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Influence of silicones surface activity on tribological properties their aqueous solutions

K e y - w o r d s

Friction coefficient, wear, ethoxylated and propoxylated organosilicone compounds.

S ł o w a k l u c z o w e

Współczynnik tarcia, zużycie, oksyetylenowane i oksypropylenowane związki krzemoorganiczne.

S u m m a r y

Aqueous solutions of ethoxylated silicones were tested in order to determine their tribological properties. The compounds varied by ethoxylation and propoxylation degrees. 1%, 4% and 10% solutions of the compounds with low ethoxy-propoxylation degree were used. The tests were performed using a four-ball machine T-02, produced by Institute for Sustainable Technologies in Radom. A significant influence of the silicones on anti-wear and anti-seizure properties of the lubricants tested was observed.

1. Introduction

Mineral oils are a standard base of lubricants. They do not satisfy, however, the strict conditions required from modern lubricants. They are not bio-degradable and are dangerous to natural environment and human beings. That is why one should aspire to replace petroleum derivatives by bio-degradable materials that could be obtained from renewable sources. In some cases water can be such a base. It is cheap, easily available, non-flammable and environmentally

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friendly. Its disadvantages are: corrosive effect, low viscosity, bad lubricity. These disadvantages can be minimized by introduction of proper additives. On the first stage chemical compounds of high surface activity that could improve lubricity are searched [1–20]. Literature data [21–25], as well as the preliminary tests [26], revealed that aqueous solutions of organosilicone compounds could be effective lubricants.

2. Structure and physical-chemical properties of silicones

Silicones are organosilicone polymers that contain oxosilane chain, built of alternant silicon and oxygen atoms. Moreover, there are various functional groups (methyl, phenyl, vinyl, alkoxyl, polyether) and atoms (i.e. hydrogen, chlorine, fluorine) attached to the silicon-oxygen skeleton. High-molecular organosilicone compounds bring together features of inorganic silicates and organic polymers. Silicone oils (also called polydimethylosiloxanes) belong to this group. First applications of silicone oils (methyl silicone, methyl phenyl silicone, methyl hydro-silicone, methyl chlorophenyl silicone, ethyl silicone, ethyl hydro-silicone) as lubricants were noted in the early 50s of 20th century. The silicones can be applied in a wide range of temperatures (-100–270°C). They have good anti-foaming properties, oxidation, chemical and UV resistance, low surface tension, neutrality to seals and lacquers. They also do not mix with other oils. The silicones dissolve badly in media that could be improved from the point of view of lubricity [21–25].

Physiological neutrality of organosilicone compounds is remarkably important when straight contact with human skin, respiratory or digestive system is possible. Because of no harmful effect on living organisms or environment these compounds can be used in food, pharmaceuticals, cosmetics and household chemistry products. Therefore they can also be used as lubricants in goods listed above.

Although silicone oils are hydrophobic, their character can be modified by substituting some of the methyl groups attached to silicon-oxygen chain by polyether groups (ethylene oxide and propylene oxide). Ethoxylated and propoxylated derivatives of organosilicone compounds are also known as polyetheric derivatives. They are classified as amphiphilic, non-ionic surfactants [27–30].

Three organosilicone compounds (manufactured by Deguss-Goldschmidt, INCI name – PEG/PPG – x/y Dimethicone), having various ethoxylation (x) and propoxylation (y) degrees were tested. The trademarks of the compounds are as follows: Abil 8843 (PEG/PPG – 14/0 Dimethicone), Abil 8851 (PEG/PPG – 14/4 Dimethicone), Abil 8852 (PEG/PPG – 4/12 Dimethicone). It should be emphasized that Abil 8843 molecule contains only ethylene oxide, without propylene oxide. The simplified structural formula of the compounds is shown in Fig. 1.

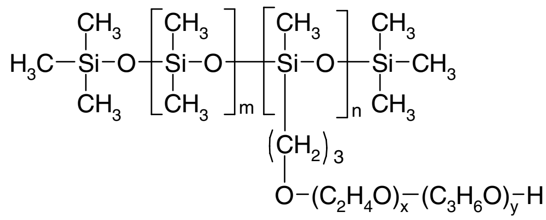

Fig. 1. Dimethicone of ethoxylation degree x and propoxylation degree y
Rys. 1. Wzór Dimethicone o stopniu oksyetylenowania x i oksypropylenowania y

The number of ethylene oxide molecules (x) attached improves hydrophillicity, while propylene oxide (y) can influence hydrophobicity. The ratio of ethylene oxide to propylene oxide conditions its solubility in polar and non-polar solvents. The above selection of compounds was dictated by their solubility in water and in some hydrophobic solvents as well as by their predicted surface activity [22–25].

3. Tribological properties of aqueous solutions of ethoxylated and propoxylated silicones

The tribological tests were performed using a four-ball machine produced by ITeE in Radom. The balls with diameter ½'' were made of bearing steel ŁH15, accuracy class 16 (roughness of the surface is R_a = 0,032μm, hardness 60÷65HRC). The apparatus and the methodology of the test have already been described [31–33].

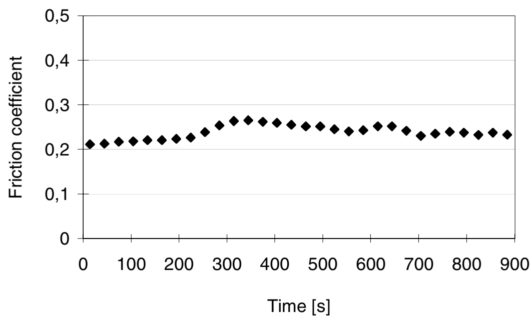

Fig. 2. Dependence of the friction coefficient on time in the presence of 10% aqueous solution of Dimethicone 14/4. Tester T02, load 2kN, rotating speed 200rpm, test duration 900 s
Rys. 2. Zależność współczynnika tarcia medium smarnego od czasu trwania testu w obecności 10-procentowego wodnego roztworu Dimethicone 14/4. Tester T02, obciążenie 2 kN, prędkość obrotowa 200 rpm, czas trwania testu 900 s

The tests were conducted under constant loads 2 and 4 kN, rotating speed of the spindle 200 rpm. The test duration was 900 s. An example of dependence of friction coefficient on time is presented in Fig. 2. The points on the graph are averages over 30-seconds time intervals. In Figs 3 and 4 additional averaging from three independent measurements was made.

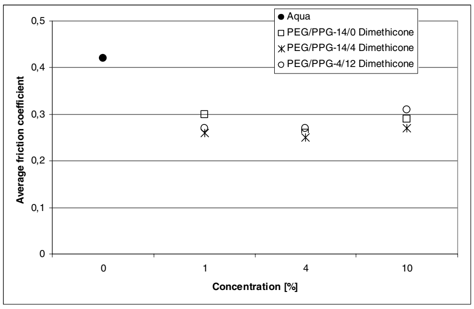

Fig.3. Dependence of average friction coefficient on concentration of the silicones with low ethoxy- and propoxylation degree. Tester T02, load 2kN, rotating speed 200rpm, test duration 900 s
Rys. 3. Zależność średniego współczynnika tarcia od stężenia związków krzemoorganicznych o niskim stopniu oksypropylenowania. Tester T02, obciążenie 2 kN, prędkość obrotowa 200 rpm, czas trwania testu 900 s

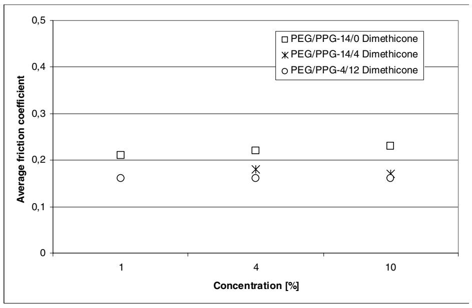

Fig. 4. Dependence of average friction coefficient on concentration of the silicones with low ethoxy- and propoxylation degree. Tester T02, load 4kN, rotating speed 200rpm, test duration 900 s
Rys. 4. Zależność średniego współczynnika tarcia od stężenia związków krzemoorganicznych o niskim stopniu oksypropylenowania. Tester T02, obciążenie 4 kN, prędkość obrotowa 200 rpm, czas trwania testu 900 s

Introduction of any silicone to water significantly reduces the friction coefficient – on average about 1.5-folds. The type of the silicone and its concentration only slightly influences the motion resistance. One can state that the smallest values of μ can be observed in 4% solutions (Fig. 3).

Under 4kN load seizure was observed in water and in 1% solution of Dimethicone14/4. The 4% and 10% solutions revealed similar course of the average friction coefficient and comparable motion resistance. The highest values of μ (increased even by 30% as compared to the remaining two compounds) were observed for Dimethicone 14/0. One should note that in the case of silicones which effectively prevented from seizure motion resistance was smaller under 4 kN, as compared to 2 kN.

After each test the wear scar diameters were measured in two directions: parallel and perpendicular to the movement. Then the averages were calculated. The measurements were performed using the reflecting microscope Polar, produced by PZO Warszawa (Poland). The values depicted in Figs 5 and 6 are arithmetic averages of three measurements.

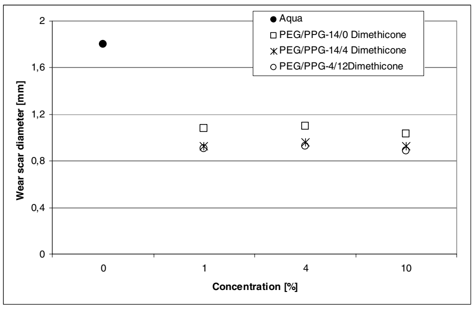

Fig. 5. Dependence of wear scar diameter on concentration of the silicones with low ethoxy- and propoxylation degree. Tester T02. load 2kN, rotating speed 200rpm, test duration 900 s

Rys. 5. Zależność średnicy skazy kulki od stężenia związków krzemoorganicznych o niskim stopniu oksypropylenowania. Tester T02, obciążenie 2 kN, prędkość obrotowa 200 rpm, czas trwania testu 900 s

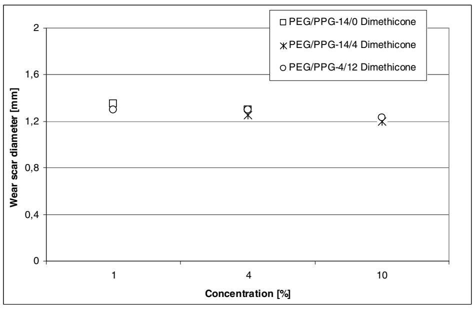

Fig. 6. Dependence of wear scar diameter on concentration of the silicones with low ethoxy- and propoxylation degree. Tester T02. load 4kN, rotating speed 200rpm, test duration 900 s

Rys. 6. Zależność średnicy skazy kulki od stężenia związków krzemoorganicznych o niskim stopniu oksypropylenowania. Tester T02, obciążenie 4 kN, prędkość obrotowa 200 rpm, czas trwania testu 900 s

The dependence of wear on concentration and type of compound is similar. Under 2 kN the wear scar diameter was considerably reduced (even 2-folds), as compared to water – Fig. 5. The highest wear can be observed for solutions of Dimethicone 14/0, but differences are not significant - about 14%, as compared to the remaining two additives.

The increase of load caused the increase of wear by approximately 20%. Under 4 kN wear only slightly depends on the type of compound. The differences do not exceed 10%. It should be mentioned that under this load wear for pure water was not measurable, as the system seized (Fig. 6).

The tests under constant loads 2 kN and 4kN reveal that the additives effectively reduce motion resistance, wear and prevent seizure. For the loads analyzed the influence of concentration and type of the compound was not noteworthy.

The profitable changes of tribological properties of the silicones tested can be explained by their high surface activity. That is why it was decided to assess surface tension and wettability of steel surface by the water solutions of ethoxylated and propoxylated silicones.

4. Surface activity of silicones solutions

Surface tension

To measure the surface tension a stalagmometric method was employed. Each point on the graph is an average of three measurements (Fig. 7). The test was performed in the temperature 22°C.

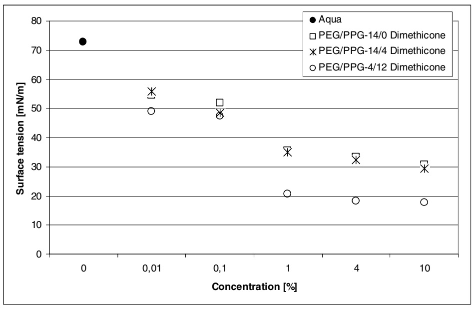

Fig. 7. Dependence of surface tension on concentration of the silicones with low ethoxy- and propoxylation degree. Temperature of the measurement 22°C
Rys. 7. Zależność napięcia powierzchniowego od stężenia związków krzemoorganicznych o niskim stopniu oksypropylenowania. Temperatura pomiaru 22°C

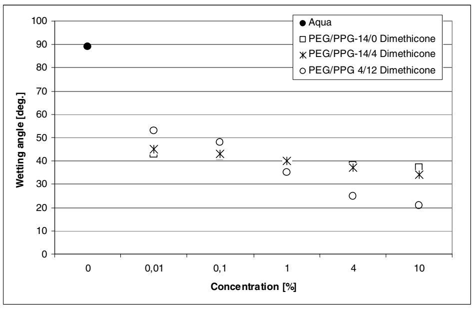

Fig. 8. Dependence of steel wetting angle on concentration of the silicones with low ethoxy- and propoxylation degree. Temperature of the measurement 22°C
Rys. 8. Zależność kąta zwilżania stali od stężenia związków krzemoorganicznych o niskim stopniu oksypropylenowania. Temperatura pomiaru 22°C

For the three solutions the surface tension (σ) is a decreasing function of concentration. The run can be divided into two intervals: from 0 to 1% and from 1% to 10%. In both intervals a linear decrease of σ was observed, but for lower concentrations the rate of decrease was quicker. The results were confirmed by the ring method (tensiometer TD1 Lauda). Therefore, one should expect that for concentrations about 1% micellar structures can turn up. As compared to water the surface tension changes are significant. The maximal value of σ is reduced even 4-folds. The lowest surface tension, as compared to water, was obtained for Dimethicone 4/12. This can be explained by higher hydrophobicity of this compound.

Wetting angle

The wetting angle of the steel surfaces by aqueous solutions of organosilicone compounds was measured using the sitting drop methodology. 0.01%, 0.1%, 1%, 4% and 10% water solutions were tested. The wetting angles in the graph are averages of three measurements (Fig. 8).

An addition of 0.01% solution of silicone caused 2-folds reduction of the wetting angle. Further increasing of the concentration (c>0.01%) affected in almost linear reduction of Θ. The slope of the line for Dimethicone 4/12 is smaller than for the two remaining solutions. The wetting angles of Dimethicone 14/0 and 14/4 are almost identical; they vary maximally by 8%. The increase of wettability of Dimethicone 4/12 is much stronger – the difference of the wetting angle between two terminal concentrations reaches up to 60%. The differences observed in wettability can be interpreted in terms of various hydrophobicities of the additives tested.

5. Discussion

In search of effective additives modifying lubricity of water derivatives of organosilicone compounds were chosen. The presence of ethylene oxide in the particle of silicone improves solubility in water while propylene oxide causes increase of hydrophobicity. The additives proposed can be classified to the group of amphiphilic compounds of high surface activity. This was confirmed by measurements of the surface tension and wetting angle. As a consequence of high affinity, a surface phase is formed in the interphase: liquid - solid. The surface phase varies from the bulk phase by composition and structure. During friction a lubricating film can be created. The film protects the cooperating surfaces from excessive wear and seizure. This reasoning was experimentally confirmed by significant decrease of motion resistance and wear in the presence of ethoxylated and propoxylated silicones, as compared to water.

The results are cognitive, because on the basis of the structure and surface activity of the compound they allow predicting changes in tribological properties which are a result of various phenomena that can occur in the friction zone. The results are a part of research that is aimed at application of aqueous solutions of the silicones as cutting fluids.

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Wpływ aktywności powierzchniowej silikonów na tribologiczne właściwości ich wodnych roztworów

S t r e s z c z e n i e

W pracy przedstawiono wyniki badań tribologicznych kompozycji smarowych, którymi były wodne roztwory etoksylatów silikonów. Związki te różniły się stopniem oksyetylenowania i oksypropylenowania. Do doświadczeń wykorzystano 1-, 4-, i 10-procentowe roztwory związków o niskim stopniu oksypropylenowania. Testy prowadzono na aparacie czterokulowym (T02), wyprodukowanym przez Instytut Technologii Eksploatacji w Radomiu. Stwierdzono znaczny wpływ pochodnych silikonu na właściwości przeciwzużyciowe i przeciwzatarciowe badanych substancji smarowych.