where, K is considered being a constant independent both on the polymer molecular weight and of the solvent. It may, however, vary somewhat with the temperature inasmuch as the unperturbed molecular extension $\overline{r_0}^2$ /M may change with temperature, where, $\sqrt{\overline{r_0}^2}$ is the unperturbed root-mean-square end-to-end distance. The term α is the molecular expansion factor (is also termed as a swelling factor). Our intention in this study is to determine the effect of different shear rates on the rheological behaviour/degree of degradation of the polymer; so the average molecular weight ratio of the sheared to the un-sheared polymer rather than the absolute molecular weight may be sufficient for the purpose of this work. Equation1 is, then, used assuming that K` is constant. Since the original polymer is shear degraded at different shear rates, the intrinsic viscosity is estimated from each set of experiments. In each set of experiments, polymer concentration of 2, 6 and 10 g dl^{-1} are used to estimate [η].

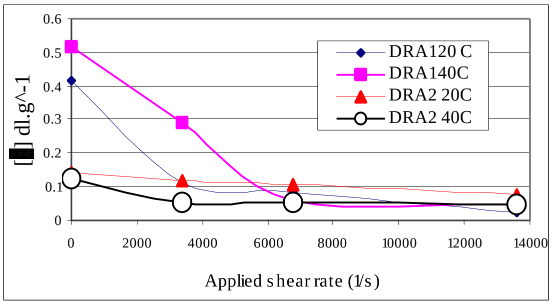

Figure 4 [η] for the different sets of the applied shear rates on DRA1 and DRA2 at 20 and 40°C.

Flory[5] stated that the exponent (a) does not fall below 0.5 in any case and seldom exceeds 0.8. Rudin et al[6] tested various polymers with different solvents, found that the exponent (a) is between 0.5 and 0.79. Park and Choi[7] found that for linear polymer system the Mark-Houwink exponent (a) is about 0.7 in a good solvent and 0.5 in the theta condition.

Intrinsic viscosity [η] is defined according to the following equation

$$[\eta]=[(\ln \eta_r)/c]_{c\to 0} \qquad (3)$$

Huggins[1] has pointed out that plots for a given polymer/solvent system vary approximately as the square of intrinsic viscosity as expressed by the following equation:

$$\frac{1}{C}\left(\frac{h}{h_0}-1\right)=[h]+k_H[h]^2C \qquad (4)$$

Where,η and η_0 are the viscosity of polymer solution and the solvent, respectively, ($\frac{h}{h_0}=h_r$, relative viscosity), C is the polymer concentration expressed as $g.dl^{-1}$ and k_H is Huggins constant. In practice it is customary to measure the relative viscosity at two or more concentrations, chosen to give

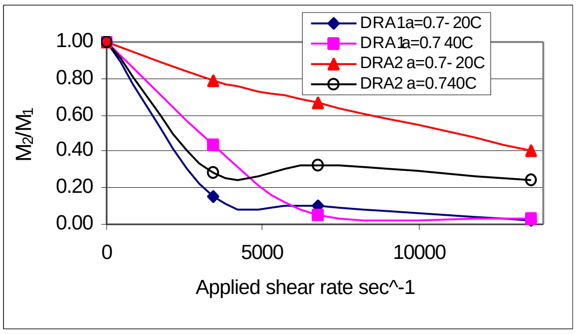

Fig.5 Molecular weight ratio (M_2/M_1) of the sheared to the unsheared polymers.

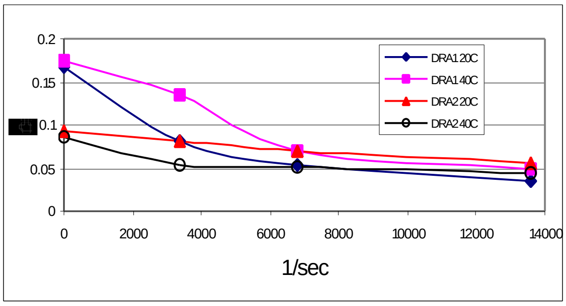

Figure 6 Volume fraction α of the swollen polymer.

relative viscosities in the range of 1.1 to 1.5, and then extrapolated to C=0. Series of shear rates are then required in order to extrapolate to very low shear rate of zero. This practice may produce errors due to forcing a real curvilinear relation into a rectilinear form. In this work power series expressions are solved directly by non-linear regression analysis^4 of the following equation

$$\frac{1}{C}\left(\frac{h}{h_0}-1\right)=[h]+k_H[h]^2C+k'_H[h]^3C+..... \qquad (5)$$

Fig.4 shows the intrinsic viscosity of different sets of applied shear rates on DRA1 and DRA2 at 20 and 40°C. Small change is observed in [η] for both polymers when they are exposed to shear rate beyond 6791sec^{-1}. In general, larger decline in [η] is shown for DRA1 compared to DRA2 as expected since the former has higher molecular weight.

It is interesting, however, to observe lower declining slope of [η] for DRA1 at 40°C than that at 20°C. A plateau is reached when the applied shear rate on DRA1 exceeded 6791sec^{-1} at 40°C while almost a plateau of the [η] has already been reached at the applied shear rate of 3395 sec^{-1} for DRA2.

DRA2 showed an opposite features where, a lower declining slope at 20°C compared to 40°C.

The ratio of the molecular weight $\frac{M_2}{M_1}$ of the sheared (M_2) and the unsheared (M_1) for the polymers are estimated using eq.1. Diesel oil used as a solvent, which is considered as a moderate solvent, so an exponent (a) value of 0.7is used^8. Fig.5 shows a relative reduction of the molecular weight as a function of the applied shears on the polymers.

The slow reduction in the molecular weight ratio at 40°C for DRA1 is in line with the observed trend with the shear viscosity measurement that is shown in Fig 2. For DRA2 the opposite effect may be explained based on that at low measured shear viscosity (<1500 sec^{-1}) both temperatures showed Newtonian behaviour for the applied shear degradation on the polymer. The low shear rate is selected to calculate the intrinsic viscosity (by the definition of the intrinsic viscosity).

An increase of about 14% of the molecular weight ratio for the sheared DRA2 at 6791sec^{-1} and 40°C is observed. This is within the experimental error of 10-15%. Alternatively, if this is a true experimental observation, it may be explained based on the molecular interactions due to the increase of the segments from the degraded polymer at shear rate of 6791sec^{-}1. This is followed by a reduction of the molecular weight when the applied shear degradation increased to 13581sec^{-1} which may be due to that the applied high shear degradation on the polymer may produce more homogeneous low molecular weight polymer solution (narrower molecular weight distribution) where the effect of the interaction may be smaller hence reduction of the flow resistance.

Equation 2 theoretically predicts that a decrease of the degree of swelling as the molecular weight increases. However, in the situation encountered in this work increase of the number of segments, due to the shear degradation, have nothing to gain by expanding, for the decrease in interaction with it self, which would be compensated by increased interference with its neighbors[5].

Rudin et. al and Ford[9] described an equation to estimate the volume fraction of swollen polymer molecules in solution from the inverse of the viscosity ratio

$$\frac{h_0}{h} = 1 - 2.5a + 11a^5 - 11.5a^7 \qquad (6)$$

where, α is the volume fraction of the swollen polymer molecule, η_0 and η are the viscosity of the solvent and polymer solution, respectively. The equation is solved for α with quadratic factorisation algorithm, where only one of the seven roots obtained is real, positive and within the range $0 \leq \alpha \geq 0.5$. Fig.6 shows the volume fraction of the swollen polymer as a function of the shear degradation applied on the polymer. This may confirm our prediction of the swelling behaviour (estimated by α). The degraded long chain molecules to smaller ones may be considered as increase in the density of molecules in the solution. As expected, α decreased as the molecular weight of the polymer decreased accompanied by increase of the number of molecules in the polymer solutions.

SUMMARY

High molecular weight polymer showed more resistance to shear degradation (at applied low shear rate 3395 sec^{-1}) at high temperature (40°C) than that at lower temperature. This is not fully understood, but intuitively, the increase of degree of swelling (higher swelling at 40 than 20°C) as the molecular weight decreases, and increase number of molecules (with a broad molecular weight distribution at low shear degradation of 3395 sec^{-1}, since not all the polymer degrades) produces varying degrees of swelling and molecular interactions. Those factors may play a role to promote resistance of the flow accordingly maintaining the viscosity as shown in Fig. 2.

On the other hand the observation for DRA2 at 40°C is similar to that for DRA1 but appeared at measured shear viscosity > 1500 sec^{-1} may support the increase of polymer interaction with solvent as well as polymer swelling which would enhance the flow resistance and regain some of the visco-elastic behaviour, but not to the same extent as for DRA1 which may have broader molecular weight distribution when a low shear degradation (3395 sec^{-1}) is applied. More work is needed to support this hypothesis/explanation.

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