

Preparation and Characterization of Lithium Grease Using 9, 10-dioxystearic Acid

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This paper aims to find a desirable new thickener for producing lithium grease. To this end, a lithium grease was prepared using self-made 9,10-dihydroxystearic acid (DHSALi) as the thickener. Then, the properties of the DHSALi-based grease were compared with the traditional lithium grease prepared from 12-hydroxystearic acid (HSA). Additionally, the differences between the two greases were discussed considering molecular structure and grease-oil gel dispersion. The results show that the DHSALi-based grease outperformed the traditional grease in terms of shear stability, consistency, dropping point, colloidal stability, wear resistance and antifricition property, despite its poor shear stability. The research proves that DHSALi is a desirable raw material of grease thickener.

1. Introduction

With more hydroxyl groups than monohydroxy stearic acid, polyhydroxy stearic acid is a highly polarized reagent capable of producing numerous types of chemicals. This acid features strong seepage force weak foaming ability and high viscosity (Li, 1993). It can be applied to wider areas than monohydroxy stearic acid, including metal working, surfactant production and the cosmetics industry (Kawashima and Li, 1992; Mohapatra et al., 2016).

In particular, polyhydroxy stearic acid has attracted much attention in the field of lubrication, thanks to its excellent resistance to wear and friction and its environmental-friendliness. Taking 12-hydroxy stearic acid (HSA) as the additive, Okable et al., (1990) observed the surface of frictional pairs using infrared reflection, discovered the formation of a polyester film by the acid, and suggested that the film enhanced the lubrication property. Hu (2001, 2002) synthesized stearic acids with different hydroxyl groups and investigated their resistances to wear and friction by adding them to liquid paraffin. Zhang et al., (1998, 1999) proved the anti-wear effects of two hydroxy stearic acids in ester oil under extreme pressure. Yang et al., (2005) created 9, 10-dihydroxystearic acid (DHSALi) and explored its lubrication property in castor oil, aiming to disclose the relation between chemical structure and lubrication property. The results show that the anti-wear, anti-friction and extreme pressure properties of oil products can be improved by using polyhydroxy stearic acid as an additive. However, polyhydroxy stearic acid has rarely been applied as a thickening agent in grease. Currently, the most popular multi-effect lubrication product is lithium grease (Zhu and Li, 2011), which is traditionally made from base oils thickened with lithium soap. The reactions include the reaction between the HSA and monohydroxy stearic acid and lithium hydroxide saponification (Zhu, 2015). The HSA shares similar molecular structure and physicochemical properties with the DHSALi. Both provide a lot of hydroxy groups that promote the formation of hydrogen bonds (He et al., 2009) between the molecules in the lithium soap. In this way, the soap fibre structure is enhanced, resulting in a greater packing capacity of the base oil. The previous studies have shown that the base oil can be thickened into grease by the DHSALi lithium soap (DHSALi).

Considering the above, the DHSALi is selected here as the raw material of the lithium soap used to thicken the base oil, and the properties of DHSALi-based grease are compared with those of the traditional lithium grease prepared using the HSA lithium soap (HSALi). Then, the mechanism of DHSALi was discussed in details.

2. Experiments

2.1 Materials

The materials for our experiments are as follows: HSALi; lithium hydroxide monohydrate (LiOH·H₂O) (AR); ethanol (AR); petroleum ether (boiling range: 60°C~90°C, 90°C~120°C); HSA (acid value: 172mgKOH/g; hydroxyl value: 145mgKOH/g; saponification value: 178mgKOH/g); DHSALi (acid value: 168mgKOH/g; hydroxyl value: 301mgKOH/g; saponification value: 169mgKOH/g); lithium hydroxide monohydrate (LiOH·H₂O) (AR); base oils: PAO25, MVI500, 200DN, dioctyl sebacate (DOS) and trimethylolpropane (TMP) ester; GCr15 four-ball steel roller mill (Diameter: 12.7mm).

2.2 Lithium grease-making through direct saponification (Direct saponification method)

The HSALi-based grease was prepared directly through saponification. First, the HSA was prepared by adding stearic acid into a specified amount of base oil and stirring and heating the mixture to about 80~100°C till the acid was fully dissolved in the base oil. Next, the lithium hydroxide solution was diluted to the concentration of $m(\text{LiOH}):m(\text{water})=1:6.7$ and maintained at 100°C~110°C for 2h to ensure complete saponification. After full saponification, the solution was heated to about 150~170°C and maintained for 30min to remove the additional water. Then, a specified amount of base oil was added again to dilute the soap base and heated up to about 200~220°C. The soap and oil mixture formed a real solution through high-temperature refining. After that, a specified amount of base oil was added quickly for quenching and the temperature was decreased to 170~180°C, followed by a 5min-long stirring at a constant temperature. Subsequently, the mixture was cooled to room temperature and turned into grease on the four-ball steel roller mill.

2.3 Lithium grease-making with prefabricated soap (Prefabricated soap method)

The DHSALi-based grease was prepared in two phases. In the first phase, 100g DHSALi was mixed with 250mL distilled water and heated to 92~95°C, forming an oil solution. Then, 12.68g LiOH·H₂O was dissolved in warm water and slowly added into the DHSALi water mixture. After that, the mixture was heated and stirred to about 95~100°C and maintained for 1h to ensure complete saponification. Next, the mixture was heated for another 1h to remove the distilled water, leaving a white semi-solid paste. The paste was relocated to a vacuum oven and dried for 30h at 65°C. The dried paste was grounded into white solid powders for further use.

In the second phase, a specified amount of base oil and the white solid powders were added into a reaction kettle. During the addition, the mixture was heated and stirred. Then, the mixture was slowly heated to 200~220°C for 40min to form a real solution, and the solution was puffed for 5min in the same temperature range. After that, a specified amount of base oil was added to quench the solution to 170~180°C with stirring. The temperature was held for 5min before the mixture was cooled naturally to room temperature. Finally, the mixture was turned into grease using the four-ball steel roller mill.

2.4 Characterization

The HSALi and DHSALi powders were characterized by a 557-type Fourier transform infrared spectrometer (FT-IR) (Perkin Elmer) at the resolution of 4cm⁻¹ and wavelength of 400~4,000cm⁻¹. The thermal properties were tested by an SDT-Q600 differential scanning calorimetry and thermogravimetry (DSC-TG) thermal analyser in nitrogen atmosphere at the flow rate of 100mL/min, heating rate of 10°C/min, and heating range of 25~500°C. The contact angle between the base oil and the soap was measured by a DSA100E contact angle meter (Kruss), whose measuring range is 0~180°.

According to the Petroleum Products and Hydrocarbon Solvents: Determination of Aniline Point and Mixed Aniline Point (GB/T 262-2010), a BF-68A aniline point tester (North Dalian), whose temperature falls between the room temperature and 170°C, was used to measure the aniline point of base oil. Considering the fibrous structure of the soap, an S-4800 scanning electron microscope (SEM) (Hitachi) was employed to observe the fibre morphology at the operating voltage of 20kV. The testing standards for grease property characterization are listed in Table 1.

Table 1: Grease testing standards

Items	Test method
Operating cone penetration (0.1 mm), Dropping point(°C)	GB/T 269-1991, GB/T 3498-2008
Shear stability, Oil separation rate of steel mesh (%)	SH/T 0122-2004, SH/T 0324-1992
Wear-resistant property, Extreme pressure property	SH/T 0204-1992, GB/T 3142-1982

3. Results and Discussion

3.1 Characterization of HSALi and DHSALi

The FT-IR spectra of HSA and HSALi are displayed in Figure 1 and those of DHSA and DHSALi are presented in Figure 2. As shown in Figure 1, the characteristic peak of -COOH at $1,698\text{cm}^{-1}$ was absent in the spectrogram of the HSA, while two obvious absorption peaks appeared at $1,581\text{cm}^{-1}$ and $1,559\text{cm}^{-1}$. The absence of the $1,698\text{cm}^{-1}$ peak is the result of the homogenization of C=O and C-O on the carbonyl group after the replacement of H^+ ion in -COOH with Li^+ ; the emergence of the $1,581\text{cm}^{-1}$ and $1,559\text{cm}^{-1}$ peaks are attributable to the dissymmetrical and symmetrical stretching vibrations (Luo et al., 2007) of -COO- . As shown in Figure 2, the characteristic peak of the DHSA at $1,709\text{cm}^{-1}$ shifted to $1,564\text{cm}^{-1}$, and two characteristic peaks appeared at $1,443\text{cm}^{-1}$ due to the dissymmetrical and symmetrical stretching vibrations of -COO- . The shape and location of any other peak were not changed at all. Hence, the HSALi and DHSALi were successfully prepared with accurate structures.

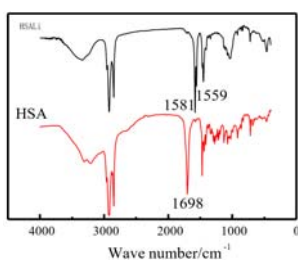


Figure 1: FT-IR spectra of HSA and HSALi

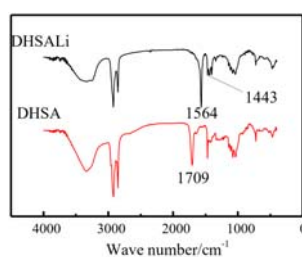


Figure 2: FT-IR spectra of DHSA and DHSALi

3.2 Compatibility of base oil and DHSALi

The HSALi and DHSALi were prepared by thickening the base oils (TMP, 200DN, DOS, PAO25 and MVI500) with 12% mass fraction of thickener through the said direct saponification method and the prefabricated soap method. In this subsection, the compatibility between base oil and DHSA is contrasted with that between base oil and HSA. The comparison results show that the HSALi boasted a stronger thickening capacity than the DHSALi, regardless of the method of lithium grease-making. The DHSALi thickening method only produced lithium grease when the base oil was DOS and TMP. Moreover, lithium grease was successfully obtained with the formula that formed real solution through high-temperature refining, while no grease was produced with the formulas that led to the stratification of the thickener and base oil. Hence, the key to the formation of lithium grease lies in the formation of real solution through high-temperature refinement.

The “similar compatibility” principle suggests that the solubility of a base oil in the thickener depends on its polarity. Among the five base oils, 200DN is a naphthene-based oil that involves cyclic hydrocarbons and aromatic hydrocarbons; MVI500 is a paraffin-based oil dominated by alkane; PAO25 is a synthetic hydrocarbon-based oil; DOS and TMP are synthetic ester-based oils. The ester-based oils have the strongest polarity, followed in descending order by the naphthene-based oil, the paraffin-based oil and the synthetic hydrocarbon-based oil. This ranking is demonstrated in the level of aniline point in Figure 3. The polarity of a base oil is negatively correlated with the level of aniline point.

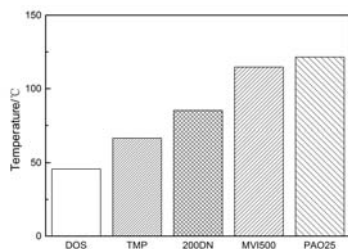


Figure 3: Level of aniline point

Figure 4 compares the contact angle between DHSALi and different base oils. This angle reflects the wettability and affinity of the thickener to the base oil. Owing to its high molecular polarity, the DHSALi was less soluble in the base oils with a weak polarity, such as naphthene-based, paraffine-based and synthetic hydrocarbon-based oils. In these oils, colloidal sol was not formed due to the uneven distribution of soap

molecules after high-temperature refining, and precipitates accumulated at the bottom in subsequent natural cooling. Thus, it is impossible to complete the transition from the colloidal state to the gel state, not to mention the generation of DHSALi-based grease. By contrast, the DHSALi was resolved well in ester-based oil, which has a strong polarity. During the process, the thickener was dispersed evenly in the base oil, forming a colloidal sol system, and eventually converted into lithium grease.

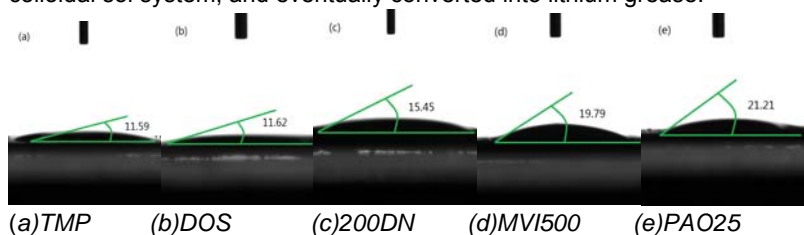


Figure 4: Contact angle between DHSALi and different base oils

3.3 Grease making and the screening of ester-based oil.

Through the above analysis, the DOS was selected as the base oil to prepare the lithium grease with 12% of DHSALi through the prescribed direct saponification method and prefabricated soap method. As shown in Figure 5 and Table 2, the lithium grease prepared through the prefabricated soap method possessed excellent properties, while that prepared through direct saponification featured poor consistence and stability. This is because the grease properties are negatively affected by the DOS hydrolysis in direct saponification.

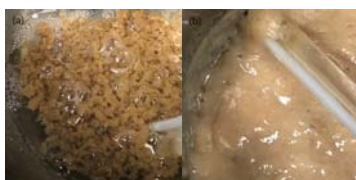


Figure 5: DHSALi-based lithium greases produced (a) direct saponification method (b) prefabricated soap method

Table 2: Basic physical-mechanical properties of lithium greases produced by the two methods

Items	Direct saponification method	Prefabricated soap method
Operating cone penetration (0.1 mm),	251	219
Dropping point(°C)	223	219
Oil separation rate of steel mesh (%)	1.69	0.50

Subsequently, the soap prefabrication method was selected for preparing lithium grease with 12% thickener, and DOS and TMP were used as the base oil to investigate the properties of the grease prepared. As shown in Table 3, the grease prepared by using DOS as the base oil possesses excellent properties. Hence, the prefabricated soap method was determined as the better way of lithium grease-making. To further investigate the grease properties, this method was adopted to produce lithium grease with 12% thickener using DOS and TMP as the base oils. As can be seen from Table 3, the lithium grease produced by DOS enjoyed better basic physical-chemical properties.

Table 3: Basic physical-mechanical properties of lithium greases produced by different base oil

Items	DOS	TMP
Operating cone penetration (0.1 mm), Dropping point(°C)	219, 219	257, 213
Oil separation rate of steel mesh (%)	0.50	1.29

3.4 Properties and mechanism of lithium grease-making using HSALi and DHSALi

Lithium greases with 6%, 8%, 10% and 12% thickener were prepared by prefabricated soap method using HSALi/DHSALi as the thickener and DOS as the base oil. The fibrous structure of the lithium grease with 12% thickener is illustrated in the SEM image in Figure 6. It is observed that the DHSALi-based grease exceeded the HSALi-based grease in fibre length, thickness, connections and clustering effect. The fibre length was 2~5nm for both greases, but the fibre diameter was 0.3~0.35nm for DHSALi-based grease and 0.02~0.05nm

for HSALi-based grease. A possible explanation lies in the numerous hydrogen bonds formed by the hydroxyl group on the DHSALi molecule, which brings about lots of fissures between adjacent grease molecules and an increase in the volume of fibres.

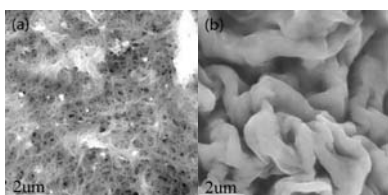


Figure 6: SEM images of the fibrous structure of the lithium greases produced by (a) HSALi and (b) DHSALi

Figure 7 describes the effect of different thickener contents on cone penetration, dropping point, and oil separation. As shown in Figure 9(a)~(b), the DHSALi-based grease had a smaller cone penetration but a higher dropping point, that is, melting point, than the HSALi-based grease. The dropping point difference was about $7^{\circ}\text{C}\sim 26^{\circ}\text{C}$. This means the dropping point of the lithium grease depends on the phase inversion temperature of the thickener. Considering the fibre structure, the DHSALi holds more adsorption oil and puffing oil than HSALi, thanks to its long, thick and wrinkled surface fibres. That is why the grease formed by DHSALi enjoys better consistency than that formed by HSALi. Comparatively, it takes more energy to separate the adsorbed oil from the fibre structure of DHSALi-based lithium grease. It can be seen from Figure 9(c) that the DHSALi-based grease lagged behind the HSALi-based grease in oil separation rate. This is attributable to the long, thick and wrinkled surface fibres of DHSALi-based grease, which increases the amount of absorbed oil and reduces that of free oil and ensures good colloidal stability. However, the presence of a certain number of fibres limits the function of the wrinkles and narrows the gap in the proportions of adsorbed and free oils between the greases produced by HSALi and DHSALi. As a result, the two greases have similar low oil separation rates.

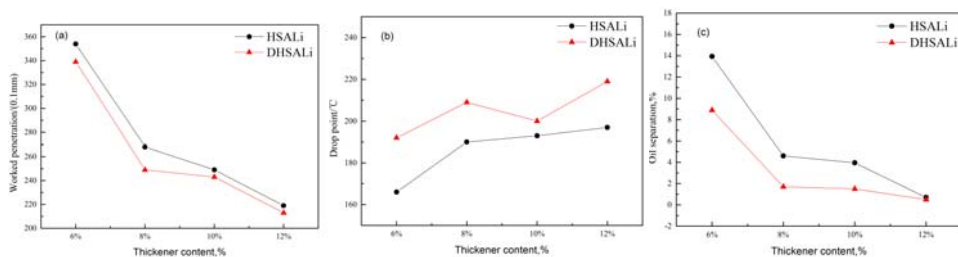


Figure 7: Effects of HSALi and DHSALi concentration on (a) cone penetration, (b) dropping point and (c) oil separation rate of lithium grease

Figure 8 compares the shear stability of the lithium greases prepared with 12% of HSALi and DHSALi. It is clear that the cone penetration of DHSALi-based grease changed by 51.60% through shearing, while that of HSALi-based grease changed by 22.07%. Because the DHSALi-based grease has a smaller aspect ratio than the HSALi-based grease, its fibres are more likely to be cut off under the external force. Once the fibres are broken, the adsorbed oil will be released, pushing up the free oil content and lowering the grease consistency. What is worse, the fibres of the DHSALi-based grease fail to form a tight and even 3D structure, adding to the degree of scattering under the external force. As a result, DHSALi-based grease is less likely to maintain the original structure of the colloid structure or good shearing stability than the HSALi-based grease.

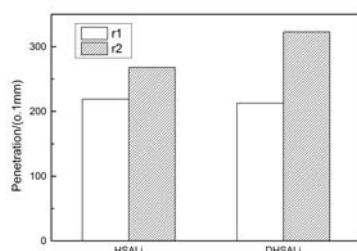


Figure 8: Shear stabilities of lithium greases with different thickeners

Figures 9 and 10 show the wear resistance, antifriction property and extreme performance of lithium greases prepared with 12% HSALi and DHSALi.

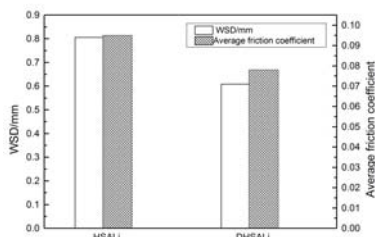


Figure 9: Wear resistances and antifriction properties of lithium greases made of different thickeners

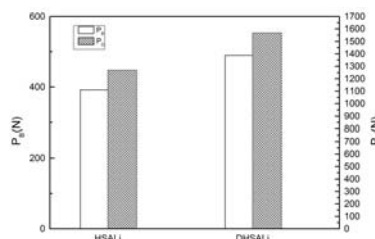


Figure 10: Extreme pressure properties of lithium greases made of different thickeners

4. Conclusions

This paper prepares a lithium grease (dropping point: 219°C) with DHSALi as the thickener. Compared to HSALi-based grease, the DHSALi-based grease achieves good stability at high temperatures, excellent consistency, good colloidal stability, and desirable results on wear resistance, antifriction property and extreme pressure performance. Nevertheless, DHSALi-based grease had poorer shear stability than HSALi-based grease, owing to its shape differences from the latter. The research proves that DHSALi is a desirable raw material of grease thickener.

Acknowledgments

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