Tribopolymer film formation on sliding electrical contacts exposed to siloxanes

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Abstract*—Investigations of mechanical shear driven organic film formation, or tribofilms, on catalytic metal surfaces in sliding electrical contacts date back to Hermance and Egan's seminal work on mated palladium contacts. In this report we describe investigations of tribofilm formation from outgassing epoxy vapors, consisting of multiple siloxane species, and from isolated constituent species including octamethyltrisiloxane (OMTS). Experiments performed in varying vapor concentrations of OMTS resulted in the formation of tribopolymer films with similar morphology and impact on electrical contact resistance (ECR) as previously published results of sliding electrical contacts in similar conditions submerged in higher molecular weight polymethyldisiloxane (PDMS) fluid. Infrared (IR) spectroscopy was used to confirm the characteristic signatures of siloxanes and silanes in tribopolymer deposits found in wear scars formed in OMTS. Comparisons to prior studies also showed that the films formed from outgassing epoxy vapor constituents (including OMTS and a multitude of other species) have similar characteristics to the silicon-carbon-oxygen (Si-C-O) films previously found to form in high molecular weight PDMS fluid-filled devices. Tribopolymer formation was demonstrated for a range of electrical contact alloy mated pairs (Paliney-7, Neyoro-G, NiPtRe). Experiments in increasing concentrations of OMTS vapor showed that a persistent tribofilm is rapidly formed under cyclic sliding contact shear that can interrupt electrical current, with a formation rate that increases with increasing concentration. Overall, this work demonstrates the ease with which trace organics can promote the formation of insulating tribopolymer films in electrical contacts and factors that can influence their growth.

***Keywords*—tribology, tribopolymer, electrical contact resistance, epoxy, octamethyltrisiloxane, friction, film, outgassing**

I. Introduction

The formation of tribopolymer film (friction polymer) on electrical contacts immersed in polymethyldisiloxane (PDMS, aka silicone oil) was described previously [1,2]. The main constituents of the tribopolymer film were Si, C, and O. The current work involves the formation of tribopolymer films from electrical contacts exposed to *gas/vapor species*, for which it is more difficult to identify an exact source if multiple polymers are used within a system. Although there is a long history in the literature on friction polymer formation from vapor species exposure [3-5], e.g. Hermance and Egan's early work on acetone, toluene, etc. on palladium contacts, there are few studies related to epoxy outgassing. Epoxies are typically considered stable in terms of outgassing that might affect electrical contacts. However, the use of amine curative agents [6] (for example, aminopropyl-piperazine) in certain epoxies may give rise to the possibility of offgassing and subsequent surface deposition which, when combined with frictional sliding, could lead to tribopolymer film formation. Table 1 shows the offgassing products from epoxy EA9394 (Loctite) analyzed by residual gas analysis (RGA).

The current work focuses on friction testing, tribopolymer film characterization, and electrical contact resistance (ECR) measurements on precious metal alloy contacts. First, experiments were conducted with offgassing of a commercial epoxy. Later, experiments were performed in an individual vapor species $C_8H_{24}O_2Si_3$, octamethyltrisiloxane (OMTS), identified from chemical analysis of the epoxy offgassing products. This work highlights the importance of considering offgassing when designing sensitive electronic components with nearby epoxies, in particular, if elevated temperature curing cycles are employed.

II. Experimental Procedure

A. Tribology Experiments

Initial friction experiments were run in an environment with a high/near-saturation concentration of epoxy vapor species using precious metal electrical contact alloys Paliney-7 and Neyoro-G. Paliney-7 is a complex palladium based alloy and Neyoro-G is a Au/Cu based alloy [7]. The test setup was a custom-built high-throughput tester (HTT). The system uses a dead-weight load and strain gage friction force measurement method and a high precision linear actuator to generate a reciprocating motion resulting in a typical sliding contact speed of 1 mm/s. In the first series of experiments, freshly mixed two-part epoxy adhesive known as EA9394 (Loctite) was placed in a 4 inch diameter glass container, which was placed in the chamber, sealed and allowed to cure for 2 hours prior to beginning a sliding contact experiment. A Paliney-7 flat coupon polished to about 20 nm average roughness was mated against a

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Neyoro-G spherically tipped cylindrical pin with 1/16 inch tip radius, and both surfaces cleaned in an ultrasonic bath of isopropyl alcohol followed by an O_2 plasma treatment. The experiment consisted of reciprocating sliding contact with a 1 mm long stroke at a contact force of 100 mN.

Follow-on experiments were conducted in the presence of offgassing OMTS. This low molecular weight siloxane species was identified among the offgassing products from EA9394 by RGA, Table 1. Thus, the tests were meant to identify the behavior of an individual "bad actor" species, rather than the mixed complex chemistry of the outgassing epoxy itself. A series of tribochemical formation experiments were performed using the same sphere-on-flat contact pairs of Paliney-7 and Neyoro-G, as well as a NiPtRe alloy (Deriney-72). The concentration of OMTS was controlled by either 1) coarse control with a bubbler mixing system or 2) finer control with a permeation tube system, shown schematically in Fig. 1.

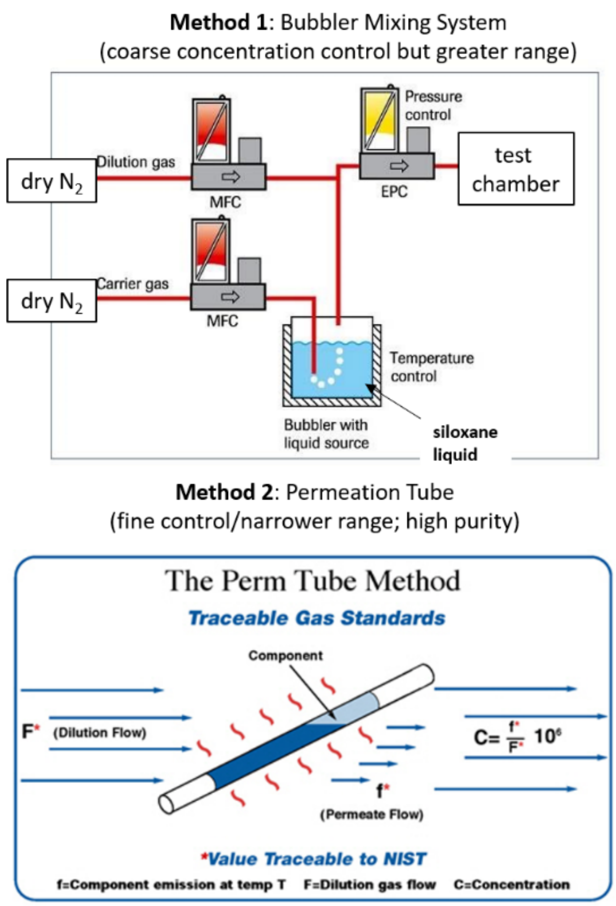

Fig. 1. Schematic diagrams of (top) coarse siloxane vapor concentration control via a bubbler mixing system (https://www.bronkhorst.com) and (bottom) fine, ppm/ppb control via a permeation tube system. (https://kin-tek.com)

B. Electrical Contact Resistance (ECR) and Microstructural Characterization

In both sets of experiments, the wear tracks were then interrogated at a lower contact force of 50 mN using a 4 wire measurement, where the tip was rastered across the tracks incrementally to generate an electrical contact resistance (ECR) map. Finally, the wear tracks (tribopolymer films) were characterized using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) at low accelerating voltage of 5kV, useful for identifying thin films and light elements.

III. Si-C-O Tribofilm Formation

A. Initial Experiments, Epoxy Outgassing

Fig. 2 shows the friction experiment results, SEM micrographs, and EDS maps of the wear track formed in an environment saturated with the outgas species from curing/cured EA9394 epoxy. The friction coefficient obtained with the Paliney-7/Neyoro-G contact pairs varied randomly from ~0.25 to >0.5 during the reciprocating test up to 1000 cycles. The buildup of tribopolymer film is apparent, especially at either end of the wear track. Note, especially in backscatter SEM contrast, the tribopolymer film appears dark (light Z elements) relative to the high-Z precious metal alloy surface. The EDS maps clearly show Si, C, and O, indicative of "Si-C-O" tribofilm formation, again mainly at the ends but also in the center of the track to a lesser extent. Note the experiment was repeated a second time with the same results.

Fig. 3 displays the ECR map obtained from two wear tracks produced under outgassing EA9394 epoxy conditions. The background ECR on the surface of the Paliney-7 substrate is generally 0.100 Ohms or less. Within the wear track, the ECR is much higher with isolated locations of 1 Ohm or greater due to the buildup of the insulative tribopolymer film. The maps confirm that the friction polymer is present not only at the ends but throughout the center of the wear track as well.

The results in Figs. 2 and 3 show that insulative Si-C-O tribofilm, similar to that found during previous investigations in silicone oil [1,2], is formed in laboratory experiments under conditions of outgassing EA9394 epoxy. Further analyses of the cured epoxy and the Si-C-O film were performed using infrared (IR) spectroscopy, discussed only briefly here. The curing/cured epoxy was found to give off water and carbon dioxide, as well as methanol produced during the curing reaction. Importantly, silane signatures were also detected in the gas phase and the silane/siloxane peaks were consistent with octamethyl-cyclotrisiloxane (OMTS). The reactive silanes given off by the epoxy are considered unusual but are believed to come from a bonding agent added to the epoxy formulation [6]. IR analysis of the tribofilm residue from the wear tracks also showed IR bands consistent with siloxane formation, including 1) $Si\text{-}CH_3$ bond deformation, 2) Si-O-Si bond stretch, and 3) $Si\text{-}CH_3$ asymetric stretch. The siloxane signatures were the same as those found from the outgassing epoxy itself.

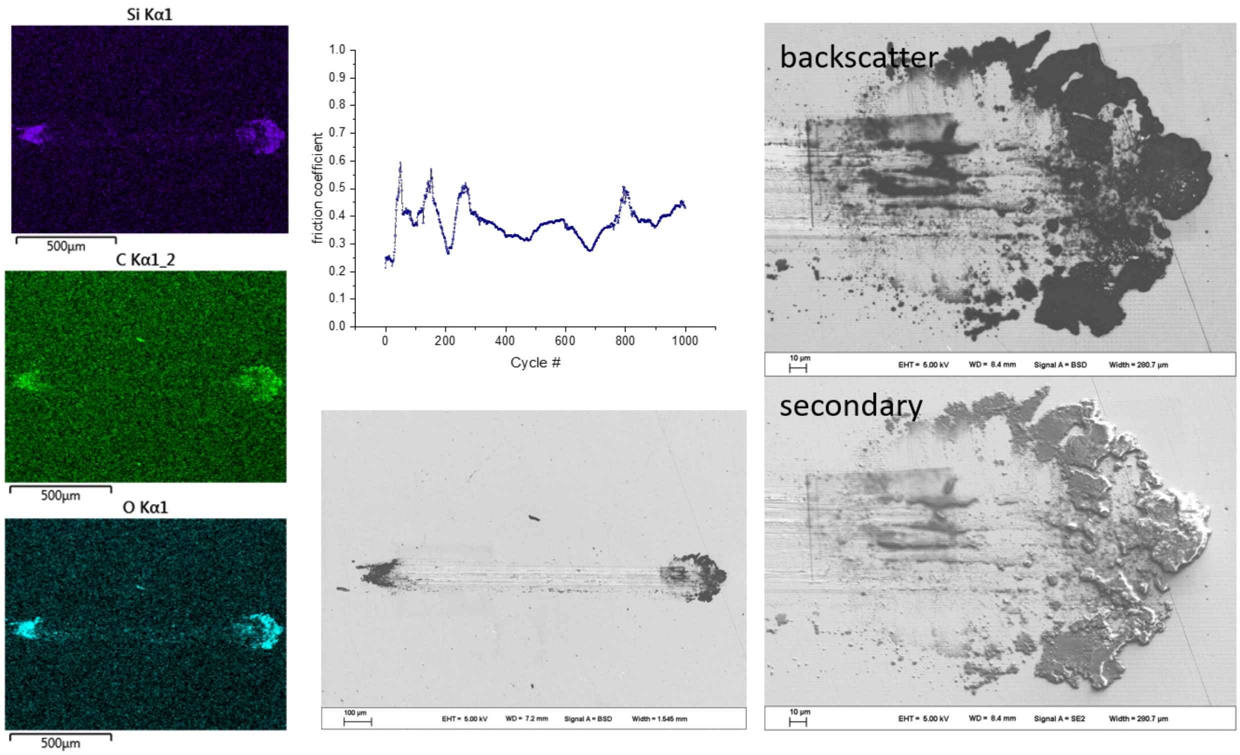

Fig. 2. SEM/EDS micrographs and friction data for the friction experiment in an environment saturated with a mixture of outgas species from cured/curing EA9394 epoxy.

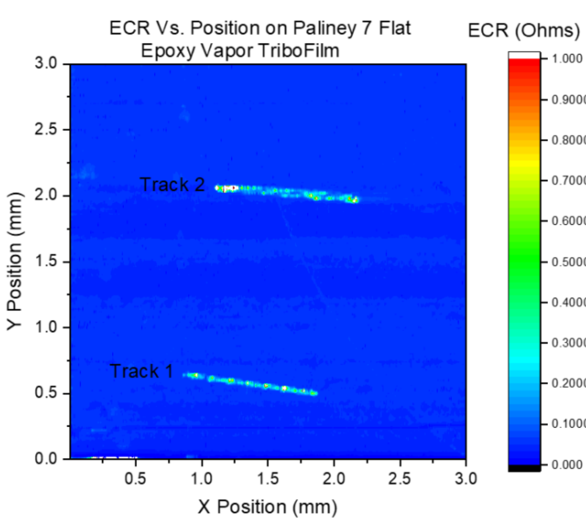

Fig. 3. Electrical contact resistance (ECR) map showing the impact of tribofilm formation experiments described above; regions in white correspond to ECR values > the limit of 1 ohm, including an open contact condition, contrasting with typical values of 10-50 milliohms.

B. Tribofilm Formation in Near-Saturation Octamethyltrisiloxane (OMTS) + Dry N_2 Environment

Since OMTS was identified as a prominent siloxane species from compositional analysis of epoxy curing outgassing experiments, this low molecular weight siloxane species was isolated for additional investigation. The objective was to identify the behavior of individual "bad actor" species, rather than the mixed complex chemistry of the outgassing epoxy itself. The tribochemical formation experiments were performed using the same sphere-on-flat contact pair configuration and the same methods were employed to control the environment concentration (Fig. 1 above).

Representative cycle-average friction data and SEM micrographs are presented in Fig. 4 for a bubbler mixed OMTS near-saturation experiment. A 1 specific cubic foot per hour (SCFH) flow rate of dry N_2 was mixed with a stream of 5 SCFH OMTS-saturated dry N_2. This mixture consisted of near-saturation (80% of p_{sat}) OMTS. The friction response was similar to that of the mixed epoxy outgas and air environment, shown in Fig. 2, though this series of experiments were performed to a total of 10k (rather than 1k) cycles. The SEM images show a significant build-up of Si-C-O tribopolymer along the periphery and near the ends of the sliding contact track. The tribopolymer volume is more significant and its distribution more uniform compared to the mixed epoxy outgas test, presumably due to the 10x higher number of sliding contact cycles.

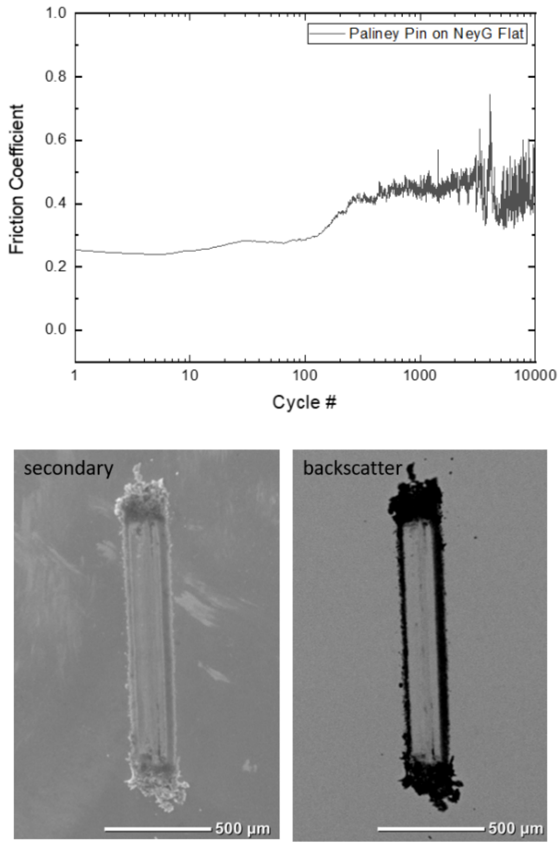

Fig. 4. (Top) plot of cycle-average friction coefficient data for a mated Paliney-7 and Neyoro-G contact and (bottom) secondary and backscatter SEM micrographs of the wear tracks generated in an environment consisting of dry N_2 and 80% of saturation vapor pressure OMTS.

C. Siloxane Vapor Concentration-Dependent Tribopolymer Film Formation (0.1 to 100% of Saturation – including Liqud Immersion)

A series of experiments was performed to systematically investigate the impact of siloxane vapor species concentration using OMTS and dry N_2 mixtures and the same contact conditions (100 mN contact force, 1 mm/s sliding speed) and mated alloy pairs (Neyoro-G and Paliney-7). Both the permeation tube and bubbler mixing systems were employed to cover this range of concentrations. Cycle-average friction coefficient data is shown in Fig. 5. Secondary SEM images and ECR maps are shown in Fig. 6. The 100% OMTS concentration resulted in condensation and the formation of a liquid meniscus around the contact between the spherically tipped pin and flat substrate. A key conclusion from this data is that the formation of an in-track, persistent tribofilm that can interrupt electrical current seems to increase with increasing concentration with the exception of the 100% condition, where there is evidence of significantly greater buildup but overall less impact within the track. It is possible that the tribofilm formed in a fully-saturated or practically liquid-immersed condition is not as well-adhered as the film that is formed in a siloxane vapor containing environment.

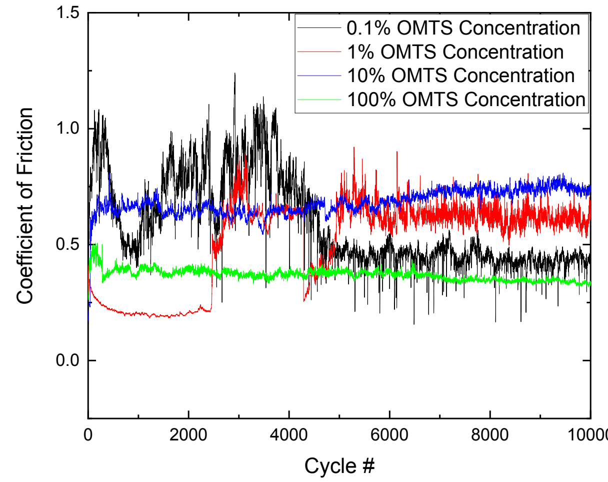

Fig. 5. Cycle-average friction coefficient data for experiments at concentrations of OMTS in dry N_2 covering four decades.

D. Summary and Conclusions

This report summarized the experimental work on tribofilm formation from an outgassing epoxy and an individual chemical species (OMTS) isolated from the offgas products. This work confirmed that tribofilm formation from outgassing of vapor species from epoxy can be reliably reproduced in the laboratory. Experiments with outgassing epoxy samples showed that tribopolymer films with similar morphology and effects on electrical contact resistance (ECR) were formed as compared to previous work in (liquid-phase) PDMS silicone oil [1,2]. Microchemical and SEM analyses also showed that the films formed from outgassing epoxy vapor have similar characteristics to the Si-C-O films studied previously in PDMS fluid-filled devices. Other experiments summarized here show that an individual chemical vapor species, OMTS, also produces tribopolymer films on mated pairs of Paliney-7 and Neyoro-G, as well as a NiPtRe alloy (Deriney-72). Experiments with increasing concentration of OMTS showed that a persistent tribofilm is formed that can interrupt electrical current and seems to increase with increasing concentration with the exception of the 100% condition, where there is evidence of significantly greater buildup but overall less impact within the track. It is possible that the tribofilm formed in a fully-saturated or practically liquid-immersed condition is not as well-adhered as the film that is formed in a siloxane vapor containing environment. Overall, the studies described here warrant further research on tribopolymer formation from outgassing of polymeric materials.

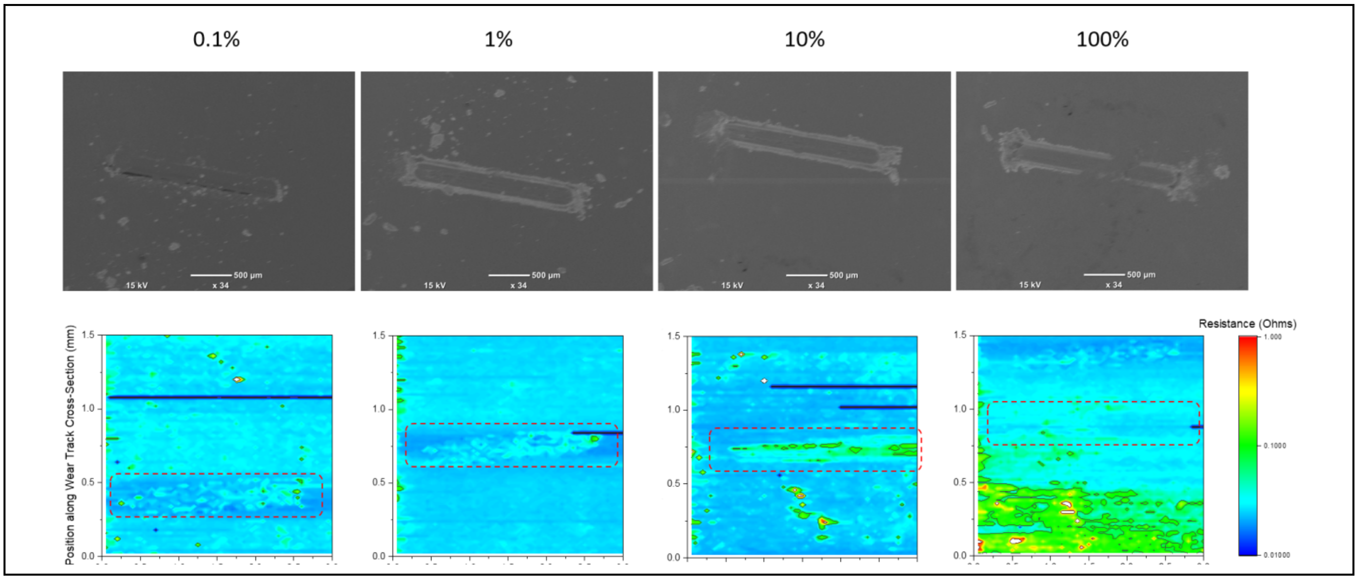

Fig. 6. (Top row) secondary SEM micrographs and (bottom row) ECR maps of wear tracks exposed to varying concentrations of OMTS vapor, including a fully-saturated condition where a liquid meniscus was observed to have formed between the contact surfaces.

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