

Silicone-polyether Copolymers as New Steam Turbine Oil Demulsifiers

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ABSTRACT

Turbine oil plays an important role in supporting optimal steam turbine performance. Some additives in turbine oil can cause emulsification when the oil is contaminated by water, so demulsibility is a very important property of the steam turbine oil. In order to improve the demulsibility of steam turbine oil, two kinds of polyether-silicone comb copolymers are synthesized and used as steam turbine oil demulsifiers. The polyether-silicone copolymers present better demulsibility properties than the demulsifiers on the market at the present time. The influences of demulsifiers on turbine oil-water interfacial tension and demulsibility time were measured. All the demulsifiers obviously decrease interfacial tension and simultaneously reduced the demulsibility time. The variation tendency of interfacial tension and demulsibility time is basically consistent. The oil-water interfacial elastic modulus and viscous modulus were also measured as a function of strain and frequency respectively. The results showed that the demulsifiers decrease the oil-water interfacial elastic modulus, which was favorable to the demulsification.

Keywords: Steam Turbine Oil, Demulsifiers, Silicone-polyether Copolymers

INTRODUCTION

Turbine oil plays an important role in supporting optimal steam turbine performance and must meet some specifications such as aging stability, hydrolytic stability, corrosion protection, demulsibility, rapid air release, low foaming, etc. [1,2]. Turbine oils contain aging inhibitors and corrosion protection agents, which offer outstanding reliability in practice if certain basic rules are observed. Modern turbine oils also contain antiwear additives and extreme-pressure additives, which protect the component from wear. However, on the other side, all these additives may also act as emulsifying agents [3]. Emulsion forming will cause the turbine oil to lose its ability to lubricate effectively, which can promote oil degradation, chemical corrosion, and

bearing fatigue. Therefore, the steam turbine oil requires excellent demulsification properties and the water content must be controlled [4,5].

Demulsibility is an important property of the oil to separate from water and resist the formation of emulsions. Adding demulsifiers is a general method to improve the oil demulsibility [6]. The common lubricant demulsifiers currently available on the market are polyethylene glycols and other ethoxylated substances, such as T1001 and DL32. However, these products are not effective in steam turbine oils in some cases and more effective demulsifier products should be developed.

Silicone polymers have a very low surface tension and high interfacial activity [7], and they possess both hydrophobic and oleophobic characteristics. These

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Article history

Received: October 26, 2014

Received in revised form: January 13, 2015

Accepted: February 25, 2015

Available online: October 20, 2016

characteristics are just what the demulsifiers desired [8, 9]. In this work, some polyether-silicone comb copolymers were synthesized and their demulsibility performances in turbine oil were tested. In order to study the emulsification and demulsification mechanism of lubricating oil, the oil-water interfacial elastic modulus and viscous modulus respectively as a function of strain and frequency were measured.

EXPERIMENTAL PROCEDURES

Synthesis of Polyether-silicone Comb Copolymers

Silicone-polyether comb copolymers were synthesized by the hydrosilylation of polymethyl hydrogensiloxane and unsaturated polyether in the presence of a platinum catalyst [10-12] (Figure 1).

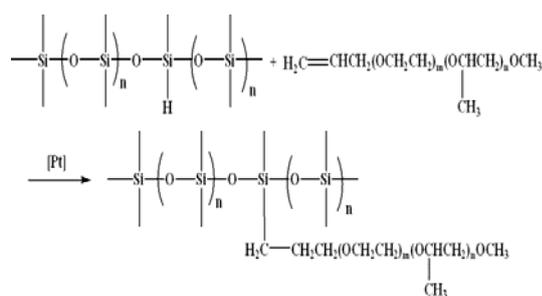


Figure 1: Synthesis of polyether-silicone comb copolymer.

Various products were synthesized with various methyl hydrogen silicone oil and allyl polyether. Two of these products (named DM1 and DM2) were evaluated in this work. The products are colorless or slightly yellow transparent viscous liquid.

Synthesis of DM1: A solution of 50.0 gr polymethylhydrogensiloxane (average molecular weight is 2000, mass percentage of hydrogen is 0.16%) and 35.2 gr allyl polyether (average molecular weight is 400) in 200 ml toluene was stirred at 95°C for 4 hrs. The toluene was removed on a rotary evaporator. Then, 50 ml petroleum ether was added to the product, and the excessive allyl polyether deposited. The petroleum ether was removed, and the final product was obtained; the yield was 92%.

Synthesis of DM2: A solution of 20.0 gr polymethylhydrogensiloxane (average molecular weight is 2000, mass percentage of hydrogen is 0.80%) and 140.8 gr allyl polyether (average molecular weight is 800) in 500 ml toluene was stirred at 95°C for 4 hrs. The toluene was removed on a rotary evaporator. Then, 100 ml petroleum ether was added to the product, and the excessive allyl polyether deposited. The petroleum ether was removed, and the final product was obtained; the yield was 93%.

The IR spectra of all the samples were characterized on a PE-325 FTIR spectrometer (Figure 2). The characteristic absorption peak of Si-H in 2150 cm^{-1} and C=C in 1647 cm^{-1} were disappeared when the chemical reaction ended.

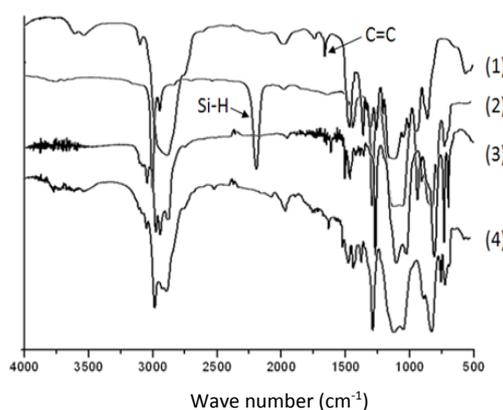


Figure 2: IR spectra of (1) polymethylhydrogensiloxane, (2) allyl polyether, (3) DM1, and (4) DM2.

Tests

The demulsibility of all the demulsifiers were tested according to the petrochemical industry standard SH/T 0191, and Figure 3 shows the sketch of the demulsibility tester. This method is designed specifically for ship oil demulsibility test. In this method, 20 ml oil is added into a 50 ml test tube with scale lines and is placed into a water bath thermostated at $24 \pm 2^\circ\text{C}$. Steaming into the oil at a specified speed continues until the total volume (oil and condensate water) is 40 ml, and then the test tube is placed into a water bath thermostated at 93.5°C . The oil and water separate and the separation time is named emulsion breaking time and recorded to indicate the

demulsibility.

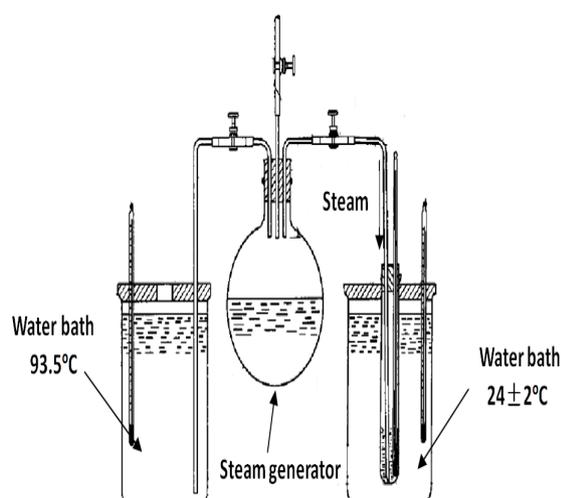


Figure 3: The sketch of demulsibility tester.

The air release property and anti-foam property are tested according to ASTM D3427 and ASTM D892 respectively.

The T1001 and DL32 are two common demulsifiers used in turbine oil. In this work, these demulsifiers were also tested for comparison.

Rheology

The interfacial tension of the oil/water is tested according to ASTM D971 on a FJZ-2 automatic interfacial tension tester.

The interfacial viscoelasticity measurements were performed using a TA Instruments AR-G2 rheometer (Figure 4). The ring was placed in the surface of the water; the oil was added afterwards. With the ring in place at the water/oil interface, the interfacial moduli were monitored by frequency sweep and strain sweep at 50°C.

RESULTS AND DISCUSSION

Demulsibility

The various demulsifiers were added to 68 # antiwear turbine oil with the mass concentration of 0.01% respectively and the demulsibility time was tested according to the petrochemical industry standard SH/T 0191(as hereinbefore described).

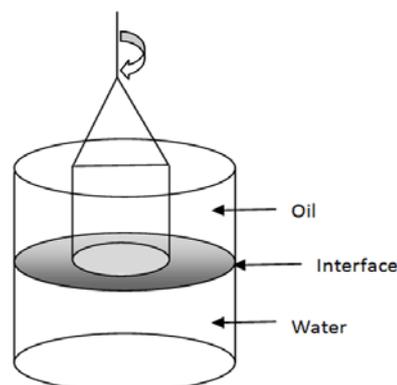


Figure 4: The sketch of the AR-G2 rheometer

The results (Table 1) showed that all the demulsifiers have the abilities to improve the demulsibility of antiwear turbine oil. The emulsion breaking time of turbine oil without demulsifier was 240 s. When T1001 and DL32 were added respectively, the emulsion breaking times of T1001 and DL32 were 178 s and 166 s, which was only a little lower than the requirement of the specification. However, when DM1 and DM2 were added respectively, the emulsion breaking times of DM1 and DM2 were 110 s and 90 s, which was far less than T1001 and DL32 and presented excellent demulsifying ability.

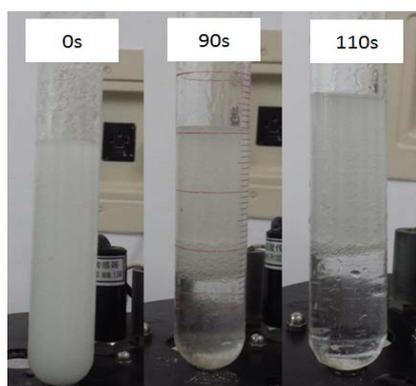
Table 1: The emulsification breaking time with different demulsifiers (0.01wt.%)

Sample	Demulsibility Time ($t \leq 180$ s)
Demulsifier free	240
T1001	178
DL32	166
DM1	110
DM2	90

Figure 5 showed the demulsibility comparison between T1001 and DM1. When T1001 was added, only about 7 ml water was separated in 90s and 20 ml water was separated after 184s. This result does not conform to the specific requirement ($t \geq 180$ s). When DM1 was added, about 15 ml water was separated in 90 s and 20 ml water was separated after 110 s. Thus DM1 shows better demulsibility than T1001.



(a) T1001



(b) DM1

Figure 5: The demulsibility comparison between T1001 and DM1.

The emulsion breaking time of various concentrations of DM1 and DM2 was also investigated. The results (Table 2) showed that the emulsion breaking time decreased with increasing concentrations of the emulsifiers. Even at the concentration of 0.003%, the demulsibility time of DM1 and DM2 are 160 s and 150 s respectively, and both have met the specific requirement. It is suggested that the optimal demulsifier concentration be 0.005%.

Table 2: The demulsibility time with various concentrations of DM1.

DM1 (wt.%)	Demulsibility Time ($t \leq 180$ s)	
	DM1	DM2
0	240	240
0.003	160	150
0.005	122	120
0.010	110	90

The Demulsifier Influence on Air Release and Antifoaming Properties

The demulsibility is a kind of surfactant and might have influence on air release and antifoaming of the oil. The air release and antifoaming of turbine oil were inspected with various concentrations of DM1 and DM2 (Table 3). The results showed that both of the demulsifiers have some impact on the antifoaming performance of antiwear turbine oil. The influence of DM2 is smaller than DM1. However, all the values meet the specific requirement ($t \geq 8$ min).

The demulsifiers influences on antifoaming were also determined and the results are displayed in Table 4. The results showed that the demulsibility has no discernible effect on antifoaming.

Table 3: The demulsifier influence on air release.

Demulsifier Concentration (%)	Air Release Value ($t \leq 8$ min)	
	DM1	DM2
0	4'40"	4'40"
0.003	4'50"	4'50"
0.005	6'40"	5'30"
0.010	7'20"	5'30"

Table 4: The demulsifier influence on antifoaming.

Demulsifier Concentration (%)	Temperature (°C)	Antifoaming	
		DM1	DM2
0	24	10.0	10.0
	93.5	10.0	10.0
	24 after 93.5	10.0	10.0
0.005	24	10.0	10.0
	93.5	10.0	10.0
	24 after 93.5	10.0	10.0
0.010	24	10.0	10.0
	93.5	10.0	10.0
	24 after 93.5	10.0	10.0

The Demulsifier Influence on the Interfacial Rheological Property of Oil/Water

Some studies have shown that the demulsibility is related to the decreased extent of oil-water interfacial tension [13-16]. The interfacial tension decreases further when better demulsibility is present.

Table 5 shows the influences of each demulsifier on turbine oil-water interfacial tension and demulsibility time. All the demulsifiers obviously decrease interfacial tension and simultaneously reduce the demulsibility time. The variation tendency of interfacial tension and demulsibility time is basically consistent. The demulsibility time decreases with decreasing interfacial tension (Table 5).

Table 5: The Interfacial tension with different demulsifiers (0.01 wt.%)

Sample	Interfacial Tension (mN/m)	Demulsibility Time ($t \leq 180s$)
Demulsifier free	9.689	237
T1001	8.155	178
DL32	7.641	166
DM1	7.465	110
DM2	7.430	90

Some researchers also suggest that the stability of the emulsion should be related to interfacial shear viscosity and the emulsion is more stable at a greater interfacial shear viscosity.

Four demulsifier additives were added to turbine oil separately and the mass concentration of every demulsifier was 0.01%. The interfacial elastic modulus was tested by frequency sweep and strain sweep. The results (Figure 6) showed that the interfacial elastic modulus of the turbine oil without demulsifier was the greatest and all the demulsifiers obviously decreased the interfacial elastic modulus to varying degrees. Among them, DM1 and DM2 decreased the interfacial elastic modulus more than DL-32 and T1001. These results suggest that decreasing the interfacial elastic modulus should be favorable to the demulsification.

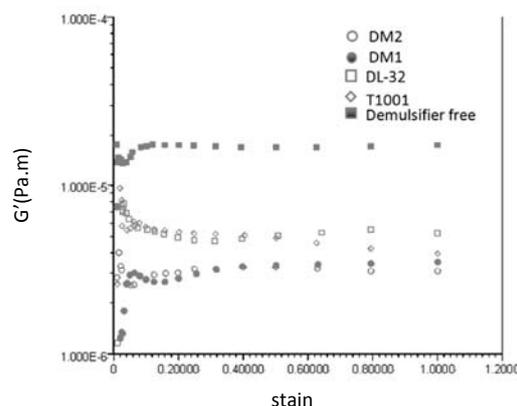


Figure 6: The influence of various demulsifiers on interfacial elastic modulus with strain sweep and frequency sweep.

The interfacial viscous modulus was also tested by frequency sweep and strain sweep. The results (Figure 7) showed that all the demulsifiers had no significant effect on interfacial viscous modulus.

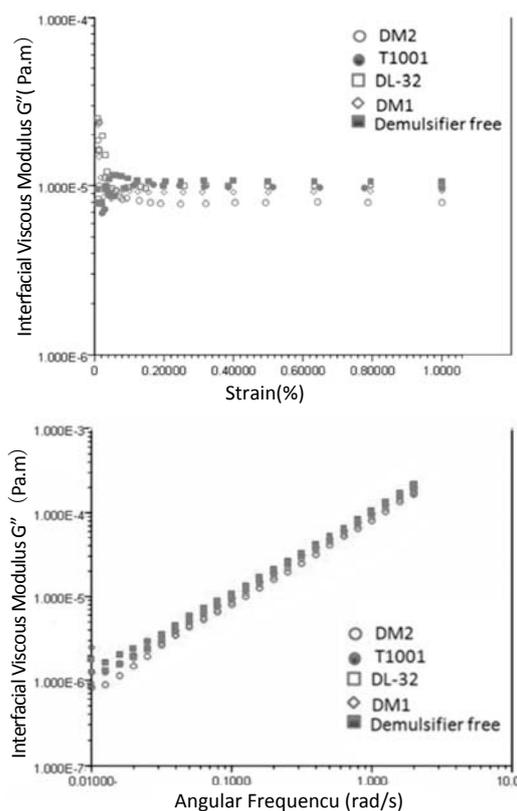


Figure 7: The influence of various demulsifiers on interfacial viscous modulus with strain sweep and frequency sweep.

CONCLUSIONS

Silicone-polyether copolymers synthesized in this paper, namely DM1 and DM2, present better

demulsibility properties when used as steam turbine oil demulsifiers compared to commercial ones. This is probably due to the characteristics of silicone oil such as very low surface tension and high interfacial activity.

All the demulsifiers obviously decrease interfacial tension. The variation tendency of interfacial tension and demulsibility time is basically consistent. The demulsibility time decreases with the decreasing of interfacial tension.

All the demulsifiers decrease the interfacial elastic modulus to varying degrees and the results suggest that decreasing the interfacial elastic modulus should be favorable to the demulsification.

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