Influences of Saponification Time on the Physical Properties of Mineral Oil-Based Magnetorheological Grease

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Abstract: This study was conducted to investigate the influences of saponification time on the physical properties of mineral oil-based magnetorheological greases (MRGs). Three types of mineral oil-based MRG were prepared by applying different saponification time in this work. Then the physical properties, thermal stability and colloidal performance were tested. Besides, the micro-morphology was observed to analyze the microstructures of MRGs. The experimental results prove the formation of entanglement soap fibers micro-network. The oil separation on pressure and worked penetration of MRG decrease with the increase of saponification time, while the centrifugal stability becomes better. DSC-TG-DTG tests exhibit three endothermic peaks and reveal a double-stage thermal decomposition process. It also indicates that the MRG under 2 hours saponification has the smallest thermal decomposition and highest decomposition temperature, which demonstrates a good thermal stability.

1. Introduction

Magnetorheological greases (MRGs) are typically prepared by dispersing ferromagnetic particles in non-magnetic grease medium[1]. As well as magnetorheological fluids[2,3], due to the directional alignment and elongated aggregates of ferromagnetic particles under external magnetic field, MRGs manifest significant magnetorheological performances. This sudden and reversible viscosity conversion has attracted considerable interests in many scientific areas. Moreover, greases are generally highly structured suspensions with relatively high viscosity[4,5], which allows ferromagnetic particles to suspend stably and homogeneously, therefore, has much better suspension stability compared to typical magnetorheological fluid. Because of these unique characteristics, MRGs brings breakthrough progress in many industrial application areas, such as the aerospace industry, motor industry, and precise work.

The performance of MRG is not only related to its components, but also the microstructures. The structural skeletons of grease are typically formed during its preparation process[6,7], therefore, suitable structural and physical properties of MRG may be achieved from a process optimization. However, most of MRGs were prepared by directly mixing ferromagnetic particles into commercial greases nowadays[9-12], thus, the effects of processing on the microstructure and physical properties of MRGs were almost neglected. In this study, in order to verify the hypothesis that the physical properties and microstructures of MRGs can be modified by the preparation process, the effects of the saponification time on the physical properties, thermal properties and centrifugal stability of MRGs...
were tested. Meanwhile, the relationship between saponification time and microstructures were also studied which can probably explain the influences on macroscopical performances of MRGs by preparation process.

2. Materials and methods

2.1. Materials
12-Hydroxystearic acid and lithium hydroxide were selected as saponifying agents. Carbonyl iron (CI) particles, consist of more than 99.5% pure iron, with the mean diameter 3.5μm, were used as magnetic particles. All of those components are commercially available. The mineral oil HVI150 used as base oil was supplied by Yiping lubrication Oil Company, China.

2.2. Measurement and analysis method
MRGs were prepared in an open-atmospheric vessel using a controlled heat cover. The preparation method of MRG was described as follow: firstly, the total calculated number of 12-hydroxystearic acid and one third of total mineral oil were charged into an open vessel to manufacture 0.5 kg of lithium MRG. The mixture was continuously stirred and heated up to about 90°C, until all of 12-hydroxystearic acid was melt. Afterwards, lithium hydroxide solution was slowly added for about half an hour and the saponification reaction occurred under about 100°C ~120°C with the reaction times of 1 hour, 2 hours, 3 hours, respectively. Once the reaction finished, the mixture was continuously heated up to between 120°C ~140°C for another half an hour to dehydrate. Then, the mixture was diluted with the preheated another one third of mineral oil before the addition of carbonyl iron at the temperature of about 160°C. Once the addition of carbonyl iron was completed, it was heated up to a maximum temperature between 200°C to 210°C in order to make the 12-hydroxystearate completely melt. Afterwards, the remaining one third of mineral oil was added during a controlled cooling step over a period of about 20 minutes. Finally, after the room temperature was reached, a homogenization treatment was applied for three times. The final soap concentration of MRG was 7% (w/w).

The colloidal performance of MRG was determined using the universal penetrometer, drop point tester and oil separation on pressure tester according to the GB/T 269, GB/T 3498, GB/T 392, respectively. The centrifugal stability of MRGs was conducted by a high-speed centrifuge at 3520r min⁻¹. The thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) was performed using a SDT-Q600 model thermal analyzer (TA Company, America). The measurements were conducted at a constant heating rate 10°C min⁻¹ in a dynamic nitrogen atmosphere (flow rate 50 mL min⁻¹) in the temperature range from 25°C to 600°C. Microstructure morphology of soap fibers was observed at 15 kV with a S-3700N model scanning electron microscope (HITACHI, Japan). About 5 mg of each sample immersed in hexane was centrifuged for 5 minutes at the speed of 3250r min⁻¹ to extract the mineral oil. This operation was repeated several times until mineral oil was extract completely. Then, the sample was dried at room temperature. Finally, the micrographs were made at 5000 power magnification after the sample was coated with gold.

3. Results and discussion
Table 1 shows the colloidal performances of MRGs with different saponification time. The results reveal that the drop points of MRGs are almost the same as each other, but the worked penetration decreased obviously, which means a decreased viscosity with the increase of saponification time. It proves an increased consistency of MRGs and may suggest that stronger microstructures were established inside MRGs with the prolonging of saponification time. Moreover, the oil separation on pressure of MRGs under 2 hour-saponification is the lowest among all the samples. It indicates a better integrality of structure skeletons in 2 hour-saponification sample. More number of soap fibers were generated in 2 hour-saponification sample which leads to denser entanglement network, as a result, higher micro-structural strength was obtained.
Table 1. The effect of saponification time on the colloidal performances of mineral oil-based MRG

| Reaction time (h) | Drop point (°C) | Worked penetration (0.1mm) | Oil separation on pressure (%) |
|------------------|----------------|---------------------------|-------------------------------|
| 1                | 194            | 261.7                     | 12.28                         |
| 2                | 196            | 252.7                     | 11.84                         |
| 3                | 195            | 245.4                     | 11.86                         |

Figure 1 shows the centrifugal stability (sedimentation ratio vs. centrifuge time) of different saponification time samples. A decreasing tendency of sedimentation ratio can be observed, however unlike its analogue MRFs\[8\], the sharp decrease in sedimentation ratio at the beginning can not be observed in MRGs. It is a strong evidence that the soap fibers hinder the fast aggregation induced by polar attractions among ferromagnetic particles. Moreover, as shown in figure 1, the centrifugal stability of MRGs increases with the increase of saponification time. When the centrifugal time is less than 20s, the MRGs under 2 hour-saponification exhibit good centrifugal stability. However, with the centrifugal time increased (more than 60s), MRGs under 2 hour-saponification begin to stratify distinctly. This result prevents that the soap fiber microstructures inside MRGs are likely to imposes the gaps among ferromagnetic particles thus restricts the aggregation and sedimentation. However, these micro-skeletons will be broken under long-time centrifuge, as a result, MRGs begin to stratify and deposit.

Figure 2 shows the TG-DTG-DSC curves of MRGs degraded in N₂ atmosphere. Table 2 gathers the main characteristic parameters derived from the thermal analysis curves. As can be seen, DSC curves of MRGs exhibit three endothermic peaks at 208 (T₁), 320 °C ~340 °C (T₂) and 465 °C ~485 °C (T₃), respectively. Corresponding to TG curves, MRGs have almost no mass loss occurred at T₁ temperature, and T₁ is slightly larger than the drop point (Table 1). Therefore, the first endothermic peak(T₁) represents the point of lithium soap melting (main peak at about 208 °C). The higher endothermic peak temperature (T₂) corresponds to the maximum degraded mass loss as showed in the TG curves. Aforementioned results prove the thermal decomposition of MRGs in this range of temperature. The last endothermic peak(T₃) is corresponding to tiny mass loss in the TG curves, which may suggest the second-stage thermal decomposition of MRG as can be found in DTG curves.

As for the derivative function curves of TG(DTG curves in Fig. 2), two DTG peaks can be observed, one obvious peak between 330 °C ~340 °C and another weak peak between 465 °C ~475 °C. This result also prevents the double-stage decomposition process of MRGs. It is obvious that the first-
stage decomposition process is primary one, thus the maximum decomposition velocity and its peak temperature of this stage are listed in Table 2. The MRG under 2 hour-saponification shows the smallest decomposition but the highest decomposition temperature, which suggests a good thermal stability. Moreover, MRG under 2 hour-saponification shows the highest $T_{5\%}$ and $T_{50\%}$ in TG curves. $T_{5\%}$ represents the temperature that 5% thermal degradation occurs while $T_{50\%}$ denoting 50% degradation. This result may be another evidence for the great thermal stability of MRGs under 2 hour-saponification[13].

![Fig. 2. The DSC-TG curves of MRG with different saponification time](image)

| Reaction time (h) | TG | DTG | DSC |
|------------------|----|-----|-----|
| $T_{5\%}/^\circ C$ | $T_{50\%}/^\circ C$ | $T_p/^\circ C$ | $V_p/% \text{ min}^{-1}$ | $T_1/^\circ C$ | $T_2/^\circ C$ | $T_3/^\circ C$ |
| 1 | 260.9 | 344.2 | 334.4 | 8.525 | 208.9 | 337.0 | 478.8 |
| 2 | 261.1 | 348.8 | 339.2 | 7.577 | 208.4 | 337.1 | 481.2 |
| 3 | 260.5 | 346.8 | 336.4 | 7.629 | 208.9 | 338.3 | 469.9 |

Figure 3 shows the micromorphology of MRGs with different saponification time. Generally, the crystallized soap particles in MRGs, usually in the form of rods, platelets or fibers, arrange themselves to form a rather complex microstructure. Meanwhile, single soap particles tend to establish entanglement network among structure skeleton, and with the increase of saponification time, single soap particles seems to deplete and making microstructures stronger. Moreover, as previously mentioned, microstructures formed by soap particles restrict the direct connect thus impose the gaps among ferromagnetic particles, so that help ferromagnetic particles remaining homogeneous and stable dispersion in the MRGs. It may be the reason for the better centrifugal stability and thermal stability of MRGs under relatively long saponification time.
4. Conclusion

The influences of saponification time on physical property, centrifugal stability, thermal stability and microstructure of MRGs were studied in this work. The experimental results can be concluded that MRGs studied in this work are likely to form entanglement network among soap fibers and impose the gaps among ferromagnetic particles, as a result, these microstructures help ferromagnetic particles remaining homogeneous and stable dispersion. MRGs exhibit three endothermic peaks and a double-stage thermal decomposition process. Moreover, with the prolongation of saponification time, the oil separation on pressure and worked penetration of MRG decreases. The consistency of MRGs microstructures increase thus centrifugal stability becomes better, especially, the MRG under 2 hours-saponification shows a good thermal stability, compact entanglement structure and high physical performance.

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