Potential of SiO_2 nanocomposite as DRA of oil

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Abstract. Poly-olefin as drag reduce agent (DRA) with more than 6 million molecular weight would lost most of drag reducing capacity after shearing degradation. Composites combining many unique physical and chemical properties could offer possible way to develop DRA with better performance. The potential of Poly-olefin/SiO_2 nanocomposite as DRA were investigated in our research. Modified SiO_2 and poly-olefin were combined together. Drag reducing rate and anti-shearing were analyzed through experimental loop system. It was shown by drag reducing test that synthesized composite DRA had higher drag reducing and flow increase performance, and it presented better anti-shearing ability. By adding SiO_2, the flow increase rate of nanocomposite had raised 29.7%, the drag reducing rate had raised 18.6%, and the anti-shearing had raised 200%. It was thought that synergistic effect had occurred after combination of nano SiO_2 and poly-olefin, which could upgrade the composite DRA performance.

1. Introduction

Drag reduce agent (DRA) is a kind of chemical additive applied in fluid drag reduction. Polymer-based DRA applied in oil pipeline can increase the throughput or reduce pressure, and improve the safety, flexibility and economy in pipeline operation [1]. After decades of development, the main components of the present-used oil reduce is advanced poly α-olefin with more than 6 000 000 molecular weight. In addition, the poly α-olefin with higher and more concentrated molecular weight offers better performance [2], but would lost most of drag reducing rate after shearing degradation, which need add fresh DRA in order to maintain the drag reduction performance [3]. From the technology and production view, improving the drag reduction and anti-shearing performance of DRA is of great practical significance.

Composited material is made of two or more than two kinds of materials with different physical and chemical properties [4~6]. Polymer-based nanocomposites refer to the materials using organic polymer as the matrix, and inorganic nano materials as strengthening agent. Nano-materials have special surface effect, volume effect and quantum size effect, and therefore, the polymer-based nanocomposites have strong interfacial binding force, giving themselves outstanding mechanical performance, and thermal, electrical, and magnetic properties [7].

This research put forward a concept for the first time, by which it was guided that composite materials were introduced into the oil DRA. The method to prepare composite DRA by combining nano-SiO_2 with poly α-olefins was systematically explored, and the drag reduction and anti-shearing performance of the as-prepared composite DRA were evaluated. Meanwhile, the influences of SiO_2 content and surface modification were also investigated.

2. Experimental

2.1 Preparation of the nanocomposites.

A certain amount of nano-SiO_2 was dried at 80 ^{o}C for 24 h, and then resolved into NMP under ultrasonic for 1 h. Then SCA (KH-550, KH-560, KH-570, A-172) of 1 ml was slowly added under stirring at 80 ^{o}C for 1 h. At 120 ^{o}C, the solvent evaporated completely, and the powdery organic modified nano-SiO_2 was obtained.

Poly-olefins and anhydrous ethanol were under ultrasonic for 0.5 h. Then the dried maleic anhydride (at 80 ℃ for 10 h) was added into the solution, and then under ultrasonic for 10~30mins, and the grafted poly-olefins with anhydride was obtained as the interfacial compatibilizer [8-10].

The above as-obtained compatibilizer was added into poly-olefin slurry, which was then added into with the modified nano-SiO_2. The slurry were slowly stirred at 80℃ for 2 h, and the composite oil DRA was obtained.

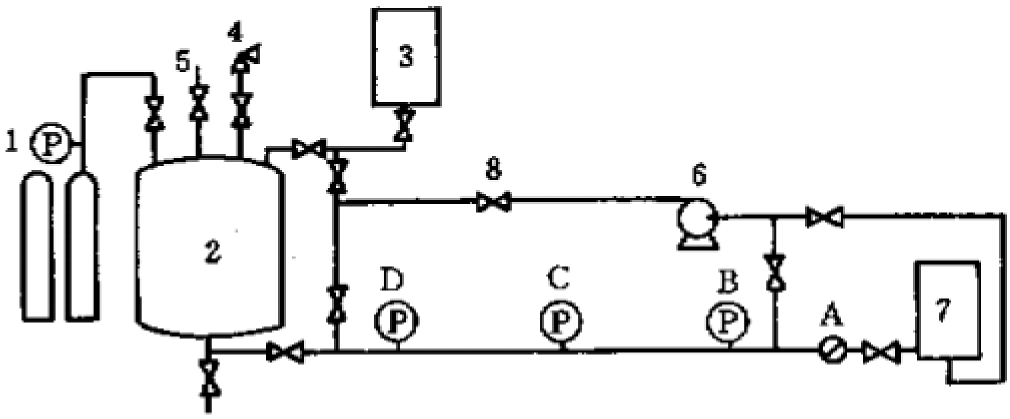

Fig.1 The apparatus for the performance evaluation of DRA
1-N_2; 2-pressure surge tank; 3-dilution tank; 4-safety relief valve; 5-air relief valve; 6-grear pump; 7-reflux accumulator; 8-ball valve; A-flow sensor; B,C,D-pressure sensors.

2.2 Drag reducing performance.

The apparatus for the performance evaluation of DRA was shown in Figure 1. Considering that the drag reducing rate has no direct relationship with the physical property of fluid, but affected by flow parameters, such as Reynolds number, diesel was selected as evaluated fluid. Evaluation procedure is as follows:

(1) Measuring the flow rate before (Q_0) and after (Q_1) addition of DRA;

(2) Calculating the flow increase rate: $TI=(Q_1-Q_0)/Q_0 \times 100\%$

(3) Calculating the drag reducing rate: $DR=[1-1/(1+TI)^{1.79856}] \times 100\%$

(4) Investigating the anti-shearing performance: The DR results from the unsheared and sheared DRA, and unsheared and sheared composite DRA were plotted, and the anti-shearing performance was evaluated according to the tendency and slope of the curve.

3. Results and Discussion

3.1 The influence of SCA

The influence of different SCA on the flow increase rate and drag reducing rate was investigated. Figure 2 indicated the important role of SCA on the modification of SiO_2 and the flow increase rate and drag reducing rate of composite DRA. Obviously, except for A-172, the other SCAs all increased the flow increase and drag reducing performance. For flow increase, the best SCA is KH-550 and KH-560 with certain ratio. It was proposed that KH-550 can improve the wetting and dispersion of SiO_2 nanoparticles in polymer, and KH-560 can improve the compatibility, dispersibility and flowability of the adhesives. The synergistic effect between KH-550 and KH-560 could be introduced, which can play a positive role in combining SiO_2 and poly α-olefin.

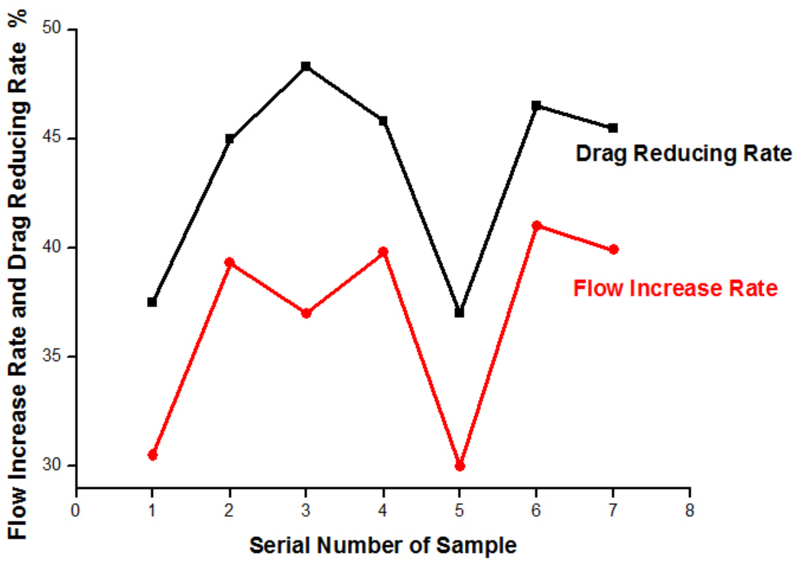

Fig.2 The influence of SCA to the flow increase rate and drag reducing rate.
1: unmodified SiO_2; 2: KH-550; 3 KH-560; 4: KH-57; 5: A-17; 6: KH-550 and KH-560 with certain ratio; 7: KH-570 and KH-560 with certain ratio

3.2Anti-Shearing performance

The untreated DRA and composite DRA were sheared in rotary vane type centrifugal pump for three times, and the anti-shearing performance of the sheared DRAs were investigated with the results shown in Figure 3.

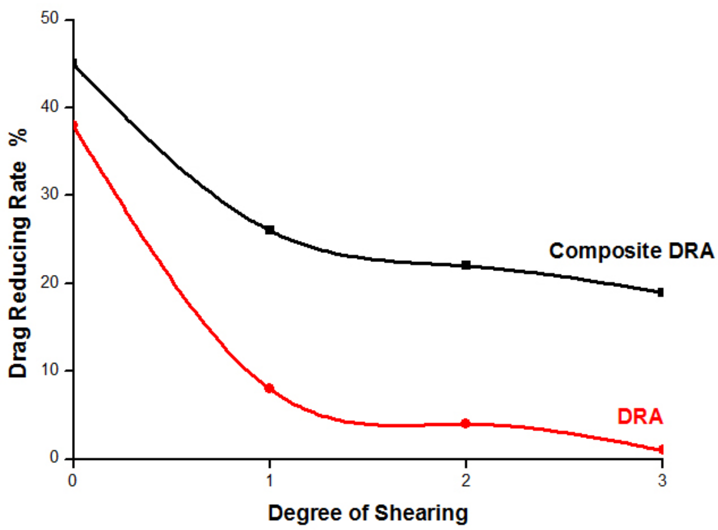

Fig.3Anti-shearing performance of the untreated DRA and nanocomposite.

After being sheared in centrifugal pump for first time, the drag reducing rate of untreated DRA deceased greatly to 20% of the fresh untreated DRA, indicating a poor anti-shearing performance. However for the composite DRA, after first time shearing treatment in centrifugal pump, the drag reducing rate deceased to 60% of the fresh composite DRA, and to 53% after second time shearing, and to 50% after third time shearing, indicating that the composite DRA have a much better anti-shearing performance due to the SiO_2-polyer matrix synergetic effect. However, the drag reducing rate of composite DRA decreased about 40% after the first time shearing, which demonstrated that SiO_2 and ploy matrix combined not so well, and the method should be further improved.

From the above results, a synergetic mechanism was proposed. Inorganic material (nano SiO_2) is hydrophilic, while poly α-olefin is hydrophobic, thereby limiting the combination of them. Through surface modification, SiO_2 was covered by a hydrophobic layer, which improves its comparability with poly α-olefin, and thereby increasing the SiO_2-poly α-olefin interfacial binding strength. In addition, the modification increased the specific surface area of SiO_2, making it better dispersed in poly α-olefin, and combined stronger with poly α-olefin, which plays a role of strengthening agent. Finally, the drag reducing, flow increase and anti-shearing performance were improved.

4. Conclusions

(1) The simple blending of nano SiO_2 and DRA can't enhance the drag reducing and flow increase performance.

(2) Using the anhydride-grafted poly α-olefin as interfacial compatibilizer, the SCA-modified nano-SiO_2 can combine well with DRA, thereby improving the drag reducing and flow increase performance.

(3) Based on the synergistic effect of SiO_2 and polymer matrix, anti-shearing performance of the composite oil DRA was enhanced greatly.

5. References

[1] Guan Zhongyuan,Li Chunman,et al.Research and Application of EP Drag Reducer,Oil & Gas Storage and Transportation,2001,20(8) 32~34.

[2] Shi Yulin,Li Huiping,Zhou Qixiong,et al.Synthesis of Drag Reducer for Crude Oil from α-Olefin over $TiCl_4/Al(i\text{-}Bu)_3$[J].Petrochemical technology,2006,35(4) :371~375.

[3] Li Guoping,Li chunman,Zhang Zhiheng et al.Pipeline Chemical Additive Technology[M].Beijing:Petroleum Industry Press,2010:12~20.

[4] Wang Jun,Zong Yongcai,Feng Chunxiang.Pyrolysis of Polycarbosilane/Nano Nickel Powder[J].Applied Chemistry,1997,14(2):90~92.

[5] Shen Chunyin,Zhang Zhongxiu,Sheng Jisheng.Composites and Dispersion Stability Mechanism of Polymer/Nanoparticle[J].Chemistry and Adhension,2000,(4):178~181.

[6] Jing Xinli,Zheng Maosheng,Jin Zhijie et al.Study on Praperation and Properties of PMMA-SiO_2 In-Situ Composites[J].Polymer Materials Science & Engineering,1998,14(4):62~64.

[7] Richard Feynman.The Man Who Dared to Think Small[J].Scinece,1991,254(29):1300~1301.

[8] Yin Lisong,Zhang Jinxiu.Interface of Rigid Inorganic Particle/Polymer Composit[J],Materials Review.2002,3:44~47.

[9] Masao S,Yasutoshi T,Tensile yield stredd of polypropylene composites filled with ultrafine particles,journal of Materials Science,1993(18):1758~1762.

[10] Kim G M,Michler G H.micromechanical deformation process in toughened and particle-filled semicrystalline polymer,polymer,1998,39(23):5689~5693.