On the drag reduction effect and shear stability of improved acrylamide copolymers for enhanced hydraulic fracturing

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HIGHLIGHTS

- NaAMPS content in the drag reducer backbone improves friction reduction.
- Drag reduction of NaAMPS copolymer was described with an empirical correlation.
- NaAMPS content does not affect polymer chains mechanical degradation.
- No limit to polymer mechanical degradation was detected.
- The most common correlation for polymer mechanical degradation does not apply.

ABSTRACT

Polymeric drag reducers, such as partially hydrolysed polyacrylamide (PHPAAm), are important chemical additives in hydraulic fracturing fluids as they can significantly decrease the frictional pressure drop in the casing (by up to 80%), resulting in an increase of the injection rate that can be delivered to the fracturing point. The incorporation of sodium 2-acrylamido-2-methylpropane sulphonic acid (NaAMPS) moieties into polyacrylamide (PAAm) can further improve the performance of fracturing fluids by addressing some compatibility issues related to the use of PHPAAm, e.g., the sensitivity to water salinity. In this study, three types of poly(acrylamide-co-NaAMPS) and pure PHPAAm were investigated with respect to polymer induced drag reduction and mechanical polymer degradation in turbulent pipe flow in a pressure-driven pipe flow facility. The test section comprised a horizontal 1” bore circular cross-section pipe. The facility was modified in order to allow long time/length experiments by automatically recirculating the polymer solution in a closed-loop through the test section. The presence of NaAMPS groups in the copolymer backbone is found to increase the ability of PHPAAm to reduce frictional drag while the vulnerability to mechanical degradation remains unaffected. The drag reduction of NaAMPS copolymer solutions can be described by a modified version of Virk’s correlation (1967), extended to include the effect of Reynolds number. Polymer mechanical degradation is found to proceed until the friction reducer is almost ineffective in reducing drag. This phenomenon is in contrast with the most common correlation for polymer degradation, which predicts the existence of an asymptotic (but finite) limit to the reduced drag reduction.

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1. Introduction

Hydraulic fracturing techniques recently achieved resounding success in increasing fossil fuels extraction, particularly of shale gas, and will play a major role in growing non-OPEC production in the near future (Energy Information Administration, 2013). Fracturing fluids typically comprise several additives to enhance their performance. Among these additives, polymers of acrylamide (AAm) have been extensively used in the oil and gas industry. Polycryliclamides are used in hydraulic fracturing applications to reduce the frictional resistance in turbulent pipe flow, an effect known as drag reduction, which was first described by Toms (1948). The net result of this effect is a decreased pressure drop inside the casing that decreases the pressure of the injected fluid.
at the wellhead for a fixed injection rate, or allows increased rate at the same wellhead pressure. These higher injection rates widen and extend the cracks present in the rocks that conduct gas in the wellbore.

It is expected that the extensive use of PAAm-based additives will be maintained if not increased in the near future; partially because PAAm copolymers can be also implemented in multiple applications, such as fluid loss control (Shenglai and Yuhuan, 2013), flooding (Vermolen et al., 2011), hydraulic fracturing treatments (Kot and Bismarck, 2010; Kot et al., 2012), and partially because the stricter legislations covering oil-based drilling will probably encourage the use of water-soluble additives.

Prior to the development of multiple hydraulic fracturing treatments in horizontal wells, fracturing fluids were typically composed of pure water with possibly 2% KCl or even lower amounts of KCl substitutes such as tetramethylammonium chloride. As a drag reducer for these fluids, PHPAAm gave acceptable results. However, the current industrial operations rely heavily on the use of reclaimed waters containing salts and this poses a challenge for PAAm based drag reducers. First, in the case of PHPAAm, a higher salt content can decrease the drag reduction by shielding the electrostatic charge along the polymer backbone and therefore reducing its hydrodynamic radius, which is directly related to the drag reducing power; see in this respect, for example, the study of Liberatore and co-workers (Liberatore et al., 2003; Liberatore and McHugh, 2005). Most important, at temperatures exceeding 60 °C PAAm undergoes hydrolysis resulting in the formation of acrylate groups. If the concentration of acrylate groups is high, the polymer backbone becomes incompatible and it is no longer effective in reducing drag (Seright et al., 2010).

Poly(AAm-co-NaAMPS) possess a better brine compatibility, being less sensitive to hydrolysis (Kelland, 2009) and, therefore, has the potential to be employed in a larger number of oil or gas fields. For this reason, a series of patents was filed relating to NaAMPS copolymers, in parallel to ongoing research studies (George and Gerke, 1985; Funkhouser and Norman, 2002). The benefits of the NaAMPS copolymers with respect to temperature stability and divalent metal tolerance are nowadays established. However, relatively few studies have focused on the ability of NaAMPS copolymers to reduce frictional drag. Studies of this kind were pioneered by McCormick and co-workers (McCormick et al., 1990; Mumick et al., 1994), who studied the influence of the molecular structure of four different AAm copolymers, with different degrees of hydrophobicity and ionic charge, on the level of measured drag reduction for Reynolds numbers (Re) up to 30,000. More recently Shah and co-workers investigated the drag reduction of NaAMPS copolymers in straight and coiled tubing (Shah et al., 2006) and the effects of temperature and salinity on the measured level of drag reduction (Shah and Vyas, 2009). Apart from the insightful aforementioned studies, experimental data on the range of conditions encountered in the field (e.g. Reynolds numbers, polymer concentrations, NaAMPS contents) are still lacking. In addition, aspects such as resistance to mechanical degradation have not been investigated yet and require further attention. Obtaining such data on the drag reduction of NaAMPS copolymers is essential to assess the economic advantage of these drag reducers in terms of pumping cost and effect.

In the present experimental study we explore further the use of poly(AAm-co-AMPS) as drag reducing agent using a pressure-driven pipe flow facility with a relatively large pipe diameter and flow rates more closely simulating the conditions encountered in the field; data are reported at Re up to about 250,000. In particular we isolate and investigate the effect of NaAMPS content, polymer concentration and Reynolds number on drag reduction performance. A correlation is proposed to relate the drag reduction of NaAMPS copolymers to concentration and Re. In addition, the experimental facility was modified to allow automatic recirculation of the polymer solution inside the test section thus offering the possibility of running the experiment multiple times. This modification allowed us to provide unique data on polymer mechanical degradation that is hereby used to study the long term shear stability of poly(AAm-co-NaAMPS) and PHPAAm. The results were also compared with the most common correlations for polymer degradation.

2. Experimental methods

2.1. Apparatus

Drag reduction was measured by means of a recirculating, pressure-driven pipe flow facility. An important feature of this facility, used for the first time in the present study, is that it was upgraded from being manually controlled to fully automated to allow for long term experiments. A detailed description of the manually driven pipe flow facility has been provided by Zadrazil (2011, 2012); here we limit ourselves to a brief presentation of the basic parts and functions of the apparatus.

Fig. 1 shows a schematic illustration of our drag reduction test facility. The rig is composed of two tanks (Tank I and II in Fig. 1), the main pipe test section and various measurement systems. Connections between each element are allowed by both pneumatic and manual valves (labelled by the letters “V” in the figure). Tank I (approximately 330 L) is used to prepare a polymer test solution at atmospheric pressure and is equipped with a low-speed impeller (approximately 60 rev/min) and a temperature sensor. It should be noted that the measurements were carried out at ambient temperature, i.e., 20 ± 2 °C. Tap water was provided from a connection to an outside network and the volume of water used was measured by a turbine flow meter (labelled "F愉" in Fig. 1). Once prepared, the polymer solutions were transferred to the second tank (Tank II), before being pushed through the main pipe test section. Tank II can be pressurised by a connection to a 6 bar laboratory compressed air supply and is equipped with measurement and control systems for water level and pressure.

Pipe flow is achieved by the pressure difference between Tank II and Tank I after the former is pressurised. The use of a pressurised tank instead of a centrifugal pump was preferred in order to minimise the mechanical degradation of the polymer chains prior to the test section (Den Toonder et al., 1995). Tank II is connected directly to the test section, which consists of a 1-in. ID stainless steel pipe. The length of the test section is 7.1 m. The relative roughness (k/D, where k is the absolute roughness and D is the inside pipe diameter) of the stainless steel pipe used in our work has been determined to be 8.75 · 10⁻⁴, which is typical for this material. After the test section a plastic hose of larger diameter (1½-in) allows a return connection to Tank I, thus closing the recirculating flow loop.

A magneto-inductive flow meter (Sitrans F M Magflo MAG5000, Siemens) was used to non-intrusively measure the liquid flow rate. A series of pressure drop measurements were made along the test section by 6 membrane differential-pressure transducers (Deltabar S, Endress-Hauser). Specifically, the pressure drop was measured at set distances ∆t from the test section inlet, with a reference tap at 1.76 m, and subsequent measurement taps at 1.96, 2.96, 3.96, 4.96, 5.96 and 6.96 m from the inlet.

2.2. Materials

Three copolymers of AAm and NaAMPS with the code names DP-OMC-1001, DP-OMC-1002 and DP-OMC-1007 having a weight
average molecular weight of 9 million Da (as measured and stated by the manufacturer, based on the standard constants from the Mark-Houwink equation relating to PAAm) were provided by BASF. All copolymers were supplied in the form of a solid powder. In field applications the friction reducers are added to the pumping solution mostly in emulsion form, nevertheless, the use of a solid powder helped here in forming uniform and reproducible test solutions. The experimental results and their direct transferability to friction reducers in the field are expected to be independent following complete dissolution of the polymer. In our campaign, dissolution was checked by a series of tests with samples that were dissolved for different times and it was confirmed that after 6 h further dissolution did not affect the results. Each of the copolymers is referred to here by an abbreviation which characterises the different NaAMPS content within its structure as determined by elemental CHNS analysis, namely: NaAMPS-AAm-3 (2.7% molar NaAMPS content), NaAMPS-AAm-10 (10% molar NaAMPS), and NaAMPS-AAm-15 (15.3% molar NaAMPS). PHPAAm of molecular weight 9 million Da was used as a reference for comparison (corresponding to 0% AMPS content).

2.3. Procedure

Polymer solutions of different concentrations were prepared in Tank I by filling the tank with tap water and sprinkling the polymer powder over a large solvent area. Tap water was used over salty water for convenience due to the large volumes involved and because drag reduction of NaAMPS copolymer was found in previous studies to be weakly dependent on salinity (Shah and Vyas, 2009). The polymer powder was weighed with an accuracy of ±0.1 mg using an analytical balance. The solutions were stirred for approximately 24 h prior to conducting any experiment in order to allow the polymer to fully dissolve and the solution to homogenise. If the polymer is not fully hydrated, the likelihood of finding large aggregates within the solution is high. Such a heterogeneous solution increases the level of drag reduction and partially invalidates the conclusions drawn from the results (Wyatt et al., 2011a, 2011b). It is worth noting, however, that an initially homogeneous solution does not guarantee the absence of aggregates as shear-induced aggregate formation could arise a posteriori in the flows of interest. This effect has been reported in our previous studies (Zadrazil, 2011) and by other research groups (Vlachogiannis et al., 2003). These shear-induced aggregates are expected to appear in the present experiments and also likely to occur in actual field applications.

Once a solution was prepared, a sample was taken and its dynamic viscosity determined using a rheometer (Physica MCR301, Anton Paar GmbH) equipped with a concentric cylinder measuring geometry. The rotor diameter and gap between the rotor and the stator were 27 and 1.1 mm, respectively. All the solutions, including those at 100 ppm, showed Newtonian behaviour within the investigated shear rate range (10–1000 s⁻¹); shear thinning behaviour, typical of a non-Newtonian polymer solution, was observed for higher polymer concentration (above 200 ppm). The Newtonian behaviour of acrylamide copolymers is attributed to the presence of ions in the solutions which have been demonstrated to reduce the zero shear rate viscosity for low concentrated solutions (Wyatt et al., 2011a, 2011b). Rheological measurements in distillate water have otherwise shown shear-thinning behaviour for 100 ppm PHPAAm solutions (Liberatore et al., 2003). The dynamic viscosity used was an average of six measurements taken at different shear rates, from 10 s⁻¹ up to the onset of Taylor flow. Lower shear rates were discarded because of the noise showed by the rheometer, which increased exponentially under approximately 1 s⁻¹, making accurate measurements difficult.

The procedure was conducted once or, when investigating polymer degradation, repeated multiple times using the same polymer solution. It started by transferring the polymer solution, which had been prepared in Tank I, to Tank II. Tank II was then pressurised to initiate flow through the pipe section. The polymer solution was collected after passing through the test section at the end of the pipe in Tank I, and returned to Tank II from which it re-entered the test section. A control panel communicating with a computer interface controlled the equipment, by setting a constant velocity in the test section that was maintained throughout the experiments, and recorded the data.

The level of drag reduction (given as a percentage) was calculated using Eq. 1:

$$DR = \left( \frac{\Delta P_s - \Delta P}{\Delta P_s} \right)_{U_{\text{const}}},$$

where $\Delta P_s$ is the pressure drop of the pure solvent (i.e., water)
through the pipe, $\Delta P$ the pressure drop of the solution containing the drag reducing polymer and $U$ the bulk velocity in the test section. The value of DR reported in this paper was an average of the results obtained from four of the six pressure transducers across a time interval after discarding the lowest and the highest values (the error of the four pressure transducers with respect to the calculated drag reduction was 3% on average). One measurement cycle ended when 80% (by volume) of the solution flowed from Tank II to Tank I. The reproducibility of the results was determined twice by preparing, testing and comparing three different fresh solutions of 25 ppm PHPAAm and 100 ppm NaAMPS-AAm-10. The DR values of the various polymer solutions were within 5% of the average value. All the other solutions were tested once.

The automated control system was programmed to allow for the automatic and successive execution of the mentioned cycle. This enabled the investigation of the decrease of DR in each subsequent run and gave an estimate of polymer mechanical degradation.

### 3. Results and discussion

#### 3.1. Effect of NaAMPS content

Figs. 2–4 show the DR, defined by Eq. 1, as a function of the bulk velocity of the solution in the test section for solutions of PHPAAm, NaAMPS-AAm-3, NaAMPS-AAm-10 and NaAMPS-AAm-15 with polymer concentrations of 10, 25 and 100 ppm (i.e., parts per million by weight), respectively. To give a general idea of the flow condition, a secondary horizontal axis reports, for each bulk velocity, the relative $Re_\text{c}$ for the pure solvent, calculated using the density and dynamic viscosity of pure water at 20 °C (1000 kg/m$^3$, 1.013 cP). As mentioned previously, the molecular weight was the same for each studied polymer ($M_w \approx 9$ million Da). All profiles show a typical dependence of DR on $Re_\text{c}$; initially DR increases steeply with $Re_\text{c}$ and at high $Re_\text{c}$ the effect levels off. Generally, when comparing NaAMPS-AAm-3 and NaAMPS-AAm-10, the two copolymers exhibit similar DR values (within the experimental error), and the two NaAMPS copolymers outperform PHPAAm, especially at low $Re_\text{c}$. It seems that the presence of NaAMPS groups in PAam produces a beneficial effect, with drag reduction levels higher than the ones achieved when using PHPAAm, which is commonly used in the oil and gas industry. The beneficial effect of NaAMPS is more evident with NaAMPS-AAm-

![Fig. 2. Dependence of drag reduction DR on bulk velocity $U$ and solvent Reynolds number $Re_\text{c}$ for $C=10$ ppm NaAMPS copolymer solutions.](image)

15, which has the highest measured DR of all three polymer concentrations considered, reaching almost 75% DR for the 100 ppm solution at $U \approx 9.7$ m/s ($Re_\text{c} \approx 250000$). The positive effect of NaAMPS groups is more evident in Fig. 5 that shows the Fanning friction factor,

$$f = \left(\frac{\Delta P}{\rho D^2 U^2} \right),$$

(2)

as a function of $Re_\text{c}$, for three 100 ppm NaAMPS copolymer solutions. In this expression, $\rho$ is the density of the solution. It is noted that the same $Re_\text{c}$ will correspond to different bulk velocities in the case of solutions with different dynamic viscosities. The two lines in Fig. 5 represent the Prandtl-von Kármán law for turbulent flow:

$$\frac{1}{\sqrt{f}} = 4 \log(Re_c) - 0.4,$$

(3)

and Virk’s maximum drag reduction asymptote (Virk, 1975), respectively:

$$\frac{1}{\sqrt{f}} = 19 \log(Re_c) - 32.4.$$

(4)

Considering Fig. 5, the Fanning friction factor $f$ measured for NaAMPS-AAm-15 is clearly below that of the other two polymers. It is apparent that NaAMPS-AAm-15 solutions clearly outperformed NaAMPS-AAm-10 and NaAMPS-AAm-3 in decreasing
dicted by the Einstein equation for viscosity. The net result of this
NaAMPS copolymers produces a more viscous solution, as pre-
in the previous paragraph. The larger hydrodynamic volume of
dynamic viscosity is due to the larger hydrodynamic volume of the
friction reduction capabilities of NaAMPS-AAm-15. The increase in
viscosity). The resulting increase in viscous drag moderates the
behaviour of all the three NaAMPS copolymers is similar for velo-
duced by which the polymer interacts with the turbulent
The difference in DR between the various copolymers however
develops with increasing polymer concentration; for the results
related to 100 ppm polymer solutions, reported in Fig. 4, the
behaviour of all the three NaAMPS copolymers is similar for veloci-
ties greater than 5 m/s (or approximately, \( Re_s > 125,000 \)). This
observation can be explained by the fact that, at relatively high
polymer concentration, NaAMPS-AAm-15 solutions are more vis-
cous than NaAMPS-AAm-3 solutions (see Table 1 for the dynamic viscosity). The resulting increase in viscous drag moderates the friction reduction capabilities of NaAMPS-AAm-15. The increase in
dynamic viscosity is due to the larger hydrodynamic volume of the
PAAm in solution when NaAMPS groups are present, as mentioned
in the previous paragraph. The larger hydrodynamic volume of
NaAMPS copolymers produces a more viscous solution, as pre-
dicted by the Einstein equation for viscosity. The net result of this
effect is that, when relatively high polymer concentrations are
used (> 10 ppm), the most efficient friction reducer is obtained by
incorporating just few NaAMPS groups (3% molar content).

3.2. Effect of polymer concentration and Reynolds number

DR as function of polymer concentration \( C \) for NaAMPS-AAm-10 is shown in Fig. 5. The concentrations studied were 10, 25, 50, 75 and 100 ppm. DR was found to be more dependent on the polymer concentration at low bulk velocities than at high bulk velocities; when increasing the NaAMPS-AAm-10 concentration from \( C = 10 \)–100 ppm, at \( U=2 \) m/s (\( Re_s \approx 50,000 \)) the value of DR increased from 34% to 63%, while at \( U=8 \) m/s (\( Re_s \approx 200,000 \)) the increase in DR with increasing polymer concentration was smaller by 10%. Again the effect of polymer concentration is twofold: higher polymer concentrations increase the overall hydrodynamic volume of the molecules in the flow and facilitate the formation of aggregates intensifying the drag reduction effect. This positive effect terminates when the solutions are close to satu-
ation (i.e., polymer overlap concentration) and further increases in
concentration lead only to viscosity increases with a detrimental effect
on the drag reduction capabilities.

In general, the variation of DR with polymer concentration was
found to follow a characteristic trend highlighted by plotting \( C/DR \)
as a function of \( C \) (Fig. 7). The results are well described by straight
lines. This type of relationship between polymer concentration

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Table 1: Dynamic viscosities of investigated polymer solutions.

| Polymer concentration [ppm] | 10  | 25  | 100 |
|-----------------------------|-----|-----|-----|
| PHPAAm                      | 1.013 | 1.014 | 1.056 |
| NaAMPS-AAm-3                | 1.014 | 1.016 | 1.113 |
| NaAMPS-AAm-10               | 1.014 | 1.017 | 1.198 |
| NaAMPS-AAm-15               | 1.016 | 1.047 | 1.443 |

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Fig. 5. Fanning friction factor \( f \) as a function of Reynolds number \( Re \) for \( C = 100 \) ppm NaAMPS copolymer solutions.

Fig. 6. Dependence of drag reduction DR on polymer concentration \( C \) for NaAMPS-AAm-10 (medium NaAMPS content) solutions at different bulk velocities \( U \), which approximately correspond to a range of \( Re_s \), from 50,000 (2 m/s) to 200,000 (8 m/s).

Fig. 7. Dependence of drag reduction DR on polymer concentration \( C \) for NaAMPS-AAm-10 (medium NaAMPS content) solutions.
and DR was already described by Virk (1967) who investigated the drag reduction performance of polyethylene oxide (PEO) solutions. His results for PEO of different molecular weights were shown to collapse on a general profile of the type:

$$\frac{C}{DR} = DR_{int} + \frac{DR_{int} C}{C_{int}}.$$  \hfill (5)

which describes the aforementioned linear relation in Fig. 7. The constants DR\textsuperscript{int} and C\textsubscript{int} are two parameters related to the flow rate, polymer–solvent interactions and flow geometry and do not depend on the polymer concentration. C\textsubscript{int} is the “intrinsic” polymer concentration while DR\textsubscript{int} is the “intrinsic” drag reduction, defined as the initial increment in DR per unit of polymer concentration:

$$DR_{int} = \lim_{c \to 0} \frac{DR}{C}.$$  \hfill (6)

It seems from Fig. 7 that the validity of Eq. 5 can be extended also to poly(AAm-co-NaAMPS) in pipe flow geometries.

In an effort to produce a simple correlation to describe DR as a function of both polymer concentration and Reynolds number for NaAMPS copolymer we extended Eq. 5 to incorporate the effect of Re\textsubscript{s}. In particular, Eq. 5 can be rearranged to:

$$\frac{1}{DR} = a(N_{Res}) + \frac{b(N_{Res})}{C},$$  \hfill (7)

where a and b is a set of parameters different from C\textsubscript{int} and DR\textsubscript{int} and function of Re\textsubscript{s}. In our experiments the dependence of DR on Re\textsubscript{s} for diluted polymer solutions was found to follow a relationship similar to Eq. 7:

$$\frac{1}{DR} = a'(C) + \frac{b'(C)}{N_{Res}},$$  \hfill (8)

where a’ and b’ are two other set of parameters depending on the concentration. By comparing Eqs. 7 and 8, it can be demonstrated that the parameters a and b have to be both written as the sum of a constant and a term which is proportional to the reciprocal of Re\textsubscript{s}. If a and b are both written in these terms, Eq. 7 can be rearranged to include four different constants:

$$\frac{1}{DR} = \frac{1}{DR_{lim}} + \frac{K_0}{N_{Res} C} + \frac{K_1}{N_{Res}} + \frac{K_2}{C}.$$  \hfill (9)

In this form, Eq. 9 was confirmed as describing approximately our set of experimental data for the studied copolymers solutions (see Fig. 8 for NaAMPS-AAm-10).

The first constant in Eq. 9 is 1/DR\textsubscript{lim} where DR\textsubscript{lim} is the drag reduction limit, which is only a function of the type and geometry of the used test section, e.g., pipe diameter, and is defined as:

$$DR_{lim} = \lim_{N_{Res} \to \infty} DR_{max}.$$  \hfill (10)

where DR\textsubscript{max} is the value of drag reduction calculated, for a given Re\textsubscript{s}, at the maximum drag reduction asymptote. To clarify Eq. 10, DR\textsubscript{max} can be regarded as the maximum drag reduction achieved at a given Re\textsubscript{s}; for smooth pipes it is equal to the value predicted by Virk’s maximum drag reduction asymptote. In general however, the maximum drag reduction asymptote is usually different from Virk’s maximum drag reduction asymptote because of the non-ideal conditions of the apparatus used. For example, in rough pipes the maximum drag reduction asymptote is found to be lower than Virk’s maximum drag reduction asymptote, see for instance Virk (1971). In practice DR\textsubscript{max} is found, for each Re\textsubscript{s}, by increasing the polymer concentration until no further increase in DR is detected. Once DR\textsubscript{max} is plotted as a function of Re\textsubscript{s} it appears that its value increases with increasing Re\textsubscript{s} until an approximately constant value is reached. This value is DR\textsubscript{lim} and, in practice, is found by measuring DR\textsubscript{max} at high Re\textsubscript{s}. In our experiments, above Re\textsubscript{s} ~ 200,000, DR\textsubscript{max} becomes practically constant (approximately equal to 81%) and can be assumed to be equal to DR\textsubscript{lim}.

Eq. 9 can be used to approximately quantify DR of fresh NaAMPS copolymer solutions once the parameters K\textsubscript{0}, K\textsubscript{1} and K\textsubscript{2} are known. In our rig the values of K\textsubscript{0}, K\textsubscript{1} and K\textsubscript{2} for NaAMPS-AAm-10 copolymer solutions are 5.81 \times 10^3, 6.78 \times 10^2 and 6.12 \times 10^{-2}, respectively. Even if the present correlation can be used as an indication of DR for NaAMPS-AAm-10 copolymer solutions, the parameters K\textsubscript{0}, K\textsubscript{1} and K\textsubscript{2} depend to some extent on the experimental setup, namely the diameter and roughness of the pipe, and experimental conditions adopted, e.g. temperature and salinity. It is likely that, as research progresses, the dependence of drag reduction (and so of K\textsubscript{0}, K\textsubscript{1} and K\textsubscript{2}) on the experimental setup and conditions will be established. Indeed, recently, Shah and Kamel (2010) investigated the drag reduction of a high molecular weight NaAMPS copolymer (Nalco ASP-820), in different pipe diameters, i.e., \frac{1}{2}, \frac{1}{4}, \frac{2}{3} and \frac{1}{8}-in. Their results showed that the friction factor correlations developed for \frac{1}{2}-in. straight tubing can be reasonably applied to larger diameter tubing, within their application range. Regarding the experimental conditions, such as the quality of the solvent and the temperature, some insights in this regards have been given also by Shah and Vyas (2009). For the specific polymer solution and experimental conditions used in their study the influence of salinity and temperature on drag reduction was not pronounced at high Re\textsubscript{s}.

3.3 Polymer mechanical degradation

Fig. 9 shows the DR of consecutive drag reduction measurements for polymer solutions recirculating in a closed loop multiple times at Re\textsubscript{s} ~ 200,000. For all investigated polymer solutions a drop in drag reduction was observed, as would be expected if mechanical degradation of the polymers occurs, resulting in a decrease in DR by approximately 10% over 8 runs. No significant difference in the rate of the drop in drag reduction was detected between poly(AAm-co-AMPS) and PHPAAm. From these results it appears that the presence of NaAMPS groups in PAAm did not affect the vulnerability of the polymer to mechanical degradation, which would be expected since the polymer backbones of PHPAAm and poly(AAm-co-AMPS) are identical, and so should be their shear stability.

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Results from a series of drag reduction experiments for 25 ppm NaAMPS-AAm-10 solution featuring a higher number of passes (231) are also shown in Fig. 9. Polymer mechanical degradation, as
evidenced by the drop in drag reduction, appears to proceed until the polymer is almost ineffective in reducing drag. Even though the rate of decrease in \( DR \) decreases with the number of passes (indicating a decrease in the rate of polymer mechanical degradation), the profile seems to approach zero \( DR \) asymptotically for a very large number of passes. The observed behaviour cannot be predicted by the correlations for polymer mechanical degradation found in the literature, in particular the correlation proposed by Brostow (1990; 2008):

\[
\frac{\lambda_{t}}{\lambda_{0}} = \left[ 1 + W \left( 1 - e^{-ht} \right) \right]^{-1},
\]

where \( \lambda \) is the time dependent drag reduction efficiency, equal to \( DR \):

\[
\lambda = \left[ 1 - \frac{f_{t}}{f_{0}} \right].
\]

\( \lambda_{0} \) being the drag reduction efficacy at time zero and \( h, W \) two empirical constants with \( h \) being a function of polymer concentration. According to Eq. 11, as \( t \to \infty \), \( \lambda \) (and \( DR \)) approaches a constant value different from 0 (in fact from Eqs. 11, \( \lambda \to \lambda_{0} / (1 + W) \)), in contrast to our experimental findings.

Although the absence of a lower limit below which the polymers cannot be degraded further has been reported by others, for instance by Bello et al. (1996) and Sung et al. (2004) for experiments conducted in rotating disk apparatuses, the aforementioned correlation shown in Eq. 11 is considered relatively accurate in the general literature (Zhang et al., 2011; Lee et al., 2010). A reason for the discrepancy from the expected behaviour of Eq. 11 could arise from the different type of flow geometry (and consequently, the different turbulence character) used in different studies. Indeed, Eq. 11 has been mostly considered in the context of rotating apparatuses in which the flow is notably different from the one occurring in a pipe, as in our case; on the other hand, few experiments have been performed on the mechanical degradation of polymer solutions in a pipe flow over extended time scales. A series of repetitions of the same experiment with different polymers in our experimental facility always led to the same conclusion: that polymer mechanical degradation does not seem to stop at a given level of \( DR \), but gradually and eventually approaches a near-zero value for the investigated flow conditions (i.e., the combination of \( Re_{c}, C_{s} \), and polymer type). It is our opinion that the overall picture requires some clarification in order to establish the origin of the discrepancy in the literature. Taking a step further, we noticed that all the degradation profiles acquired in our facility assumed the shape of a parabola in the \( DR - \ln(t) \) diagram. In particular, using Brostow’s notation, the data were found to fit an equation of the following type:

\[
\frac{\lambda}{\lambda_{0}} = 1 + W_{0} \ln^{2} + W_{1} \ln t,
\]

where \( W_{0} \) and \( W_{1} \) are two empirical constant.

It is interesting to compare the current experiment with a typical situation encountered during hydraulic fracturing. If we assume that mechanical polymer degradation takes place only in the 7.1 m test section, these multiple-pass experiments would correspond to a single experiment where a friction reducing solution passes through a 1.6 km long pipe with an average wall shear stress \( \tau_{w} \) of 102 Pa (\( \tau_{w} = \rho U^{2} / 2 \)). This is similar to field applications where friction reducers flow for several kilometres while being subjected to a wall shear stress of the order of 10^{2} Pa. Of course, a direct comparison with field applications is to be done with precaution because the former assumption is probably too optimistic and part of the polymer degradation is likely to take place also outside the test section. Nevertheless it would appear that the level of polymer degradation in a corresponding hydraulic fracturing treatment is very high and does not stop, with an overall drag reduction, \( DR_{\text{tot}} \), achieved in a well of length \( L \), given by:

\[
DR_{\text{tot}} = \frac{1}{L} \int_{0}^{L} DR \, dl.
\]

In order to choose the best drag reducer for a hydraulic fracturing treatment it is therefore very important to take into account how \( DR \) changes along the well length, i.e., polymer degradation, as it is possible that \( DR \) can reach relatively low values deep down the well. Moreover, it is possible that the drag reducer which was proven to have the highest \( DR \) in experiments conducted using fresh solutions, might be relatively inefficient in a hydraulic fracturing treatment. As a last comment, we report that the major parameter which affected polymer mechanical degradation in our experiments was the polymer concentration: the higher the polymer concentration the lower the rate of decrease in \( DR \), an effect also mentioned in previous studies (Moussa and Tiu, 1994). The different polymer concentrations were compared at the same \( Re \) in order to achieve the same degree of turbulence. It appears that varying the polymer concentration could offer the right approach to decrease polymer degradation and enhance the overall drag reduction across the pipe length.

4. Conclusions

The drag reduction and shear stability performance of poly (AAM-copolymer) solutions in turbulent pipe flow was investigated experimentally using a pressure-driven pipe flow facility. Specifically, three types of poly(acrylamide-co-NaAMPS) and pure PHPAam were investigated with respect to polymer induced drag reduction and mechanical polymer degradation at Reynolds numbers up to about 250,000, achieved in a 1-in. horizontal pipe. The facility also had the capability of conducting long length/time experiments by automatically recirculating the polymer solution in a closed-loop circuit through the test section. The main findings of the present study are:

- The NaAMPS content in the polymer backbone improves the efficiency of PAAm to reduce frictional drag in turbulent pipe flow. In particular, poly(AAm-co-NaAMPS) containing 15% NaAMPS resulted in the lowest Fanning friction factor values and the highest measured \( DR \). Increasing the NaAMPS content...
in the copolymer resulted in an increased dynamic viscosity of the polymer solution, with solutions of poly(AAm-co-NaAMPS) containing 15% NaAMPS being the most viscous, which resulted in a partial decrease of the relative efficiency of NaAMPS-AAm-15 to reduce frictional drag. Due to this effect, the most efficient drag reducer at concentration higher than 10 ppm, was NaAMPS-AAm-3, with just 3% molar mass of added NaAMPS groups.

- The DR of the NaAMPS copolymers increased with increasing polymer concentration and Re. The DR dependence on polymer concentration was found to follow the same correlation reported by Virk (1967) for PEO. This correlation was extended to take into account the effect of Re, resulting in the correlation for NaAMPS copolymers described by Eq. 9.

- No significant difference with respect to the vulnerability to mechanical degradation was detected between poly(AAm-co-NaAMPS) and PHPAAm, indicating that the presence of NaAMPS in the polymer backbone does not significantly affect the susceptibility of the polymer chains to mechanical degradation.

- An experiment carried out over 231 runs with a 25 ppm NaAMPS-AAm-10 solution showed the absence of a limit to polymer mechanical degradation with a decrease in DR that continued until the polymer had little effect on the turbulent flow. This is in contrast with the most common correlation for polymer degradation. The observed phenomenon also means that investigating mechanical polymer degradation is essential in order to select the optimal friction reducer in drag reduction applications, as opposed to use the most performing friction reducer found by testing and comparing fresh solutions.

### Nomenclature

- **DR** Amount of drag reduction
- **DRint** Intrinsic drag reduction
- **DRmax** Maximum drag reduction
- **DRlim** Drag reduction limit
- **DRtot** Overall drag reduction over a length
- **C** Concentration, ppm
- **Cint** Intrinsic concentration, ppm
- **D** Diameter, m
- **Tw** Wall shear stress, Pa
- **f** Fanning friction factor
- **k** Absolute roughness, m
- **U** Velocity, m/s
- **Δl** Distance, m
- **L** Length of a well, m
- **ΔP** Pressure drop of the drag reducer solutions across Δl, Pa
- **ΔP0** Pressure drop of the pure solvent across Δl, Pa
- **Re** Reynolds number
- **Re0** Solvent Reynolds number
- **ρ** Density, kg/m³

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### Acknowledgements

This work was supported by the UK Engineering and Physical Sciences Research Council (EPSRC) [grant number EP/K003976/1]. The authors also gratefully acknowledge the financial support provided by Halliburton Energy Services. Data supporting this publication can be obtained on request from cep-lab@imperial.ac.uk.
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