

## ENHANCED DRAG REDUCTION PERFORMANCE OF NANOCOMPOSITES: THE EFFECTS OF SURFACE MODIFICATION OF NANO SILICA

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### ABSTRACT

In this paper, nanocomposite was synthesized with nano silica and poly- $\alpha$ -olefin, and the effects of surface modification to the nano silica on its drag reduction performance were investigated. The dosage coupling agent, Y-aminopropyltriethoxysilane, and the modification temperature were studied intensively through surface hydroxyl and oil adsorption analysis. The test results indicated that the hydroxyl number of the silica was decreased by Y-aminopropyltriethoxysilane modification, with improved lipophilicity and oil adsorption. At 50°C, the optimum Y-aminopropyltriethoxysilane dosages were 15% for Nano-Si-10, 5% for Nano-Si-20, and 10% for Degussa-R972. The modification significantly changed the nano silica surface properties and enhanced the interaction with poly- $\alpha$ -olefin. Through drag reduction and shear resistance tests by rotating disk 40 mins degradation and testing loop 2 times shearing, it was shown that the nanocomposite possessed good drag reduction and excellent shear resistance properties.

**Keywords:** nano silica, surface modification, nanocomposite, drag reduction, shear resistance

### 1. INTRODUCTION

Energy loss caused by flow friction is a concern in many types of fluid transportation application. Numerous technologies have been investigated to decrease friction and energy loss, such as changing the inner surface finish, improving fluid rheological properties and adding surfactants or polymers, etc. For the crude oil and oil products transportation, adding trace quantities of drag reduction agents (DRA) can not only improve capacity by 20%-60%, but also can reduce pressure loss. Currently, the most popular DRA for oil is poly- $\alpha$ -olefin, which is characterized by a long main chain with short side chains and may be several millions in molecular weight (MW). After dissolution in the oil, the poly- $\alpha$ -olefin molecule is oriented by the shear stress within the fluid. Radial pulsations in the fluid are inhibited by elastic deformation of the polymer chain, which reduces the flow resistance and friction energy loss[1-4]. However, poly- $\alpha$ -olefins with high MW are easy to be irreversibly degraded by shear stress. Hence, after intensive shearing, such as at laminar boundary layers, pumps, pipeline elbows and other large velocity gradient locations[5,6], the

DRA should be re-supplied to maintain its drag reduction performance. Optimizing this procedure is a practical problem for DRA research and application.

Nano materials are widely used in the materials field because of their special properties, which originate from their structure and size in nanometer range. Nanocomposites fabricated with base materials, with nano materials as promoters, have been the subject of increasing attention [7-9]. With their nanometer size, large surface area and high surface energy, it is easy for nanomaterials to lose their character because of self-agglomeration. However, poly- $\alpha$ -olefin is a typical non-polar material. In consequence, therefore, nano particles do not disperse well in poly- $\alpha$ -olefin.

Coupling agents commonly are used for surface modification in order to increase the dispersibility of nano silica in polymers[10], and have been applied successfully into poly-acrylate, polyurethane, polyethylene, plastic, rubber and other polymers[11-16]. These polymers show improved application performance and some functionalization properties. Ac-

ording to the requirements for the application of the nanocomposite, the surface of the nano silica particles was modified to prepare the nanocomposited DRA[17,18]. In the present study, the modification conditions and consequent drag reduction performance were investigated.

## 2. EXPERIMENTAL

### 2.1 Materials

Nano silica particles with a size of 10 nm (denoted as Nano-Si-10) and nano silica with a particle size of 20 nm (denoted as Nano-Si-20) were obtained from the Sichuan Jicai Science and Technology Company. Nano silica (Degussa-R972, Aerosil) was obtained from the Degussa Company, Germany. The silane coupling agent, Y-aminopropyltriethoxysilane, (KH550, an industrial product) was obtained from the Chenguang Reagent Company. The drag reducing agent (poly- $\alpha$ -olefin, slurry) was obtained from the Langfang Weipu Pipeline Technology Corporation. Dioctyl phthalate (an analytical reagent), was obtained from the Wuxi Yatai Lianhe Chemical Company.

### 2.2 Methodology

#### 2.2.1 Surface modification

The nano silica was dispersed in 95% ethanol with a 1% mass ratio, as 'Solution 1'. KH550 was dissolved in 95% ethanol with 5% mass ratio, designated as 'Solution 2'. Solution 1 then was further dispersed using an ultrasonic treatment at 40kHz and 180w for 10 min. The pH of Solution 2 was regulated to pH 3~4 using dilute hydrochloric acid and the solution then was hydrolysed for 30 min. Solutions 1 and 2 then were mixed together and were reacted under ultrasonification at 25°C for 60min. The mixed solution was dried in the atmosphere at 40°C for 4 h, and dried under vacuum at 80°C for 24 h. Finally, it was washed 5 times with 95% ethanol and dried under vacuum at 80°C for 24 h.

#### 2.2.2 Preparation of Nanocomposited DRA

The as-modified nano silica samples were added in the DRA suspension of poly- $\alpha$ -olefin at a weight concentration 2%(w/w). A 20% mass ratio of compatibilizer[19] then was added. The suspension was stirred at 50°C and 60 rpm for 6 h in order to obtain a nano silica/poly- $\alpha$ -olefin composited DRA suspension.

### 2.3 Characterization

#### 2.3.1 $S_{BET}$ , TEM and TGA

Surface area ( $S_{BET}$ ) and pore size were calculated

on the basis of the low-temperature  $N_2$  adsorption isotherm measured by a Tristar 3020 automatic adsorption instrument (USA). Transmission electron microscopy (TEM) images were taken using a JEOL JEM-2100 (Japan), with accelerating voltage of 200 kV. The samples for TEM observation were prepared by deposition of an ultrasonically dispersed suspension of a  $SiO_2$  particles in ethanol on a carbon-coated copper grid. Thermal gravimetric analysis (TGA) was conducted using a TG Q50 instrument (TA company, USA.). Approximately 4.0mg of the sample was weighed and placed in Pt sample pan, then heated under a 60ml/min  $N_2$  flow from 40 to 900°C at a rate of 20°C/min.

#### 2.3.2 Measurement of the hydroxyl number on the nano silica surface[20]

Each nano silica sample of 2 g was placed in a conical flask and 25 mL ethanol and 20% 75 ml NaCl solution were added respectively. After stirring to disperse the particles, 0.1 mol/L HCl or 0.1 mol/L NaOH was used to adjust solution pH to 4. Then, the pH was adjusted to 9 with 0.1 mol/L NaOH until the pH value remained unchanged for 20 s. The hydroxyl number on the nano silica surface (per square nanometer) was calculated as per Equation 1:

$$N = (CVN_A * 10^{-3}) / (S * m) \quad (1)$$

where:

C: Concentration of NaOH (mol/L)

V: consumed volume of 0.1 mol/L NaOH when pH from 4 to 9

$N_A$ : Avogadro's constant

S: Specific surface area of nano silica ( $nm^2/g$ )

m: Mass of nano silica (g)

#### 2.3.3 Oil adsorption value

An empty beaker and rod were weighted to obtain the value of  $m_1$ . Nano silica in the beaker with the rod was weighed as  $m_2$ . Then, dioctyl phthalate was gradually added in and stirred to cluster until no excessive dioctyl phthalate leaching was evident, an weighted to obtain the  $m_3$  value. The oil adsorption value,[21,22] was calculated as Equation 2:

$$D = \frac{m_3 - m_2}{m_2 - m_1} \times 100 \quad (2)$$

### 2.4 Drag reduction test

Several references[23-25] reported a the use of a rotating disk device for drag reduction testing, and one

was set up in the laboratory as shown in Fig. 1. The stainless steel rotating disk was 13 cm in diameter and 0.3 cm in thickness. A stainless steel container with a diameter of 17 cm and a height of 7.5 cm, had a volume of 1701.5 cm<sup>3</sup>. The container (with a cover) was placed in a water bath to maintain a constant temperature.

The drive motor shown in Fig. 1, which had a PLC speed control, had a range of 0~3000 rpm. A torque sensor with range a range of 0~5 N•m and an accuracy of 0.0001 N•m was installed between the motor and the rotary shaft. The torque of a test fluid was measured and collected from the rotating disk device.  $T_s$  was resistance torque of diesel at 25°C.  $T_p$  was the resistance torque after adding DRA. Then, the drag reduction rate (DR%) was calculated using Equation 3:

$$DR\% = \frac{T_s - T_p}{T_s} \times 100 \quad (3)$$

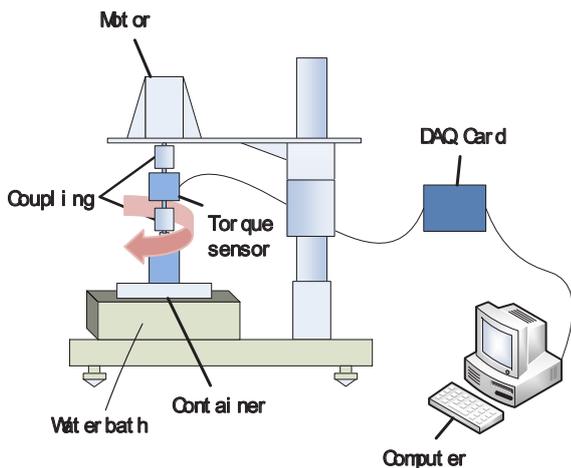


Fig. 1: Rotating disk device for drag reduction test

The test loop was set in laboratory according to Chinese Standard SY/T6578 2009. Compressed nitrogen was used as the power of fluid, and diesel was the test fluid. The pressure drop without DRA was  $\Delta P_0$ , and the pressure drop with DRA was  $\Delta P_1$ . The drag reduction rate (DR%) was calculated according to Equation 4:

$$DR\% = \frac{\Delta p_0 - \Delta p_1}{\Delta p_0} \times 100\% \quad (4)$$

### 3. RESULTS AND DISCUSSION

#### 3.1 Chemical and physical properties of nano silica

The nano silica samples were degassed at 400°C for 4 h, until the pressure was less than 1 Pa. The N<sub>2</sub> adsorption isotherms at -192°C were obtained using

the Tristar 3020. The specific surface area was obtained by employing the BET equation from the as-obtained adsorption isotherm (Fig. 2). It was observed that Nano-Si-10 had the highest adsorption quantity, which meant it had the biggest surface area of 213.10 m<sup>2</sup>/g and the smallest particle size 28.15 nm, as shown in Table 1. Conversely, Nano-Si-20 had the lowest surface area, which was confirmed by the TEM analysis.

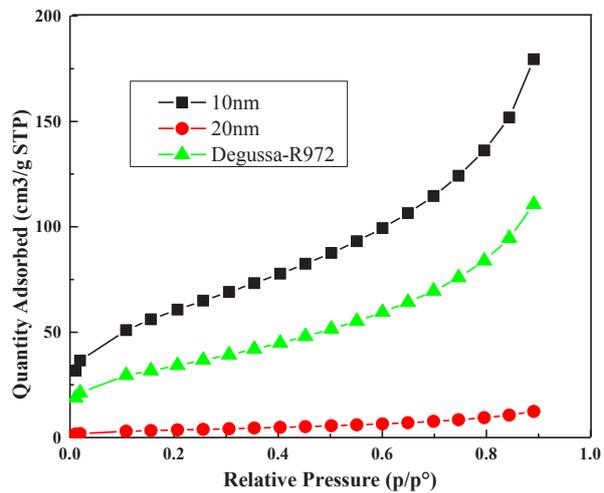


Fig. 2: N<sub>2</sub> adsorption isotherm of nano silica

Table 1: Surface area and particle size of nano silica

Silica Sample	Surface area (m <sup>2</sup> /g)	Particle size (nm)
10 nm	213.10	28.15
20 nm	13.15	456.15
Degussa-R972	121.15	49.52

The TEM images of the nano silica samples are shown in Fig. 2. Clearly, the nano silica sample of nano-Si-10 sample had a size distribution around 8~15 nm. For Nano-Si-20 material, most of particles arranged from 18 to 24 nm. The particle size for the Degussa-R972 was 12~18 nm. It also could be observed that most of the silica had aggregated, which was caused by interaction between the particles. Hence, the particle size as obtained from the N<sub>2</sub> adsorption calculation was larger than the size as measured in the TEM.

TGA analysis of the unmodified nano silica is shown in Fig. 3. It can be observed that there were two weight loss regions for all samples. The weight loss at ≤120°C was attributed to the desorption of the free water from the particle; the loss at 200~700°C was the integrated water loss and hydroxyl dehydration from the silica. For Nano-Si-20 material, it lost approximately 3.8% by weight before 120°C and another 2.5% weight at 200~700°C, which indicated

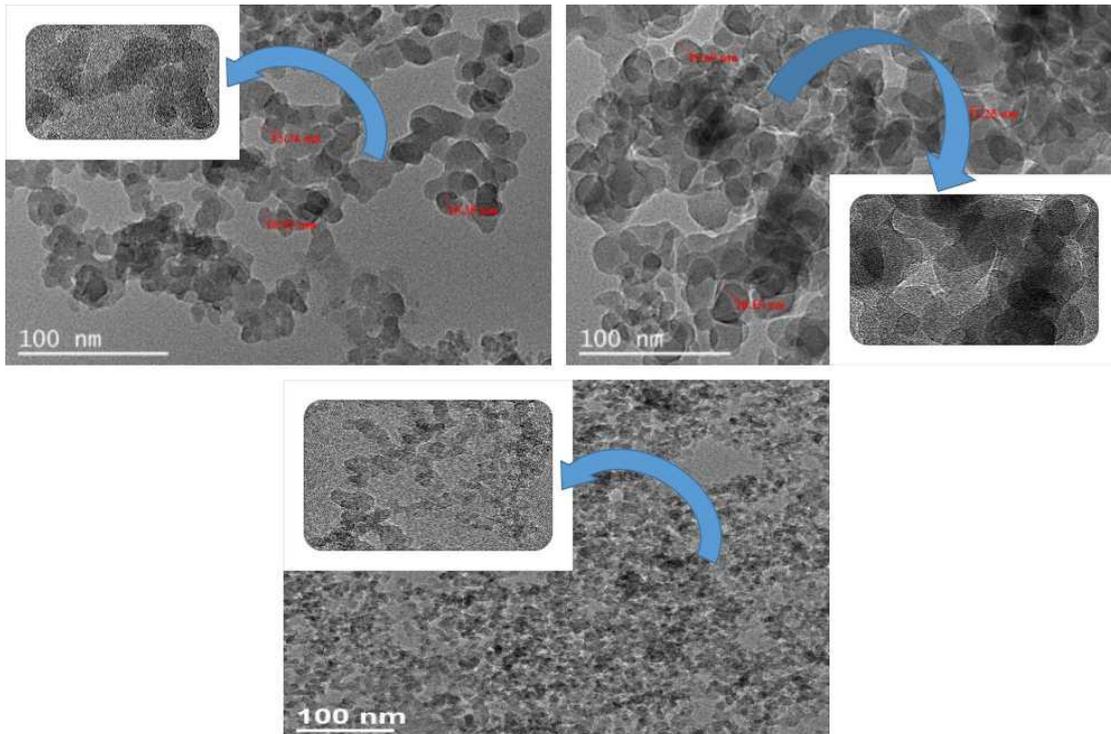


Fig. 3: TEM images of nano silica samples

the free water and hydroxyl group contents. For the other two samples, Degussa-R972 lost much more weight than did the Nano-Si-10. Degussa-R972 exhibited higher hydrophilicity than the Nano-Si-10.

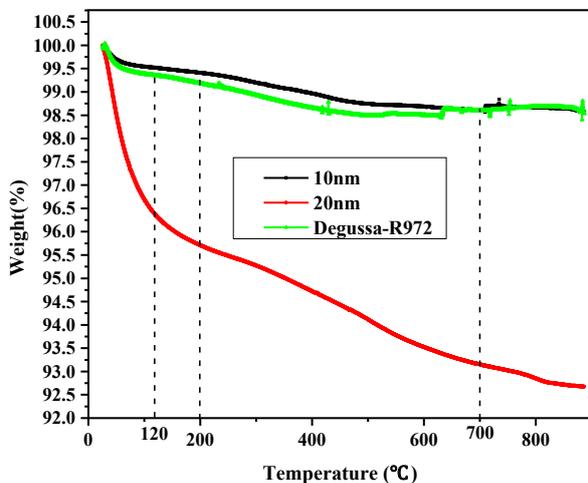


Fig. 4: TGA analyses

Some hydroxyl groups on unmodified silica surface exhibited high surface energy and hydrophilic properties, whereas the poly- $\alpha$ -olefin possessed a hydrophobic surface. In order to make silica disperse well in poly- $\alpha$ -olefin, the nano silica was modified with KH550. After organic groups grafting, the silica surface could eliminate the hydroxyl radicals and enhance its hydrophobicity[20,22], as shown in Fig. 5.

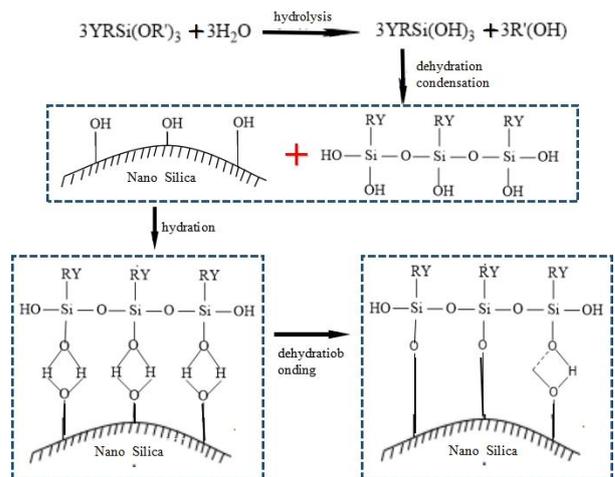


Fig. 5: Schematic procedure of coupling agent interaction with nano silica[20]

### 3.2 Influence of coupling agent modification

The influence of KH550 dosage was studied initially for nano silica modification (at 50°C). The hydroxyl number and oil absorption value were measured. As evident in Table 2, with an increase in KH550, the hydroxyl number of the silica gradually decreased for Nano-Si-10. At 15% KH550 dosage, the minimum hydroxyl number occurred, which meant the best hydrophobic surface property had been achieved. For Nano-Si-20, the lowest hydroxyl number occurred at 5% KH550 and for the Degussa-R972 the optimum KH550 dosage was 10%. Combining the N2 adsorption and TGA analysis, it is straightforward

**Table 2:** Influence of KH550 dosage

Nano silica	10 nm		20 nm		Degussa-R972	
KH550 dosage (%)	Hydroxyl number (/nm <sup>2</sup> )	Oil adsorption ( ml/g )	Hydroxyl number (/nm <sup>2</sup> )	Oil adsorption ( ml/g )	Hydroxyl number (/nm <sup>2</sup> )	Oil adsorption ( ml/g )
0	1.66	2.02	4.53	0.16	3.21	0.85
5	1.23	2.43	<b>0.42</b>	<b>0.64</b>	1.03	1.13
10	1.01	2.88	0.48	0.65	<b>0.52</b>	<b>1.26</b>
15	<b>0.58</b>	<b>3.53</b>	0.95	0.51	0.61	1.27
20	0.86	3.15	1.57	0.47	1.73	0.98
25	1.35	2.74	1.86	0.42	1.94	0.91

to conclude that Nano-Si-20, with smallest surface area but the most weight loss, needed the lowest KH550 dosage. With increase in KH550 dose rate, more silanol was produced by KH550 hydrolysis. In that case, the condensation reaction to siloxane amongst the silanol would increase, which reduced or hindered the interaction between silanol and the nano silica. In consequence, the hydroxyl number of the silica surface increased when KH550 was above optimum dose ratio.

For the oil adsorption values shown in Table 2, the effect of KH550 on modification was further confirmed. At the optimum KH550 ratio, more oil was adsorbed due to the decrease in hydroxyl number on the nano silica surface, with increase in the concentration of KH550. Additionally, the greatest oil adsorption values were 15% KH550 for Nano-Si-10, 5% for Nano-Si-20, and 10% for Degussa-R972, respectively. Beyond that, the oil adsorption values decreased with increase in the KH550 dosage. Because of replacement of the hydroxyl on the silica surface and the steric effect there were no obvi-

ous modification effects. In addition, more KH550 might cause particle agglomeration and decrease the oil adsorption value.

### 3.3 Influence of modification temperature

System temperature could affect the modification. Behavior at five temperatures between 20 and 60°C was investigated for the Nano-Si-10 modified with 15% KH550, Nano-Si-20 with 5%, and Degussa-R972 with 10% KS550. It can be observed from Table 3 that the oil adsorption value increased with increasing temperature. Inversely, the hydroxyl number gradually decreased with increasing temperature. High modification temperature favoured surface lipophilicity. The reason was that silanol from the hydrolysis stage was apt to adsorb on silica surfaces and maintain a balance between adsorbing and desorbing, but not silicon hydroxyl replacement, at low temperature. At higher temperatures, silanol with enough energy could replace silicon hydroxyl, while when the temperature was above 50°C there was no distinct improvement by the modification mechanism. This was attributed to high temperature

**Table 3:** Influence of modification temperature

Nano silica	10 nm		20 nm		Degussa-R972	
temperature ( °C )	Hydroxyl number (/nm <sup>2</sup> )	Oil adsorption ( ml/g )	Hydroxyl number (/nm <sup>2</sup> )	Oil adsorption ( ml/g )	Hydroxyl number (/nm <sup>2</sup> )	Oil adsorption ( ml/g )
20	1.22	2.41	0.97	0.41	0.44	0.76
30	1.10	2.56	0.73	0.53	0.56	1.09
40	0.94	3.07	0.51	0.58	0.57	1.24
<b>50</b>	<b>0.58</b>	<b>3.53</b>	<b>0.42</b>	<b>0.64</b>	<b>0.52</b>	<b>1.26</b>
60	1.35	2.89	0.65	0.62	0.59	1.18

affecting the replacement balance between the silanol and the silicon hydroxyl. Therefore, the optimal modification temperature was 50°C.

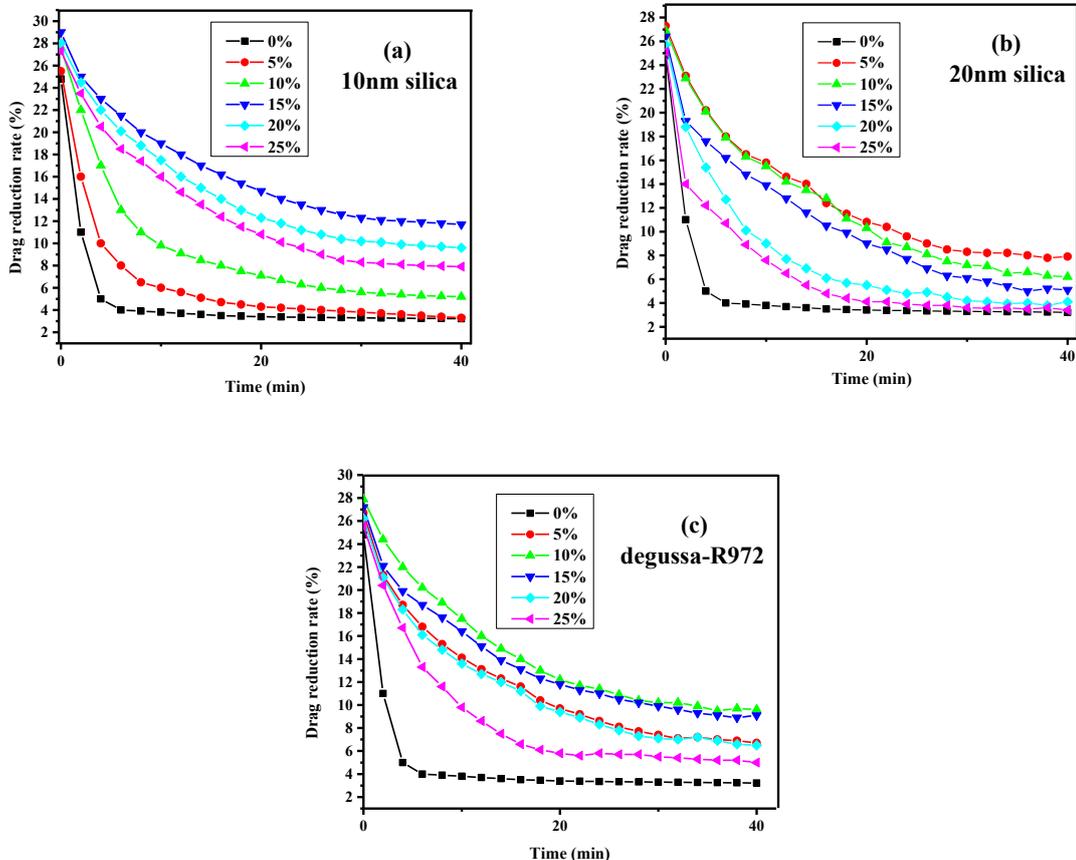
### 3.4 Drag reduction performance of the nanocomposite

Silica/poly- $\alpha$ -olefin nanocomposites were prepared with the modified SiO<sub>2</sub>, interface phase solvent and DRA slurry of poly- $\alpha$ -olefin<sup>[20-21]</sup>. At 25°C, with diesel as the solvent and a DRA concentration of 50 ppm, the torque of test fluid was measured and collected from the rotating disk device.

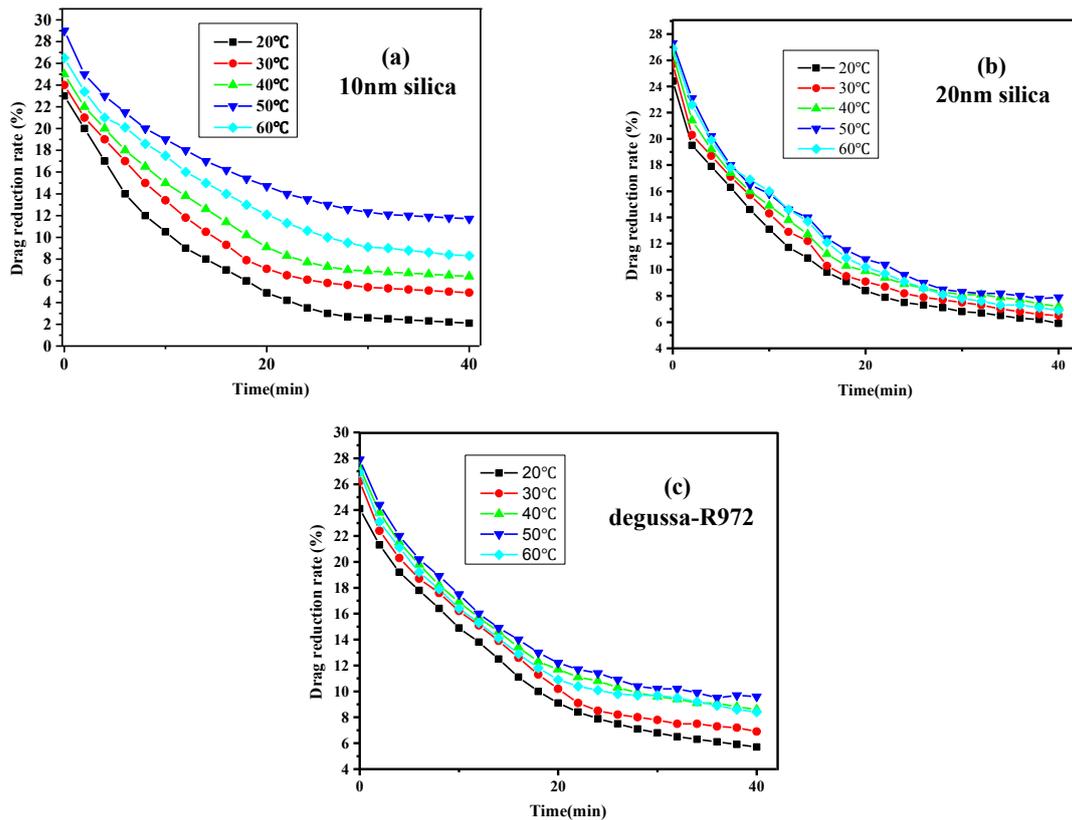
The influence of KH550 dosage on the drag reduction and shear resistance of the nanocomposite were investigated, as shown in Fig. 6. As the preparation process could improve dispersion of the nanocomposite DRA, so all three nanocomposites exhibited a slightly higher drag reduction rate than the poly- $\alpha$ -olefin. For Nano-Si-10, with increase in the KH550 dosage, the drag reduction rate improved until a concentration of 15% KH550. The equivalent readings were 5% KH550 for Nano-Si-20 and 10% KH550 for Degussa-R972, which agreed with silica modification results presented in Section 3.2.

Shear resistance can be reflected in the residue drag reduction rate after shear degradation. It could be observed that all of the nanocomposites showed better shear resistance than the poly- $\alpha$ -olefin. The modification had an influence on the shear resistance of the nanocomposites, where nanocomposites with well-modified nano silica would show excellent shear resistance performance. The best shear resistance samples were 15%, 5% and 10% KH550 modified for the Nano-Si-10, Nano-Si-20 and Degussa-R972, leaving 11.7%, 7.9% and 9.6% drag reduction rates, respectively, after 40 min of shear degradation by the rotating disk.

The influence of modification temperature on drag reduction and shear resistance was investigated for the three nanocomposite samples. It can be observed from Fig. 7 that higher temperature was helpful in generating a better drag reduction and shear resistance performance, though modification temperature had less influence than KH550 dosage. The optimum performance was 50°C for all three nano silica types, as discussed in Section 3.3. After 40 mins of the shear degradation procedure, it left an 11.7% drag reduction rate for the best nanocomposite of Nano-Si-10.



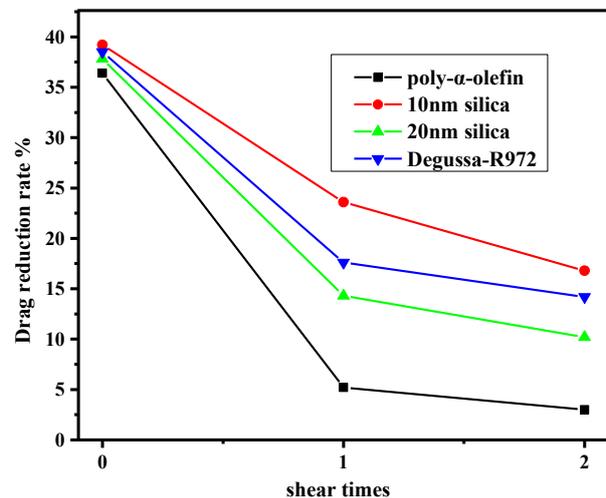
**Fig. 6:** Influence of KH550 dosage on the drag reduction of nanocomposites during the rotating disk tests: (a) Nano-Si-10, (b) Nano-Si-20, (c) Degussa-R972



**Fig. 7:** Influence of the modification temperature on drag reduction of nanocomposites by the rotating disk: (a) Nano-Si-10, (b) Nano-Si-20, (c) Degussa-R972

In this investigation, the test loop also was used to evaluate the performance of DRA in laboratory. The nanocomposites (50°C, 15% KH550 for Nano-Si-10, 5% KH550 for Nano-Si-20, 10% KH550 for Degussa-R972) with the best performance in the rotating disk rig were tested. At 25°C, the DRAs were sheared twice by a centrifugal pump in the test system. The test loop results are shown in Fig. 8. The nanocomposites had better drag reduction rates than the poly- $\alpha$ -olefin. This was because DRA dispersion in the diesel was accelerated by the stirring procedure during nanocomposite preparation. After being sheared the first time by the centrifugal pump, the drag reduction rate of the poly- $\alpha$ -olefin had decreased from 40% to 4.2%. This result indicates that most of the poly- $\alpha$ -olefin had degraded. However, when sheared for a second time, there was just 2.3% drag reduction rate. Nevertheless, the nanocomposites still had 23.6% drag reduction rate after the same procedure, nearly 60% drag reduction capacity remained for 15% KH550 Nano-Si-10, and 38% drag reduction capacity for 5% KH550 Nano-Si-20, and 46% drag reduction capacity for 10% KH550 Degussa-R972. Additionally, a 16.8% rate remained (more than 40% drag reduction capacity) after two times cycles of shearing for 15% KH550 Nano-Si-10, 27% for 5% KH550 Nano-Si-20, and 37%

for 10% KH550 Degussa-R972. Therefore, it could conclude that the nanocomposites possessed good shear resistance characteristics.



**Fig. 8:** Shear resistance of the nanocomposite in the test loop

The above results of the rotating disk and test loop showed that the silane coupling agent very evidently improved the non-polarity of the nano silica and promoted the interaction between the nano silica and the poly- $\alpha$ -olefin. Meanwhile, the stronger surface potential produced by the modification pro-

cess on the nano silica facilitated connection with a chemical bond to the poly- $\alpha$ -olefin. The strength and effect of the nanocomposites could be improved by enhanced physical entanglement of the macromolecules, which would transfer exterior force and consume a large amount of impact energy.

#### 4. CONCLUSIONS

According to the requirements for DRA applications, the effects of nano silica surface modification on nanocomposite performance were investigated. Through the characterization of unmodified nano silica, studies on modification conditions, drag reduction and shear resistance performance tests, it was concluded as follows:

(1) Hydroxyl number on nano silica surface and oil adsorption value shown that hydrolysis product silanol by KH550 replaced hydroxyl on nano silica surface. Higher KH550 concentrations and temperatures were favourable for surface lipophilicity. The optimal modification conditions were 50°C, and 15% KH550 for Nano-Si-10, 5% KH550 for Nano-Si-20 and 10% KH550 for Degussa-R972.

(2) Drag reduction results from the rotating disk rig indicated that all the prepared silica/poly- $\alpha$ -olefin nanocomposites exhibited good drag reduction and excellent shear resistance capabilities. After 40 min of shear degradation, the nanocomposites still retained more than a 15% drag reducing rate. Test loop test results showed that the nanocomposites possessed good shear resistance and the drag reduction rate was maintained at the original values of 60% and 40% for the best nanocomposite DRA, after 1 and 2 cycles of shear degradation, respectively.

(3) The coupling agent modification significantly changed the surface properties of the nano silica and promoted the its interaction with the poly- $\alpha$ -olefin. Then, molecular entanglement and chemical bond effects of the nanocomposite transfer applied force and improve the shear resistance of the fluid.

(4) The use of nanocomposites as DRAs was confirmed to be a feasible way to improve drag reduction and shear resistance performance of the additive. The conditions of surface modification and nanocomposite preparation should be investigated in detail in future studies. Additionally, the interaction between nano particles and poly- $\alpha$ -olefins should be studied to clarify and optimize the properties of such drag resistance agents.

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