Oil-soluble Drag-reducing Polymers

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Abstract

This article reviews the oil-soluble polymeric drag-reducing agents (DRAs) with an outlook to their large-scale application in petroleum industry. A general discussion on mechanism of the DR phenomenon and mechanical degradation of the drag reducers in turbulent flow is offered with an emphasis on the molecular parameters. Furthermore, low charge density associating polymers, as a new class of oil-soluble flow improvers, are described.

Key Words: Drag reduction, Oil-soluble polymer, Turbulent flow, Shear degradation, Polympholyte.

Introduction

From the time when N.S. Blatch in 1906 in an article titled as "Water Filtration at Washington" for the first time pointed out briefly to the reduction of water pressure drop due to presence of some substances, more than 40 years passed when Mysels and Toms reported separately the same phenomenon. However, in this period similar works during the flow of wood pulp fiber suspension in water had also been observed. This phenomenon which was firstly named "Toms' effect", in the area of fluid mechanics was later known as drag reduction (DR). This, by definition, is the phenomenon whereby extremely dilute solutions of some substances, mainly high polymers, fibers, soap, surfactants and their mixtures exhibit frictional resistance of turbulent flow much lower than the solvent alone.

In the last century, Reynolds found out that transition from laminar to turbulent in pipe flows takes place at particular value (≥ 2300) known as the Reynolds number (Re)

$$Re = \frac{\bar{u} D \rho}{\eta}$$

where $\bar{u}$ is the average velocity, $D$ the pipe diameter, $\rho$ density and $\eta$ viscosity of the liquid. The conventional relation for evaluating the drag reduction was defined by Savin$^4$, as at constant flow rate

$$\% DR = \left(1 - \frac{\Delta P_r}{\Delta P_s}\right) \times 100$$

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where $\Delta P_s$ and $\Delta P_p$ are pressure drops in a given length of tube for solvent and polymer solution, respectively.

Drag-reducing properties of poly(ethylene oxide) (PEO), the most effective synthetic homopolymer, was discovered by Fabula\(^5\) in 1963. During the period of 1965-1980, there was a spurt in research activity on drag reduction by researchers drawn from diverse fields such as turbulence, rheology, hydraulics, polymer and material science, so a large number of flow improvers (drag-reducing agents, DRAs) were discovered. However, high polymers have emerged as the most efficient drag reducers and shown the greatest potential for various applications. During the two last decades, extensive efforts were concentrated mainly on the effect of polymers on turbulent structure by Doppler-anemometry, flow visualization, flow through sudden contraction, nonhomogeneous flows, extensional viscosities, theoretical attempts to correlate drag reduction with rheological properties, and molecular parameters in flow, besides the areas pursued in the earlier period.

The range of applications of drag reduction has increased tremendously. Possible areas include oil well fracturing operations, crude oil and refined petroleum products transport through pipelines, fire fighting, sewerage and flood water disposal, irrigation, hydrotransport to solids, water and heating circuits, hydraulic machinery, jet cutting, marine and biomedical applications\(^3, 6\). A large number of review articles, up to about 1980, mostly from pioneering workers\(^7-14\), and after that, along with proceedings of international conferences\(^15-18\) have been published.

In spite of the intensive studies on the polymeric flow improvers, most of the reported works have been on aqueous solutions, because they not only have no hazard of flammability and toxicity, but also offer more immediate possibilities of commercial exploitation in most applications. In addition, due to often quantity increase of any solvent used through polymer degradation, the cost of organic solvents is also appreciable.

This review focuses on the oil-soluble polymeric DRAs with emphasis on the role of molecular structure in their performance and shear stability.

**OIL-SOLUBLE DRAG-REDUCING POLYMERS**

**Variety and Large-scale Application**

Polymer drag reduction has had a rather empirical or discovery-type history. Many of polymeric DRAs have been discovered on a trial-and-error basis. Only recently, materials specifically designed for friction reduction have been developed for oil industry\(^19, 20\).

Table 1 summarizes the polymers that show DR in nonaqueous solvents and crude oil. It appears that the first successful large-scale application of polymers as flow enhancers has been in the field of crude oil research\(^20\). The Trans-Alaska-pipeline (TAPS), extending from Purdhoe Bay, Alaska, to Valdez, Alaska, a distance of 1,287 km, is one of the most significant large-scale technical examples of the benefits to be gained from the DR effect. A polymeric flow improver, CDR (an ultrahigh molecular weight $\alpha$-olefin copolymer) is injected approximately every 100 km at a concentration of 5-25 ppm in pipes with diameter up to 1.20 m. The possible levels of DR have been up to 28% which under laboratory conditions reaches to 80%\(^26, 27\). It is not necessary to separate the polymers afterwards since the amounts lie below the level of contamination, and do not show any other negative effects. Another DRA tested with TAPS, is poly(1, 2-butyleneoxide) with a molecular weight of $2.05 \times 10^6$ and a concentration of 20 ppm which has resulted in 45% drag reduction\(^30\). Although, polyisobutylene has been the earliest commercial oil-soluble DRA\(^24\), and widely exposed to various investigations, it has the disadvantage of being very shear...


**TABLE 1. Drag-reducing Polymers Applicable in Nonaqueous solvents**

<table>
<thead>
<tr>
<th>Drag-reducing agent</th>
<th>Solvent</th>
<th>Commercial Source</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyisobutylene (PIB)</td>
<td>Toluene, Benzene, Cyclohexane, Light Mineral oil, Decalin, Kerosene, Crude oil</td>
<td>Shell Oil Co.</td>
<td>20–24</td>
</tr>
<tr>
<td>CDR</td>
<td>Crude oil, Gasoline, Fuel oil</td>
<td>Conoco Inc.</td>
<td>25–27</td>
</tr>
<tr>
<td>FLO</td>
<td>Crude oil, Diesel oil, Gasoline</td>
<td>Chem Link Petroleum Inc.</td>
<td>19, 28</td>
</tr>
<tr>
<td>Ethylene-α-olefin copolymers</td>
<td>Decalin</td>
<td>—</td>
<td>29</td>
</tr>
<tr>
<td>Poly(1,2-butyleneoxide)</td>
<td>Crude oil</td>
<td>Dow Chemical Co.</td>
<td>30</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>Monochlorobenzene, Toluene</td>
<td>—</td>
<td>2, 25, 31</td>
</tr>
<tr>
<td>Homo- and copolymers of acrylates and methacrylates</td>
<td>Kerosene</td>
<td>—</td>
<td>32</td>
</tr>
<tr>
<td>Polysoprene (PI)</td>
<td>Aircraft fluid</td>
<td>Shell Oil Co.</td>
<td>33</td>
</tr>
<tr>
<td>Hydrogenated PI</td>
<td>Liquid hydrocarbons</td>
<td>—</td>
<td>34</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>benzene, Cyclohexane, Methyl ethyl ketone</td>
<td>—</td>
<td>21, 35</td>
</tr>
<tr>
<td>Mixture of PIB and isoprene rubber</td>
<td>Toluene</td>
<td>—</td>
<td>36</td>
</tr>
<tr>
<td>Mixture of PIB and polystyrene</td>
<td>Toluene</td>
<td>—</td>
<td>37</td>
</tr>
<tr>
<td>Homo- and copolymers of alkylstyrenes</td>
<td>Kerosene</td>
<td>—</td>
<td>32</td>
</tr>
<tr>
<td>Styrene-styrenesulfonate-vinylpyridine terpolymers</td>
<td>Xylen</td>
<td>—</td>
<td>38</td>
</tr>
<tr>
<td>Mixtures of metal-sulfo-EPDM and styrene-4-vinylpyridine copolymer</td>
<td>Xylene</td>
<td>—</td>
<td>39</td>
</tr>
<tr>
<td>Tri-n-butyl-tin(IV) fluoride&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Hexane, Cyclohexane</td>
<td>—</td>
<td>40</td>
</tr>
</tbody>
</table>

<sup>a</sup> A micelle-forming system.

degradable. Nowadays, CDR and FLO are only efficient flow enhancers for crude oil and refined petroleum products transportation.

The authors’ research program includes modification and optimization of polymeric DRA preparation methods, recently offered by Peiffer<sup>38</sup> and Kowalik et al.,<sup>39</sup> for using in Rey Tabriz crude oil pipeline over a distance of 600 km.

**Classification**

Polymeric flow improvers may be categorized based on different aspects. Hoyt has divided them according to their flow behaviors into three classes: homogeneous solution; two (liquid)-phase components, polymer and supporting liquid (heterogeneous polymer flows); and surfactant solutions in which the dissolved component is arranged in aggregate

![Chemical classification of oil-soluble polymeric drag reducers](image)

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form. This classification has also been applied by the other researchers\textsuperscript{9-13}.

Majority of the oil-soluble DRAs form homogeneous systems (Table 1). However, they can be reclassified according to their chemical structure (Fig. 1).

**CHEMICAL FEATURES OF DRAG REDUCTION**

**Molecular Parameters**

The precise mechanism describing how a DRA works to reduce friction is not established. It is believed these agents act by directly reducing turbulence, or by absorbing and later returning to the flowing stream energy which otherwise would have been wasted in producing the crossflows which comprise turbulence. The absorb-and-return approach has a certain intuitive attractiveness because one of the characteristics of a viscoelastic fluid is its ability to do this on a physically large scale; whether the effect exists at the molecular scale is not completely understood.

However, intention to identify the molecular parameters, which are relevant to the qualitative understanding of the flow phenomena, may lead to four molecular structures; in fact, the effective parameters on the DR efficiency are:

1) Primary structure including molecular weight (10\textsuperscript{5}-10\textsuperscript{9}) and chemical nature of the polymer.

2) Secondary structure including molecular weight distribution (MWD), branching and copolymer composition.

3) Tertiary structure including molecular shape, radius of gyration, end-to-end distance, hydrodynamical radius, and second Virial coefficient.

4) Quaternary structure including dynamic parameters in general, segment mobility, entanglements and energetic interactions (association, aggregation etc.).

All of the proposed theories for DR deal somehow with the above parameters. However, our knowledge of the effect of polymeric DRAs on turbulent flow processes is hampered by the limited understanding of turbulence itself. On the other hand, some peculiarities, i.e., apparent molecular weight due to thixotropic behavior in ampholytic polymer solutions\textsuperscript{41}, or synergistic effects in DR of some polymeric mixtures\textsuperscript{36,37}, may also be observed. Such observations, however, have been led to very important applied approaches, e.g. CDR, which is firstly synthesized by Culter et al. and reported in the patent literature\textsuperscript{42}. They polymerized a mixture of \( \alpha \)-olefins (C\textsubscript{6}-C\textsubscript{20}) using a Ziegler-Natta catalyst to obtain a linear, ultra-high molecular weight (1-40 \times 10\textsuperscript{6}) polymer. This polymer, as Culter claimed, has been the best shear resistant oil-soluble DRA. Since none of the molecular parameters of this commercial DRA (as the case of FLO), is clear and easily characterizable, they are difficult for detailed chemical investigations.

In general, polymeric DRAs are highly viscoelastic and thixotropic; and may have a viscosity at low shear rates in excess of 3 \times 10\textsuperscript{6} cp while having a viscosity 100-1000 times less at higher rates. The viscosity is somewhat affected by temperature, and increases with decreasing temperature. DRA-solvent solutions are viscoelastic, time-independent, shear degradable and non-Newtonian fluids.

Apart from the mentioned molecular ambiguity, there are some empirical facts in the solution behavior of polymeric DRAs. It is known that a DRA does not coat the pipe wall nor does it change the physical properties of the fluid. Virk\textsuperscript{43} has theorized that the coiled DRA molecule undergoes extension in turbulent flow which retards the radial loss of energy in a pipeline; thereby increasing the energy available in the axial direction of pipeline flow. The following section deals with the general aspects on the solution behavior of DRAs in turbulent flow.
Solution Behavior and Degradation of Polymeric DRAs

Macromolecules in solution are usually randomly coiled so that they form tangled and beanlike coils filled with solvent. Good thermodynamically solvents interact with the chains causing an expansion of the coil and more chain flexibility. For the exact determination of coil size, it is necessary to ensure that measurements are carried out in dilute solutions. In general, the range of dilute particle solutions and concentrated solutions may be definitely separated by a critical concentration, \( c^* \), where the geometric shape of the polymer coils are assumed to be spherical. The presence of small amounts (beneath \( c^* \)) of polymeric DRAs produce reduction in the frictional losses in turbulent flow, which has an immense field of applications. But a big snag exists: DR decreases with flow time, due to shear degradation of added polymer\(^{44}\). An easily manageable model, offered by Bouldin\(^{45}\), has been derived which can make an ad hoc prediction of the critical shear rate at which mechanical chain scission takes place (Fig. 2). Degradation occurs when all intermolecular coupling points are loosened and the discrete molecule is subjected to the velocity field as shown in Fig. 3.

\[
\begin{align*}
\dot{\gamma} &= \dot{\gamma}_0 \\
\dot{\gamma}_0 &> \dot{\gamma}_{deg} \\
\dot{\gamma} &= \dot{\gamma}_{deg} \\
\dot{\gamma}_0 &< \dot{\gamma}_{deg}
\end{align*}
\]

Fig. 3. Schematic picture of the state of solution of a non-sheared solution, a disentangled solution at the critical shear rate and a degraded sample.

This critical value can be estimated by application of the \( \eta_0-MW-c \) relationship, due to the fact that the viscosity level of a completely disentangled polymer solution is equal to the product \( c \cdot [\eta] \), i.e., the specific viscosity, \( \eta_{sp} \), is directly proportional to the effective volume fraction of polymer. Further enhancement of the shear gradient leads to a reduction in the mean molecular weight (\( MW_{deg} \)),

\[
\eta_{sp} (\dot{\gamma}) = c \cdot [\eta]_{deg} \tag{3}
\]

\[
MW_{deg} = \left( \frac{\eta_{sp}(\dot{\gamma})}{c \cdot K_n} \right)^{\frac{1}{s}} \tag{4}
\]

and consequently, in the loss of drag reduction\(^{46}\),

\[
DR_t = DR_0 e^{-Rt} \tag{5}
\]

where \( \dot{\gamma} \) is shear rate, \( [\eta]_{deg} \) is intrinsic viscosity after the flow time (t), \( R \) is the measure of the rate of decay of DR effectiveness, \( K_n \) and \( a \) are the constants of the Mark-Houwink relationship, and \( DR_0 \) and \( DR_t \) are the drag reduction at zero time and at time (t), respectively.

The DR of polymeric fluids seems to be linked to the extensibility of polymer coils. Assuming the elongational viscosity to be a determining factor for DR, Durst \textit{et al.}\(^{47}\) proposed that the elongation rate correlates with the Re of the fluid and that, therefore, the effectiveness
should be linked with the Deborah number, De. The latter is defined as the ratio of the relaxation time of the polymer (τ) to the time between two elongations (t₀).

\[
De = \frac{\tau}{t_0}
\]

The coil can be fixed between the counter-rotating of eddies and elongated in the direction of low (Fig. 4). The relaxation time should be greater or at least equal to the life time of the eddy to obtain no degradation. The life time of eddy which is proportional to t₀ and the eddy dimensions, depends ultimately on the molecular parameters and the solvent nature.

**ASSOCIATING POLYMERIC DRAG REDUCERS**

A family of novel and efficient DRAs for a variety of organic solutions, have recently been improved by Peiffer, Kowalik and their colleagues in Exxon Res. & Eng. Co.\textsuperscript{36, 39, 49} Their reports have shown that a polyampholyte (Fig. 5) can be effective as DRA for hydrocarbon solutions. For example, a terpolymer of a metal (i.e. transition metal) neutralized styrene sulfonate can interact with styrene-vinylpyridine monomer units chemically attached to the same polymer chain molecule, via a coordination chemistry-type mechanism (Fig. 6). This complex and its solution behavior in dimethylformamide (DMF) is discussed elsewhere\textsuperscript{41}.

Another example is SVC/Zn-SEPDM blends in nonpolar solvents such as xylene\textsuperscript{50}. In this system, viscosity measurements indicate that no specific interaction between the two polymers occurs when alkali or alkaline earth metal neutralized SEPDM is used. However, in a polar solvent such as DMF, the mentioned

![Diagram of polymer coil and eddy interactions](image)

**Fig. 4. Schematic representation of the elongational flow between two eddies in turbulent flow.**

Finally, it has to be pointed out that in the large-scale pipeline flow, some other different factors may cause mechanical degradation. Pumps, bends, links and obstacles to the flow, such as edges, sharp-edged links or ringblends, etc. lead macromolecules to shatter. In addition, shear degradation occurs in the entrance region, as found out by injection experiments\textsuperscript{48}.

![Chemical structures](image)

**Fig. 5. Chemical formula of the main parts of the polymeric associating DRAs. A typical composition may be as x = 0.55, y = 0.40, z = 0.05, p = 0.96, q = r = 0.04 and M⁺ = Zn²⁺/2.**
cations, i.e. Cs\(^+\), Ba\(^{2+}\), form the vinylpyridine (VP)-sulfonate complexes as well as the transition metal cations, i.e. Cu\(^{2+}\), Zn\(^{2+}\) (Fig. 6(a)). Therefore, the structure and stability of the VP-sulfonate complexes, in addition to the cation nature, depend on the polarity of solvent from the solvation point of view (the ability of separation of the ion pair by the solvent). Since a nonpolar solvent favors the formation of the ion pair, direct complexation of the transition metal (using d orbitals) with the VP group can occur (Fig. 5(b)). Such coordination complex formation has also been established in the solid state\(^{51}\).

A variety of polymer backbones will display the desirable properties. In addition to sulfo-EPDM, the sulfonation products of isoprene copolymers, SBR, block copolymers, etc., can act as the cationic part, and polymers containing basic nitrogen moieties (amine, alkyl amine or pyridine groups) may play the role of the anionic part of the interchain coordination complex. These associating polymers can provide improved DR via formation of higher molecular weight entities or even a polymeric networks rather than by high molecular weight. Consequently, such larger molecular weight structures of networks can be less sensitive to turbulente flow degradation due to the ability of the coordination-type bonding to absorb energy from the fluid itself in a reversible manner\(^{38}\) (Fig. 6). These bonds will break and subsequently reform in a flowing fluid, reducing the stress on an individual chain and, therefore, preventing a substantial and permanent deterioration in the molecular weight, especially as compared to its non-associating or non-coordinating counterpart.

Peiffer et al.\(^{38}\) have pointed out that because of a low charge density in such systems, they are often soluble in single component nonaqueous solvents, and a polar cosolvent is not always required for solvation. Partly, due to this solubility characteristic, these materials are recently recommended in drag reduction applications. Fig. 7 shows the data relating measured pressure drops to solvent Reynolds numbers for a SVC/Zn-SEPDM associating system as a good flow improver.

![Fig. 7. Typical result obtained from evaluation of SVC/Zn-SEPDM associating system in xylene at 25°C.](image)

As a result, the associating oil-soluble polymeric DRAs have two certain advantages in comparison with the conventional previous types. They are: (a) easy to prepare because of the unnecessary to achieve very high molecular weights, and (b) capable to lead to an apparent high molecular weight (as is necessary for DR) in turbulent flow, without a
high degree of degradation, due to the specific chemical nature of the interchain complexes.

CONCLUSION

Reduced pressure drops during turbulent flow can be induced by small amounts of linear, high molecular weight (> 10^5), soluble polymeric additives. Several mechanisms and models are proposed to explain the drag reduction (DR) phenomenon. They are based on either a molecular approach or fluid dynamical continuum considerations, but a unified theory of the phenomenon has not yet been proposed. However, some semi-empirical interpretations, such as the molecular stretching through elongation flow, may often be used.

Although surfactants, fiber suspensions, etc., may show the DR effect also, most of the reported works have been on aqueous solutions. The most important wide application of oil-soluble polymeric drag reducers is in the petroleum transportation through pipeline. In this case, commercial high polymers produced from unknown compositions of \( \alpha \)-olefins (C\(_6\)-C\(_{20}\)) are being used, i.e., CDR and FLO. However, during last few years, a new class of oil-soluble polymeric DRAs (low charge density polyampholytes as associating systems) has been developed and anticipated to use in the mentioned large-scale application.

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