

Antifoaming Performance of Polysiloxanes Modified with Fluoroalkyls and Polyethers

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Received 30 July 2007; accepted 28 November 2007

DOI 10.1002/app.27877

Published online 30 April 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of polysiloxanes modified with fluoroalkyls and polyethers were synthesized. Antifoaming performance of such modified polysiloxanes in the mixture of diesel and mobile fuel was studied. The effects of factors such as polyethers type, molar ratio between polyether and fluoroalkyl, hydrogen-contents and viscosity of polysiloxanes, length of fluoroalkyls, etc., on the performance of modified products were discussed. It shows that polysiloxane modified with allyl polyoxypropylene ether and hexafluorobutyl acrylate has better breaking and inhibiting foam performance, when compared with that replacing allyl polyoxypropylene ether with allyl polyoxyethylene polyoxypropylene block ether and allyl polyoxyethylene ether. And when the molar ratio between allyl polyoxypropylene ether and hexafluorobutyl acrylate is 3 : 7, modified polysiloxane has the best foam controlling performance. Low viscosity polysiloxane or low hydrogen

content polysiloxane modified with allyl polyoxypropylene ether and hexafluorobutyl acrylate has better foam controlling performance. Polysiloxane modified with longer carbon chain fluoroalkyl and allyl polyoxypropylene ether has better antifoaming performance than that modified with shorter carbon chain fluoroalkyl and polyether and lower surface tension. The change of surface tension of foaming liquid between initially added with modified polysiloxane and after testing antifoaming performance was studied, and it shows that after testing performance of antifoam, the surface tension of foaming liquid becomes bigger which is one possible reason for antifoam exhausting. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1950–1954, 2008

Key words: polysiloxane; modification; polyether; fluoroalkyl; antifoaming performance

INTRODUCTION

Foam is a system of a large number of bubbles dispersed into continuous phase, and dispersed phase is bubbles. Antifoaming agent is a kind of important auxiliaries, which is widely used in many industries to eliminate unwanted foam, such as printing, coating, dyeing, paper making, petroleum process, and so on. Up to now, silicone antifoam is being thought to be very effective in many aqueous systems.^{1–3}

However, in such industry processes as retarded coking process, diesel process, and lubricant transport silicone antifoam is not so efficient. In the last decade, some researchers applied patents of introducing some kinds of antifoam compositions used in oil system, and the main components of such antifoam include polysiloxane (PS) and polysiloxanes modified with polyether(HPS-P).^{4–7}

Synthesis and application of fluorine-containing compounds is one hot topic,⁸ because of fluoro-compounds having excellent properties such as low

surface tension, water-repellent, oil-repellent performance, etc. Jouji et al. synthesized a series of polysiloxanes modified with fluoroalkyls (HPS-F) used in cosmetic products by hydrosilation addition reaction.^{9,10} Some kinds of HPS-F or perfluoropolyethers used as one component of antifoam composition in nonaqueous systems were also discussed,^{11–13} but the performance of antifoam composition is not so satisfactory. Owen and Julianne, too, discussed synthesis of some HPS-F and their breaking foam performance in presence of silica in aqueous system, and explained the process of antifoam breaking foam, but did not study performance in nonaqueous system.¹⁴ We studied antifoaming performance of a series of HPS-F in which fluoroalkyl having different carbon number in the mixture of diesel and mobile fuel, the HPS-F has fast initial breaking foam speed and lacks inhibiting foam ability.¹⁵

Some literatures explored factors having some effects on the antifoam exhausting in aqueous systems, including entry barrier of antifoam, spreading oil and particle size, and so on.^{16,17}

To our best knowledge, the reports on the antifoaming performance and antifoam exhaust problem in oil-based system are still very few.

Here, from the view of industry, antifoaming performance of polysiloxane modified with polyethers

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Contract grant sponsor: Postdoctoral Science Foundation of Jiangsu Province; contract grant number: 0701023C.

and fluoroalkyls (HPS-P-F) was systemically studied, and the possible reason for "antifoam exhaust" was analyzed by comparing the change of surface tension of foaming liquid between initially added with modified polysiloxane and after testing antifoaming performance. Thus, HPS-P-F low the cost when HPS-F is used as antifoam directly, which provides reference for choosing suitable antifoam for oil-based systems.

EXPERIMENTAL

Material

2,2,2-Trifluoroethyl acrylate (G00), hexafluorobutyl acrylate (G01), dodecafluorobutyl acrylate (G02) were purchased from Harbin Xeogia Fluorine-Silicon Chemical Company (Harbin, China). Allyl polyoxypropylene ether (P1), allyl polyoxyethylene polyoxypropylene block ether (P2), and allyl polyoxyethylene ether (P3) were purchased from Nanjing Jinling Petrochemical Research Institute Co. (Nanjing, China) Hydrogen-containing polysiloxane (HPS) of different viscosity and different hydrogen-content were prepared in lab. Chloroplatinic acid was purchased from Xi'an Kaili Chemical Co. (Xi'an, China).

Synthesis of HPS-P1-G01

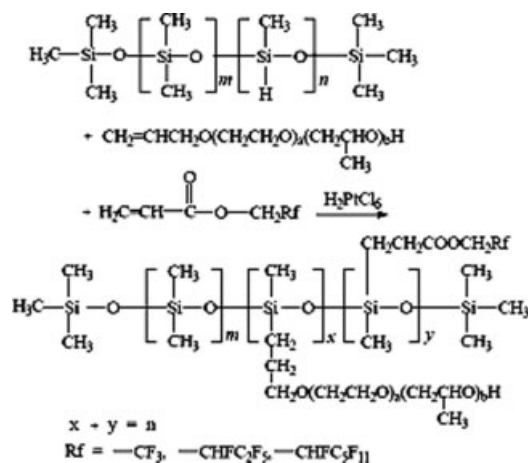
A 50-mL three-necked flask equipped with a stirrer and thermometer was charged with G01, HPS (molar mass of Si—H bond in HPS is equal to total sum of C=C double bond in both G01 and P1). Chloroplatinic acid (10 ppm) based on the total mass was added at 60°C, and then the mixture was heated to 115°C at the rate of 2–3°C per minute and maintained at that temperature for 1 h, a light-yellow transparent oil product was obtained. Changing the molar ratio between P1 and G01, a series of HPS-P1-G01 could be obtained.

IR spectra were recorded on a Bomem MB154S. IR (KBr): 2964.3, 1749, 1270.9, 1260.5, 1110.9, 1094, 1023, 802.9 cm^{-1} .

The hydrosilation addition reaction is for other substrates in the same way. With G00 and G02 replacing G01, and P2 and P3 replacing P1 to react with HPS of different viscosity and hydrogen-content, a series of modified polysiloxanes were obtained (Scheme 1). HPS-P1 is product of HPS modified only with P1, HPS-G01 is product of HPS modified only with G01, and the same for others. Surface tension was measured on JZ-200A automatic apparatus at 25°C.

Antifoaming performance test

To the graduated cylinder, which has a radius of about 2 cm, 50 mL of mixture of diesel and mobile fuel and 0.2 g of 10% (by weight) of solution of anti-



Scheme 1 Reaction of HPS modified with fluoroalkyls and polyethers.

foam (HPS-P-F) in propanone was added, then capped and shaken in upright position. The graduated cylinder was shaken for 20 strokes through an arc of 20° at a frequency of 100–120 strokes per minute. Then, the time (T^{20}) of foam collapse and volume of foam (V^{20}) were recorded. Foam volume was measured as the sum of volume of bubble and volume of liquid mixture. Foam collapse time was determined at the foam disappeared completely, measured from the end of the shaking period. Then the solution was shaken again for 100 strokes and the time (T^{100}) of foam collapse and the volume of foam (V^{100}) were measured again.

The collapse time T^{20} and foam volume V^{20} after shaking 20 strokes characterize the initial effect, and the collapse time T^{100} and foam volume V^{100} after shaking 100 strokes represent the persistence performance of the antifoam. Value of T^{20} is smaller, which indicates that initial breaking foam performance of the antifoam is better. Value of T^{100} and V^{100} is smaller, which shows that inhibiting foam performance of the antifoam is better. And value of V^{100} is bigger, which illustrates inhibiting foam performance of the antifoam is worse.

RESULTS AND DISCUSSION

Mechanism of antifoaming action of antifoam is not well known. Antifoaming performance includes both breaking foam ability and inhibiting foam ability in this article.

As shown in Table I, when shaken 20 and 100 strokes, the order of both V^{20} and V^{100} is same: HPS2-G01 < HPS2-P1 ≈ HPS2-P2 ≈ HPS2-P3 < blank experiment ≈ HPS2. When shaken for 20 strokes, the order of T^{20} is: HPS2-G01 < HPS2-P1 < HPS2-P2 < HPS2-P3 < blank experiment < HPS2,

TABLE I
Performance of HPS (HPS2) Modified with Different Groups

| | V^{20} (mL) | T^{20} (s) | V^{100} (mL) | T^{100} (s) | $\gamma^{25^\circ\text{C}}$ (mN·m ⁻¹) ^a | $\eta^{25^\circ\text{C}}$ (mPa·s) ^b |
|-------------------------------|---------------|--------------|----------------|---------------|----------------------------------------------------------------|------------------------------------------------|
| HPS2 | 68 | 95 | 72 | 91 | 21.4 | – |
| HPS2-P1 | 62 | 25 | 64 | 28 | 24.9 | 30 |
| HPS2-P2 | 65 | 32 | 63 | 40 | 25.7 | 46 |
| HPS2-P3 | 65 | 35 | 62 | 43 | 25.5 | 74 |
| HPS2-G01 | 52 | 19 | 53 | 51 | 21.8 | – |
| Blank experiment ^c | 67 | 43 | 70 | 79 | 32.0 | – |

^a $\gamma^{25^\circ\text{C}}$, the surface tension of modified products at 25°C.

^b $\eta^{25^\circ\text{C}}$, is viscosity of mixture of the product of polysiloxane modified with polyether and foaming liquid with the weight ratio 1 : 1 (2#, 750 rpm).

^c Without adding any antifoam sample.

but when shaken for 100 strokes, the order of T^{100} is: HPS2-P1 < HPS2-P2 < HPS2-P3 < HPS2-G01 < blank experiment < HPS2. It shows that HPS modified with fluoroalkyl has only excellent initial breaking foam performance, but when continuously shaken, the breaking foam speed decreases obviously. On the contrary, the product of HPS modified with different polyethers can keep excellent breaking foam performance for a long period, but the ability of initial breaking foam is not so good. And polysiloxane HPS2 almost has no foam controlling performance in the system because HPS2 is soluble in foaming system, and becomes “surface-active agent.”

Among products modified with three different polyethers, HPS2-P1 has better breaking foam performance than two others, HPS2-P2 and HPS2-P3. Viscosity of HPS2-P1, HPS2-P2, and HPS2-P3 in foaming liquid is gradually increasing with the increase of the content of ethylene epoxide in polyether. And HPS2-G01 has the lowest surface tension among four modified products HPS2-P1, HPS2-P2, HPS2-P3, and HPS2-G01. But surface tensions of all

modified products are lower than that of mixture of diesel and mobile fuel.

To combine the advantage of HPS2-P and HPS2-G01 into one product, HPS2 was modified with polyethers and fluoroalkyl in different molar ratios. From Table II, it is very clear that modified product HPS2-P1-G01 has better initial breaking foam performance and inhibiting foam performance than HPS2-P2-G01 and HPS2-P3-G01 with polyether and G01 having same molar ratio. It is possible that polyoxyethylene chain in P2 and P3 changes the dispersing state of modified products and size of dispersed particle. Propylene epoxide chain in P1 make it be more compatible with foaming media, thus HPS2-P1-G01 can be kept in suitable range of particle size. When changing the molar ratio between P1 and G01, HPS2-P1-G01 has the best foam controlling performance and fastest breaking foam speed with the molar ratio $n(\text{P1}) : n(\text{G01})$ being 3 : 7. And surface tension of modified polysiloxane with same polyether and G01 is decreasing with the increasing of content of G01 in modified product (Table II).

TABLE II
Antifoaming Performance of HPS2 Modified with Both Different Polyethers and G01

| | V^{20} (mL) | T^{20} (s) | V^{100} (mL) | T^{100} (s) | $\gamma^{25^\circ\text{C}}$ (mN·m ⁻¹) ^a |
|-----------------------------------|---------------|--------------|----------------|---------------|----------------------------------------------------------------|
| HPS2-P1-G01 (10 : 0) ^b | 62 | 25 | 64 | 28 | 24.9 |
| HPS2-P1-G01 (7 : 3) | 65 | 28 | 65 | 34 | 24.8 |
| HPS2-P1-G01 (5 : 5) | 64 | 27 | 62 | 31 | 23.7 |
| HPS2-P1-G01 (3 : 7) | 62 | 23 | 59 | 27 | 22.5 |
| HPS2-P1-G01 (0 : 10) | 52 | 19 | 53 | 51 | 21.8 |
| HPS2-P2-G01 (10 : 0) | 65 | 32 | 63 | 40 | 25.7 |
| HPS2-P2-G01 (7 : 3) | 64 | 56 | 67 | 61 | 24.3 |
| HPS2-P2-G01 (5 : 5) | 57 | 29 | 64 | 50 | 23.4 |
| HPS2-P2-G01 (3 : 7) | 58 | 36 | 64 | 40 | 22.3 |
| HPS2-P2-G01 (0 : 10) | 52 | 19 | 53 | 51 | 21.8 |
| HPS2-P3-G01 (10 : 0) | 65 | 35 | 62 | 43 | 25.5 |
| HPS2-P3-G01 (7 : 3) | 60 | 37 | 65 | 48 | 24.5 |
| HPS2-P3-G01 (5 : 5) | 63 | 40 | 62 | 45 | 23.4 |
| HPS2-P3-G01 (3 : 7) | 57 | 48 | 67 | 80 | 22.2 |
| HPS2-P3-G01 (0 : 10) | 52 | 19 | 53 | 51 | 21.8 |

^a $\gamma^{25^\circ\text{C}}$ is the surface tension of modified products at 25°C.

^b 10 : 0 is the molar ratio between of P1 and G01.

TABLE III
Antifoaming Performances of Different HPS Modified with Both Polyether and Fluoroalkyl

| | V^{20} (mL) | T^{20} (s) | V^{100} (mL) | T^{100} (s) | $\gamma^{25^\circ\text{C}}$ (mN · m ⁻¹) |
|--------------------------|------------------|-----------------|-------------------|------------------|--------------------------------------------------------|
| HPS1-P1-G01 ^a | 62 | 21 | 56 | 23 | 22.0 |
| HPS2-P1-G01 | 62 | 23 | 59 | 27 | 21.8 |
| HPS3-P1-G01 | 60 | 43 | 63 | 48 | 21.9 |
| HPS1-P1-G01 | 62 | 21 | 56 | 23 | 22.0 |
| HPS4-P1-G01 | 65 | 30 | 62 | 26 | 22.1 |
| HPS5-P1-G01 | 65 | 35 | 63 | 32 | 22.0 |
| HPS1-P1-G00 | 69 | 43 | 59 | 28 | 22.5 |
| HPS1-P1-G01 | 62 | 21 | 56 | 23 | 22.0 |
| HPS1-P1-G02 | 66 | 31 | 57 | 18 | 19.6 |

^a Molar ratio between P1 and fluoroalkyl is 3 : 7 in all modified products, and same for others.

Viscosity is one of important factors for antifoam having good antifoaming performance.^{18,19} As shown in Table III, the hydrogen content was fixed, and the viscosity of HPS was changed only, from 60 mPa · s (HPS2) to 40 mPa · s (HPS1) and 100 mPa · s (HPS3), respectively. It is possible that low viscous modified product is easily dispersed; modified product of HPS1-P1-G01 (3 : 7, molar ratio) has both better breaking foam speed and inhibiting foam performance than other two. It indicates that dispersing performance of antifoam is very important. But there is no significant change for surface tension of modified products as the viscosity of HPS changes.

Hydrogen content is another important factor for HPS. And the viscosity of HPS was set being 40 mPa · s, and the hydrogen content (H%) of HPS1 was chosen to be 0.18%, the H% of HPS4 being 0.30%, H% of HPS5 being 0.50%, respectively. As shown in Table III, with the H% changing from 0.18% to 0.50%, the value of V^{20} , T^{20} , V^{100} , and T^{100} is growing regularly, and breaking and inhibiting foam performance of HPS1-P1-G01 is better than that of HPS4-P1-G01 and HPS5-P1-G01. There is also no significant change for surface tension of modified products with the change of hydrogen content in polysiloxane.

Length of fluoroalkyl has an effect on antifoaming performance in fluorine-containing polysiloxane.²⁰ As in Table III, G01 was replaced with 2,2,2-trifluoroethyl acrylate (G00) and dodecafluorobutyl acrylate (G02), antifoaming performance of modified products were also tested. From this Table, it can be seen that modified product HPS1-P1-G02 has the best antifoaming performance among them, because of G02 having the longest fluorine-carbon chain, and HPS1-P1-G02 having the lowest surface tension. Therefore, antifoaming performance is related with surface tension of antifoam.

To conclude, the products of HPS modified with both polyethers and fluoroalkyls (HPS-P-F) have com-

mon advantage of polysiloxane modified with two modifying groups, respectively. And it has good foam breaking ability and excellent foam controlling performance (Tables I and II). Meanwhile, the cost of polysiloxane modified with fluoroalkyl as antifoam can be reduced. Dispersing property is also an important factor if antifoam will have good antifoaming performance (Table III). Besides, there are some relationships between antifoam performance and surface tension of modified products (Tables II and III).

Mechanism of antifoam exhaust in oil-based system is also not so clear. The change of surface tension of foaming liquid added antifoam between initially added with modified polysiloxane and after testing antifoaming performance was studied, as in Table IV, the surface tension $\gamma^{25^\circ\text{C}}$ of the mixture of diesel and mobile fuel is about 32 mN · m⁻¹ without any antifoam added, and the surface tension of synthesized PS-MPF is tested in Tables I-III. After the antifoam sample was added into the foaming liquid, the surface tension of foaming liquid became lower than 32 mN · m⁻¹. However, when retesting surface tension of foaming liquid after test PS-MPF breaking foam, the value became higher again, as shown in Table IV. Antifoam exist in three forms in foaming liquid: antifoam globules dispersed in foaming liquid, very thin spreading oil, and lenses floating on the solution surface.¹⁸ It is possible that before shaking test there are some spreading oils and lenses shown on the surface of foaming liquid helping break foam, but only part of them exist on the surface after shaking test. Therefore, the surface tension slightly increases again and breaking and inhibiting foam performance fell.

TABLE IV
Surface Tension of Mixture of Foaming Liquid Between Initially Added with Antifoam and After Test Antifoaming Performance

| | $\gamma^{25^\circ\text{C}(1)}$ (mN · m ⁻¹) | $\gamma^{25^\circ\text{C}(2)}$ (mN · m ⁻¹) |
|----------------------|--------------------------------------------------------|--------------------------------------------------------|
| HPS2-P1-G01 (10 : 0) | 31.4 | 31.7 |
| HPS2-P1-G01 (7 : 3) | 31.0 | 31.2 |
| HPS2-P1-G01 (5 : 5) | 30.7 | 31.1 |
| HPS2-P1-G01 (3 : 7) | 30.0 | 30.3 |
| HPS2-P1-G01 (0 : 10) | 27.8 | 28.0 |
| HPS2-P2-G01 (10 : 0) | 29.1 | 29.5 |
| HPS2-P2-G01 (7 : 3) | 28.7 | 29.9 |
| HPS2-P2-G01 (5 : 5) | 28.9 | 28.9 |
| HPS2-P2-G01 (3 : 7) | 28.7 | 28.8 |
| HPS2-P2-G01 (0 : 10) | 27.8 | 28.0 |
| HPS2-P3-G01 (10 : 0) | 28.6 | 30.0 |
| HPS2-P3-G01 (7 : 3) | 28.7 | 29.3 |
| HPS2-P3-G01 (5 : 5) | 28.5 | 29.7 |
| HPS2-P3-G01 (3 : 7) | 28.4 | 28.9 |
| HPS2-P3-G01 (0 : 10) | 27.8 | 28.0 |

$\gamma^{25^\circ\text{C}(1)}$ and $\gamma^{25^\circ\text{C}(2)}$ are the surface tension of foaming liquid between initially added with antifoam and after test antifoaming performance, respectively.

CONCLUSION

A series of polysiloxanes modified with fluoroalkyls and polyethers with different molar ratios were synthesized. Antifoaming performance of such modified polysiloxanes in the mixture of diesel and mobile fuel was studied. Results show that polysiloxane modified with polyether and fluoroalkyl has advantage of polysiloxane modified with two modifying groups, respectively. That is, modified product has fast breaking foam speed and good foam controlling performance. Meanwhile, it lowers the cost of polysiloxane modified with fluoroalkyl only acting as antifoam. The change of surface tension of foaming medium in the course of test is one reason for antifoam exhaust, which provides reference for choosing suitable antifoam for oil-based systems.

This project (0701023C) was supported by the Postdoctoral Science Foundation of Jiangsu Province.

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