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THE INFLUENCE OF MECHANICAL EFFECTS ON DEGRADATION OF POLYISOBUTYLENES AS DRAG REDUCING AGENTS

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Abstract

The mechanical degradation of high molecular weight polyisobutylene polymers (Oppanol B) was studied by exposing there dilute solutions to high speed mechanical stirring. Three Oppanol B, 150, 200 and 250 types of molecular weight, 2.5, 4.1 and 5.9million g/mole were considered in present work. The shear viscosity of Oppanol B stock solutions of concentrations, 0.5, 1.0 and 1.4w/v% was measured as function of exposure time.
It was observed, that the degradation efficiency of higher molecular weight is larger than that of lower molecular weight in a whole polymer concentrations. The time dependence drag− reduction data was compared with the observation of shear degradation by stirring behavior. The decrease of drag reduction with time is in evident to the mechanical degradation observed by shear stirring and viscosity decline of polymeric additives.

***Keywords**: Turbulent drag reduction; High molecular weight Polyisobutylene; Mechanical Degradation; Viscosity lowering.*

1. Introduction

It is well known that the addition of small amount of certain polymer types to a turbulent Newtonian fluid flow can result in a drag reduction [1]. Effective polymeric drag reducing additives are considered to be flexible, linear with a high molecular weight such as polyisobutylene (PIB) [2]. However, the usage of these polymers is limited because of their susceptibility to flow induced shear degradation[3]. High molecular weight polymers are more susceptible to shear induced degradation, and polymers with linear chain structure are more vulnerable than branched polymers.

The degradation of polymers by mechanical action is a depolymerization reaction in which the activation energy is supplied by the mechanical action on the polymer. Degradation reduces the effectiveness of polymer additives because of the strong dependence of effectiveness on molecular weight [4]. Since the long chain polymer having different molecular weights will show different time dependent resistance. In other words, longer molecules are more susceptible to mechanical degradation, accompanying more rapid degradation[5].

Mechanical degradation refers to the chemical process in which the activation energy of polymer chain scission is exceeded by the mechanical action on the polymer chain and bond rupture occurs [6-7,8-14]. Degradation of polymers may be brought about either by physical factors, such as heat, light or mechanical stress or by chemical agents, such as oxygen, ozone, acids or alkalis [15]. The degradation can be prevented by avoiding high speeds in stirring or transporting polymers solutions; using the low temperature as possible commensurate with prevention of thermal degradation and using good solvents (those with high intrinsic viscosity) of low viscosity [16].

The present work deals with the experimental data for mechanical degradation and the performance of drag reducing polymers. Dilute solutions of polyisobutylene with high, different molecular weights were exposed to shear degradation using mechanical stirrer with blades. The time dependence effectiveness of polyisobutylenes as drag-reducer agents was also studied in a closed re-circulation loop to evaluate there mechanical degradation ability.

2. Experimental

The hydrocarbon soluble polyisobutylenes, grade Oppanol 150, 200 and 250 with different molecular weight of $2.5*10^6$, $4.1*10^6$ and $5.9*10^6$g/mole respectively, were acquired from BASF Company, Germany. Kerosene solvent to dissolve the polyisobutylenes was supplied from AL–Durra Refinery, Baghdad.

The dissolving of high molecular weight polyisobutylene polymers were carried out in a shaking machine of 100rpm at room temperature. This condition was used to avoid any polymer molecular degradation since the stirring device has no blade or sharp edge that could expose the polymer to high shear forces.

The polymeric solutions of different concentrations were exposed to high speed stirring at different time. The viscosity of the solutions was measured as function of time and stirring speed, to evaluate the degree of polymeric degradation. The stirrer used has a sharp edge and rotating speed. Solutions of concentrations, 0.5, 1.0 and 1.4w/v percent for poly-isobutylene were exposed to such shear degradation at 1200, 1500 and 1800 rpm stirring for different time up to 2hr. Samples were taken to measure the viscosity of the solution. All experiments were taken place at room temperature, 30–35°C. The viscosity was measured by using Brookfield DV–E viscometer, which measures fluid viscosity at a different shear rates and shearing time.

The performance of the drag reducing additives was evaluated in a laboratory scale circulation loop, as shown in figure1. The fluid container of about 0.49m^3 capacity was fitted with a positive displacement gear pump of 50.8mm diameter and 1440rpm. This type of pump was used to avoid polymer mechanical degradation which reduces usually the drag reducing efficiency. Pipe of 0.0317m inside diameter was used to perform the flow measurement . The test section was 2m long and located away from the entrance to get the fully developed region. The pressure drop in the test section was measured by U-tube manometer filled with water. The pressure drop readings before and after drag reducer addition were used to calculate the percentage drag reduction, %DR, as follows.

$$\% DR = \frac{\Delta P_{untreated} - \Delta P_{treated}}{\Delta P_{untreated}} * 100$$

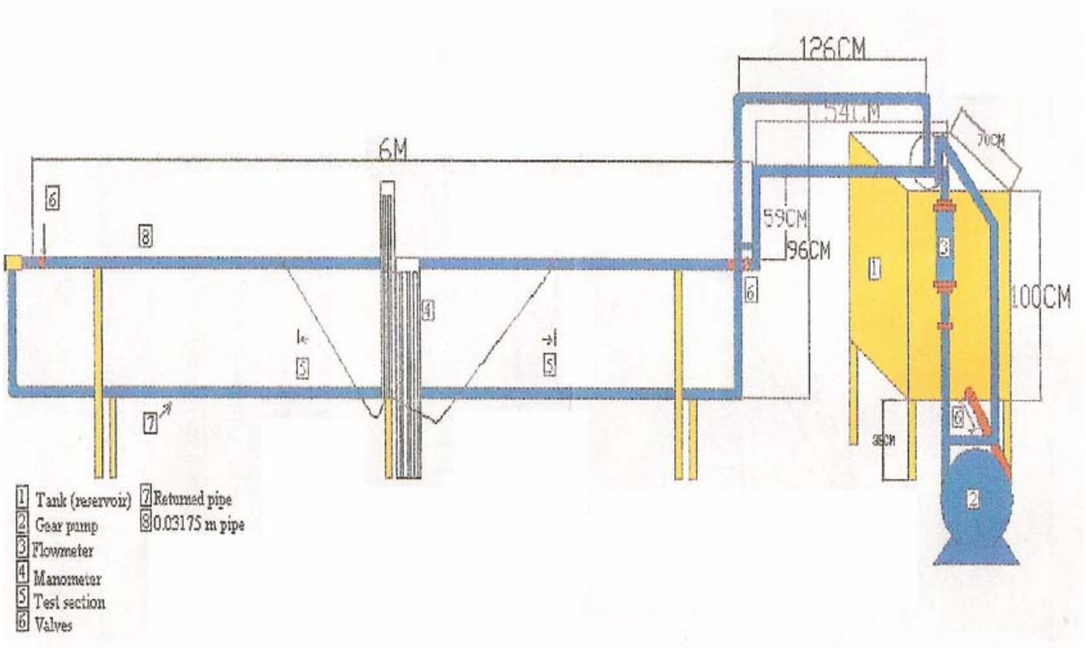

Fig. 1 Schematic diagram for circulation loop

3. Results and discussion

The viscosity changes of high molecular weights polyisobutylens polymers Oppanol B dissolved in Kerosene were investigated by exposing the dilute solutions to high mechanical stirring, 1200, 1500 and 1800rpm.Three Oppanol B, 150, 200 and 250 types of molecular weight 2.5, 4.1 and 5.9million g/mole were considered in present work.

Table 1 summarizes selected results to clarify the effect of stirring speed on viscosity lowering of 1.4wt% solutions of the three types of Oppanol polymers at 2hr exposure time. The results indicate clearly the effect of high level of shearing on viscosity reduction due to mechanical shear degradation on polymer molecules. Shearing at higher stirring speed (i.e 1800rpm) resulted on high viscosity reduction of polymeric solutions. It is well expected that the viscosity of Oppanol B solutions increase as molecular weight of polymer increase, as shown in table 1 and figure 2. Furthermore, the viscosity of polymeric solution is usually a function of concentration as shown in figure 2. As in case of Oppanol 250, the viscosity of 0.5, 1.0 and 1.4w/v% solutions are about 63cp, 293cp and 623 respectively.

Table 1: Effect of stirring speed on viscosity of Oppanol solutions at 1.4%, 2hr stirring time

rpm	B 150	B 200	B 250
-	120	232	623
1200	103	160	368
1500	89	134	317
1800	82	101	205

The decrease of polymer solution viscosity with increasing time of shearing is shown in figure 3. The experiments were carried out on 1.4%wt polymeric concentration and 1800rpm stirring . It can be concluded from this figure that a gradual lowering of viscosity is observed with increasing the exposure time due to mechanical degradation. At 60min stirring the viscosity changed dramatically from 120, 232 and 623cp to around 97, 132and 339cp for Oppanol B 150, 200 and 250 respectively. Therefore, the highest molecular weight polymer undergoes faster degradation leading to higher lowering in viscosity than the lower molecular weight polymers such as B 150.

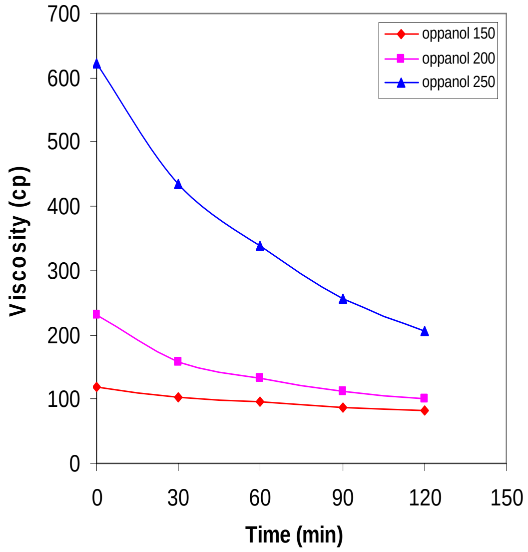

Fig. 2 Combined effect of concentrations and molecular weight on the viscosity of Oppanol B solutions

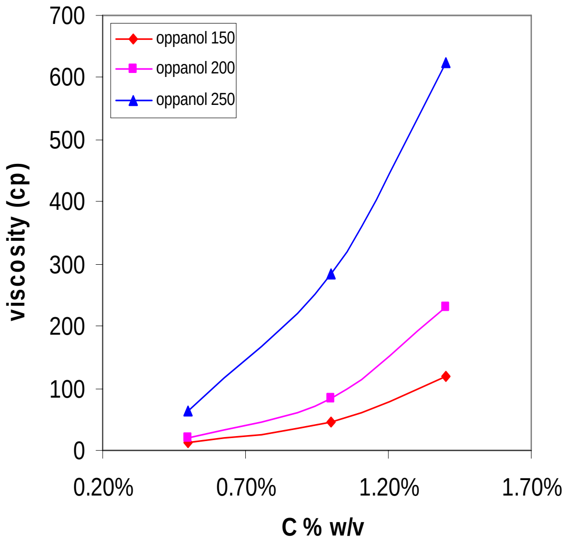

Fig. 3 Viscosity variation of Oppanol B polymers by exposing 1.4 w/v % solutions to mechanical stirring at 1800rpm

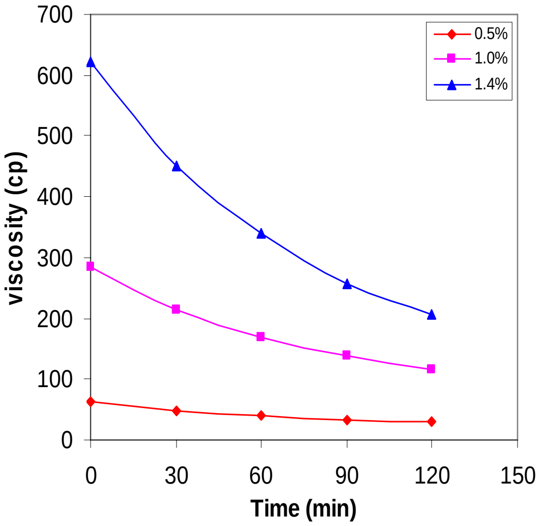

Fig. 4 Concentration effect on viscosity for Oppanol B-250 solution at 1800 rpm

The effect of concentration of polymer solutions on the scission of polymer chains by high speed stirring had been investigated by change the viscosities, as shown in figures 4 for Oppanol B 250. Three polymer concentrations were chosen, namely 0.5%, 1.0% and 1.4%w/v to evaluate the concentration dependence of shear degradation of the three Oppanol polymers by expose there solutions to high speed stirring. It was found that the low concentration solutions are less sensitive to shear degradation by mechanical stirring. The polymer chain scission is largely dependent on the concentration of polymer solution that lead to the conclusion that the polymer chains were not broken by contact only with solvent but even though by contact of a polymer chain (entanglement) with other chains [9].

As illustrated adequately in the previous paragraph, the viscosity of Oppanol B polymers undergo remarkable reduction by exposure there solutions to high speed mechanical stirring. Therefore it was worthy to compare the results of shear degradation by stirring of the three Oppanol polymers solution with the values of time dependence drag–reduction efficiency. Since the long chain polymers experience mid–point degradation, leading to the fact that the molecular chains having different molecular weights will show different time dependent resistance. The time dependence drag–reduction results for these polymers are shown in figure 5 which were carried at 6.0m^3/hr flow rate in 31.75mm I.D pipe. The figure indicates that, the low molecular weight polymers are sharply degraded within the first hour resulting in fast decrease of percentage drag–reduction. While the higher molecular weight polymer has higher resistance towards the degradation. Therefore in case of Oppanol B 250 additive, still about 9% drag reduction was achieved after 210min operation due to presence of efficient molecules, which act as drag reducer agents. The effectiveness of low molecular weight polymer B 150 was completely vanished after about one hour circulation leading to minor drag reduction , while B 200 shows little drag–reduction effectiveness after 150min circulation. It was observed previously that exposure of Oppanol B, 150, 200 and 250 polymeric solutions to high speed stirring, (1800rpm) leading to noticeable decrease in viscosity due to mechanical degradation.

The time-dependence drag reduction of Oppanol B 250 at different concentrations is plotted in figure 6 taking the time zero for maximum drag reduction. This figure indicates clearly that low concentrations will be degraded quickly compared with high concentration i.e 50ppm. Therefore the percentage DR decrease rapidly reaching to zero value after 60min for 10ppm and 120min running for 30ppm. While at 50ppm concentration there is still undegraded polymer until 220 min experimental time elapsed. Since degradation is generally attributed to mechanical breaking of the polymer chains and when a low concentration exists in the pipe a larger performance of chains are destroyed and consequently a rapid decrease in the effective drag reduction is noticed. While, for high concentrations i.e 50ppm there is still sufficient effective polymer left to cause drag reduction at the considered experimental time.

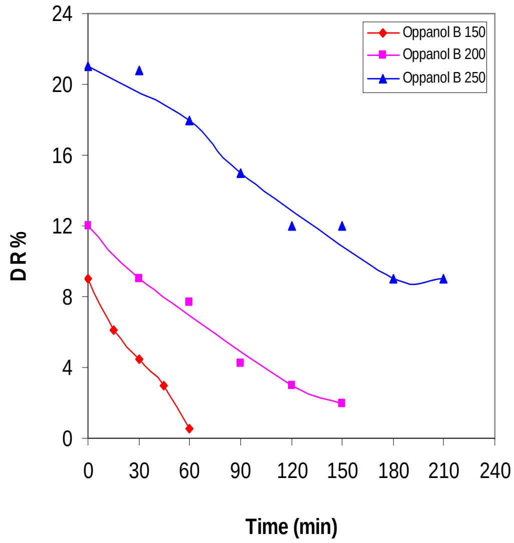

Fig. 5 Effect of molecular weight on degradation of Oppanol B additives, at Q= 6 m^3/hr, 50 ppm concentration and 31.75 mm I.D

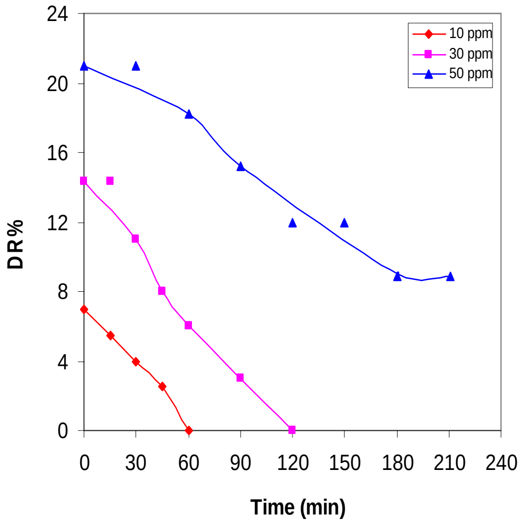

Fig. 6Time dependence of percentage drag-reduction for Oppanol B 250 at different concentration, 6 m^3/hr flow rate and 31.75 mm I.D

As already reported previously the largest lowering in the solution viscosity of Oppanol polymers due to mechanical degradation occur with polymeric solution of highest concentration, as shown in figure 4 for type B 250 polymer. Thus, the viscosity of Oppanol B 250, decreases from 63cp before mechanical stirring to about 29cp, 293cp to 116cp and 623cp to 205cp after exposure time of 2hr for solutions of 0.5, 1.0 and 1.4 w/v% concentrations respectively. Therefore the results in figure 6 is in agreement with those shown in figure 4 for the dependence of drag reduction effectiveness on the molecular polymer degradation.

4. Conclusions

The mechanical degradation of high molecular weight polyisobutylene polymers was studied by exposing there dilute solutions to high mechanical stirring. It was observed that the susceptibility of polyisobutylene to degradation increases with increasing the polymer molecular weight, concentrations, stirring speed and exposed time.

The drag – reduction efficiency of polyisobutylenes of three different molecular weights decreases dramatically with time due to shear degradation of polymer molecules under the exposed turbulent recirculation flow. The behaviour of molecular degradation during the drag–reduction experiments are in agreement with the observation for shear degradation by stirring.

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