# Composition of plasmapolymeric coatings using O2/HMDSO gas mixtures and application on elastomers for tribological improvement

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The composition of plasmapolymeric coatings (SiOx) using O2/HMDSO gas mixtures in a plasma enhanced chemical vapour deposition (PECVD) process can be widely tailored varying the mixing ratio of the process gases as well as the applied power in the deposition process. This article demonstrates the changing properties of those coatings and its capability for reduction of friction regarding elastomers for the application on seals[1]. A reduced friction of sealing rings in an automobile realizes the reduction of CO2 emission due to energy saving.

On the one hand the deposition process was varied regarding the mixing ratio of the process gases oxygen (O2) and Hexamethyldisiloxan (HMDSO) from 1:5 to 18:1 as well as the applied power from 500 W to 1500 W. On the other hand the friction of three different types of elastomers plasmapolymeric coated as well as uncoated was investigated. These three substrate types were acrylic rubber (ACM), fluoric rubber (FKM/FPM), and nitrile rubber (NBR).

The studied coated and uncoated elastomers were tested as flat plates. The friction of elastomers was investigated using an Universal Material Tester (UMT3) system[2] with oscillating Pin-on-plate contact geometries (Figure 1). The tribological tests were done in ambient conditions with a velocity of 200 mm/s and a stroke length of 11 mm. The counterparts in the tribological tests were on the one hand a 440C steel ball with a diameter of 9.5 mm and on the other hand an end plane of a steel rolling bearing with diameter of 6 mm. In the case of the steel ball a normal force of 4.7 N was used. Using the rolling bearing a normal force of 10.6 N was applied. The used normal forces represent an initial Hertzian pressure of 1.5 MPa and 0.5 MPa, respectively.

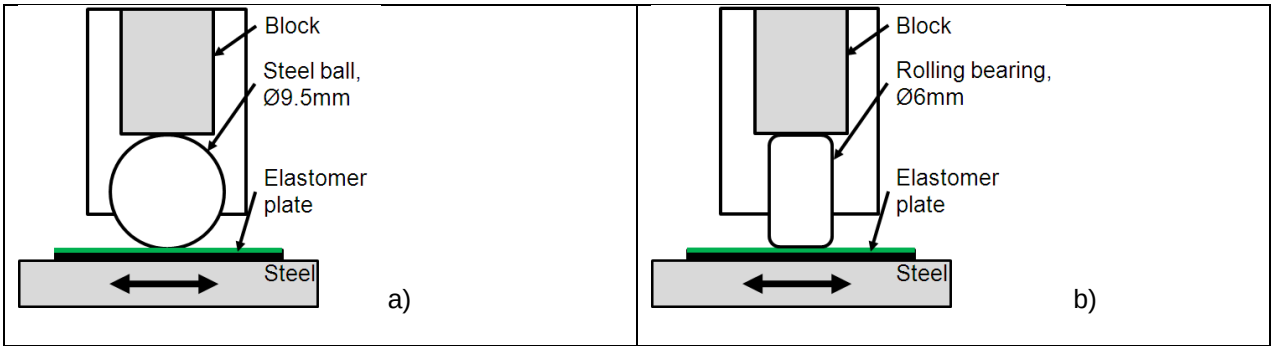



**Figure 1:** a) steel ball and b) steel pin in contact with coated or uncoated elastomer plate.

[1] Patent “Dichtungsartikel”: DE 10 2008 002 515 A1.
[2] Universal Material Tester (UMT3), Bruker formally Center for Tribology Inc., 1717 Dell Ave., Campbell, CA 95008

Determine the nanohardness and the Young's modulus of the coatings nanoindentation experiments were done. The force-indentation depth curves were evaluated using the model of Oliver and Pharr[3]. Investigating in the chemical composition mircoelementary analysis (µAnalyse[4]) techniques as well as IR spectroscopy (Bruker Equinox 55 spectrometer, detection angle 75 ° at IRRAS configuration, at least 32 scans, 4cm$^{-1}$ resolution) was used determining the bond configuration. The surface energy was calculated according to Wu[5].

The nanohardness of the coatings was tailored to slightly higher values to increase the wear resistance of the elastomeric substrates. As a result, it was found that the Young's modulus and the nanohardness of the plasmapolymeric coatings were increasing at increasing amount of $O_2$ content (Figure 2a). These mechanical properties saturated at higher $O_2$ contents due to a transition to a $SiO_2$ network.

The surface energy of the samples could be tailored varying the mixing ratio of the process gases in the deposition process (Figure 2b). The surface energy was increasing at increasing $O_2$ content as well as a decreasing amount of methyl groups (compare Figure 3).

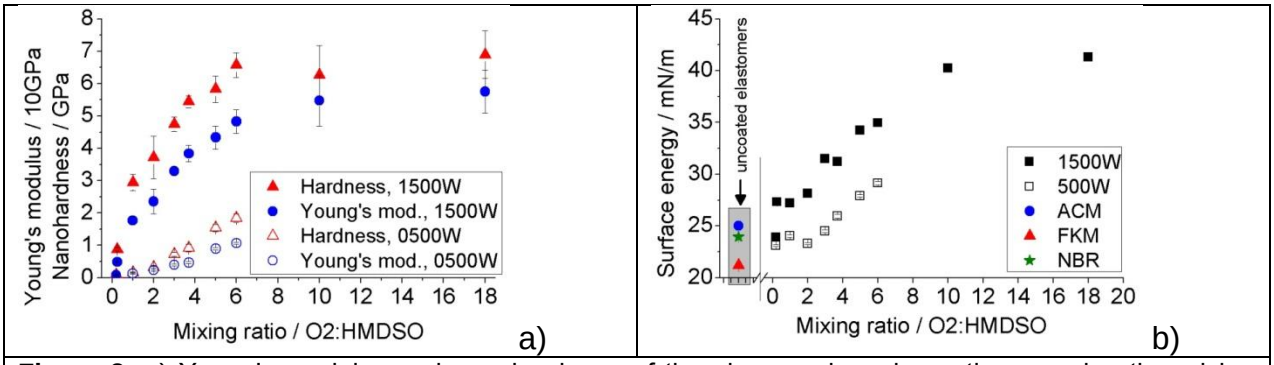



**Figure 2:** a) Young's modulus and nanohardness of the plasmapolymeric coatings varying the mixing ratio of the process gases. b) Surface energy of elastomeric substrates and plasmapolymeric coatings. The surface energy of the plasmapolymeric coating could be tailored varying the mixing ratio of the process gases.

Regarding the six methyl groups in the precursor HMDSO it was obvious to investigate in associated bonds. On the one hand the mass-% content of C as well as H was determined using µAnalyse. On the other hand the bond configuration was investigated using IR spectroscopy. It was found that the mass-% content of C as well as H was decreasing with increasing amount of $O_2$ content due to the decreasing amount of HMDSO content (Figure 3).

[3] W. C. Oliver, G. M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, J. Material Res. (1992) Vol. 7, No. 6, 1564-1583
[4] Mikroanalytisches Labor Pascher, An der Pulvermühle 1, 53424 Remagen
[5] S. Wu, Calculation of interfacial tension in polymer systems, Journal of Polymer Science Part C: Polymer Symposia (1971), Vol. 34, Issue 1, 19-30

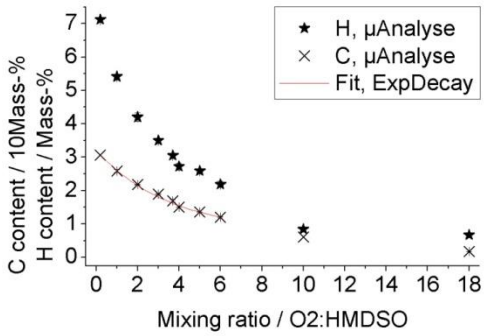



**Figure 3:** C as well as H content of the plasmapolymeric coatings. The contents can be tailored varying the mixing ratio of the process gases.

The determined IR spectra of each plasmapolymeric coating version are shown in Figure 4a. A pure HMDSO spectrum was determined using an ATR-crystal configuration additionally. In Figure 4b depicted peak positions are listed to demonstrate peak shifts. As a very brief conclusion regarding these spectras and all determined coating properties of the plasmapolymers above it is obvious that there was a smooth transition in the composition from polymer-like structure to $SiO_2$ network and furthermore a densification in the $SiO_2$ network.

The transition from polymer-like structure to $SiO_2$ network was observed regarding bonds of $CH_x$, $Si\text{-}CH_x$, and Si-O-Si. Due to missing Si-H bonds and the measured C as well as H content regarding the mixing ratio of the process gases it is obvious that the C and H was mainly bond as $CH_x$. Therewith the $CH_x$ content was decreasing increasing the amount of $O_2$ content.

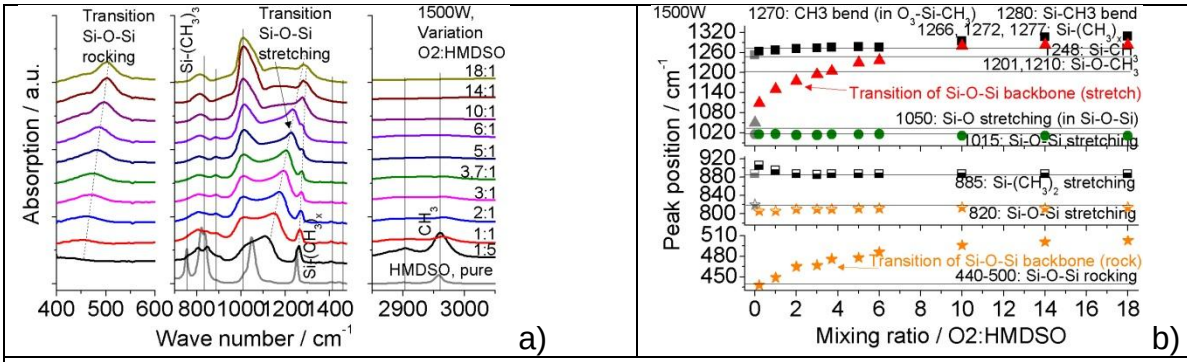



**Figure 4:** a) Depicted FTIR spectra of the plasmapolymeric coatings as well as pure HMDSO. b) Shifting of peak position varying the mixing ratio of the plasmapolymeric coatings.

The investigations in the tribological improvement of the elastomers due to the applied plasmapolymeric coatings showed a reduction of friction (Figure 5). It was found that the coefficient of friction µ could be reduced by 86 % of the uncoated elastomers from 1.24 to 0.17 using plasmapolymeric coatings at dry friction (Figure 5a). In the past an improvement of dry friction by 84 % of the uncoated elastomers from 1.24 to 0.20 using plasmapolymeric coatings applied by classical bar electrodes was shown[6]. Up to four times higher deposition rates of the large scaled electrode in the actual article

[6] Dominik Paulkowski, Klaus Vissing, Tribological improvement of elastomers using plasmapolymeric coatings, 15/1-15/14, Proceedings of Tribologie Fachtagung 2011, GfT, Göttingen

demonstrates the increased cost effectiveness of the deposition process. The significant tribological improvement and the decreased deposition time are fulfilled basic demands from the applied plasmapolymeric coatings.

Regarding sealing rings in automobiles or other elastomer devices a reduction in friction of lubricated contacts is required. It was found that the coefficient of friction µ could be reduced by 43 % from 0.14 to 0.08 at oil lubricated contact (Figure 5b) and up to 71 % from 0.80 to 0.23 at grease lubricated contact (Figure 5c-d). The nanohardness as well as the Young's modulus, the surface energy and the chemical composition of the plasmapolymeric coatings exhibit a clear dependency. That means the wear resistance could be tailored in relation to the damping behavior of the elastomers.

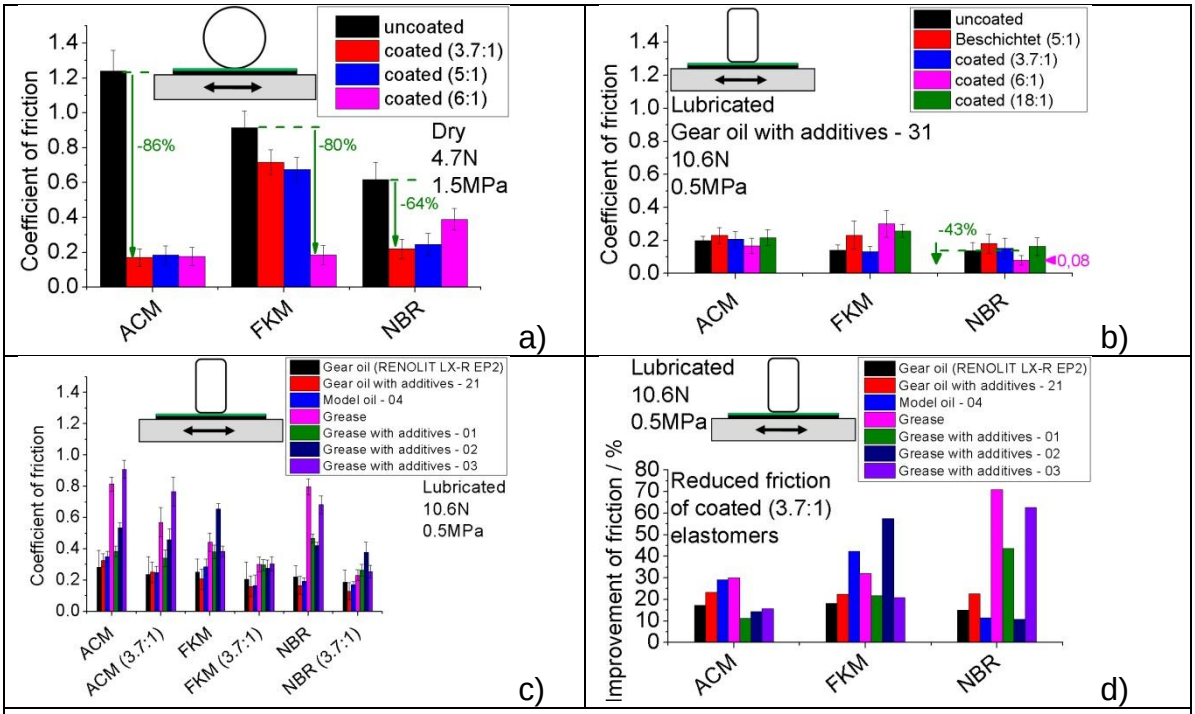



**Figure 5:** Coefficient of friction of uncoated as well as plasmapolymeric coated elastomeric substrates. The contact geometry in each case is drafted in the diagrams. a) Dry, c-d) lubricated friction. In a) and b) the reduction of friction was listed directly, in d) the improvement of c) due to the plasmapolymeric coating is listed.

It has to be noticed that the friction results revealed differences between the three coated elastomeric substrates ACM, FKM as well as NBR (Figure 5). The three elastomeric samples were chosen due to identical 75-Shore-A hardness. The main difference was the relatively higher friction of the plasmapolymeric coatings on FKM in relation to ACM or NBR. Several reasons had been discussed by the authors in the past[6].

The authors acknowledge the financial support of the Bundesministerium für Wirtschaft und Technologie (BMWi) and the participating companies. The support code was 0327499A.