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Tribology of self-lubricating SU-8+PFPE composite based Lub-tape

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Abstract

Despite of the fact that the SU-8 is a useful material for micro-fabrication of MEMS devices using the photo-lithography process, its poor tribological properties restrict its wider applications. It was postulated in our previous study that adding perflouropolyether (PFPE) lubricant to SU-8 possibly promoted chemical reaction between the molecules and also formed the boundary lubrication, which enhanced the wear durability of SU-8 by more than four orders of magnitude. The same SU-8+PFPE composite were used to fabricate a stand-alone laminate film called "Lub-tape", which has two layers of ~90 µm thickness each. The top and bottom layers were made of SU-8+PFPE composite and pristine SU-8, respectively. The lub-tape has reduced the initial coefficient of friction by ~7 times and increased wear life by more than five orders of magnitude of SU-8. It can also improve the tribology of any given surface. The Lub-tape can be used to protect all surfaces against friction and wear.

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Keywords: Polymer tribology; SU-8 composites; PFPE; lub-tape; chemical bonding;

Nomenclature	
SU-8+PFPE	PFPE lubricant blended with SU-8
PFPE	Perflouropolyether
Lub-tape	Lubrication Tape
Wt%	Weight percentage
μ_i	Initial coefficient of friction
μ_s	Steady-state coefficient of friction
N,n	Number of sliding cycles, wear life
At%	Atomic percentage
Greek symbols	
γ_s^d	Polar surface free energy (mN/m)
γ_s^p	Dispersive surface free energy (mN/m)
θ	Contcat angle (°)

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1. Introduction:

Tribology (i.e. friction and wear) is becoming an important factor while designing any micro-electro mechanical systems (MEMS). MEMS are micro sized devices, which are designed to perform variety of operations in various fields including automotive, bio-engineering, bio-medical and military etc. The surface forces are becoming highly detrimental to operation of these devices, as the surface area-to-volume ratio becomes large. However, these forces are capable of stopping the operation of the device against its inertial forces [1]. Though the Si has been conventional MEMS structural material for the past few decades, this could change with SU-8 as the mainstay structural material for certain applications. SU-8 is a negative thick-film photoresist patented by IBM in 1989[2]. SU-8 consists of three basic components: (a) an EPON^{TM} SU-8 epoxy resin; (b) a solvent such as gamma-butyrolactone (GBL) and (c) a photoacid generator such as triaryl sulfonium salts. Each SU-8 molecule consists of an average of 8 epoxy groups (and hence the name SU-8). SU-8 has many advantages over Si, such as bio-compatibility, compatible with micro-fabrication process by its unique UV sensitive property and more hydrophobic [3]. Despite of above mentioned advantages, it has two major drawbacks. Those drawbacks are its poor tribological and mechanical properties.

Very few works can be found on improving the tribology of SU-8. Jiguet et al [4] have studied the effect of silica particles reinforcement with SU-8 and heat treatment of SU-8. The improvements in tribology from reinforcement are very marginal, but the heat treatment improved tribology considerably. Few other studies by Singh et al [5, 6], notable is the two-step surface modification process, which uses the oxygen-plasma treatment of SU-8 surface, followed by coating of lubricant such as perfluoropolyether (PFPE). The tribology of the SU-8 improved significantly by this method. Another one is chemical-modification of SU-8 surface by treating chemically with ethanolamine-sodium phosphate buffer, followed by the coating of PFPE lubricant. The wear life is increased considerably, which attributed to end groups bonding between PFPE and ethanolamine.

PFPE has several superior properties such as high chemical and thermal stability, resistance to oxidation, low vapor pressure, self-replenishment property, hydrophobic nature, good lubricity and good adhesion with different substrates [7]. Therefore, it was used as a lubricant filler material in our recent study [8], where SU-8+PFPE composites have shown the significant reduction in the initial coefficient of friction and increased the wear life by more than four orders of magnitude. It was postulated that the SU-8 and PFPE molecules might undergo a chemical reaction and form an ether bond.

The present lub-tape is a variation of the SU-8+PFPE composite and consists of two layers, ~90 μm each; top layer is SU-8+PFPE and bottom one is pristine SU-8. The pristine SU-8 has high frictional properties, hence it can be easily stuck to the targeted surface. The top composite has low frictional properties, so that can be exposed to any counterface coming in contact. The PFPE concentration in the composites was increased from 5 wt% to 10 wt% and then the tribological behavior was evaluated. Observed tribological behavior will be discussed in succeeding sections.

2. Materials and Experimental Procedure:

Over-head projector (OHP) sheet wafers were cut into ~3 cm x 3 cm pieces and were thoroughly cleaned with soapy water, distilled water and isopropyl alcohol (IPA), respectively, and finally dried with N_2 gas. The cleaned OHP sheet wafers were then subjected to the spin-coating immediately. The SU-8 used for the sample preparation was SU-8 2050. For the preparation of the "Lub-tape" films, SU-8 was spin-coated onto OHP sheet wafer at an initial speed of 500 rpm for a duration of 5 seconds, followed by an increase in the spinning speed to 3000 rpm for a duration of 60 seconds which results in SU-8 films with a thickness of ~75 microns. Thicknesses of the films were measured using WYKO NT1100 optical profiler (Vecco Instruments Inc, USA). The spin-coated SU-8 films were then subjected to the pre-baking at a temperature of 65 ^{o}C for 4 minutes, and then followed by at 95 ^{o}C for 9 minutes. The pre-baked SU-8 films were then again subjected to spin-coating of SU8+PFPE nanocomposite over the pre-baked SU8 film at an initial speed of 500 rpm for a duration of 5 seconds, followed by an increase in the spinning speed to 3000 rpm for a duration of 60 seconds which results in SU-8+PFPE film with a thickness of ~75 microns. The spin coated SU-8+PFPE films over SU8 films on the same wafer were then subjected to the pre-baking at a temperature of 65 ^{o}C for 4 minutes followed by 95 ^{o}C for 9 minutes, respectively. Then, the spin-coated SU8+PFPE nanocomposite film along with the bare SU8 film was subjected to UV (ultra-violet) rays (wavelength: 365 nm and power: 210 mJ/cm^2) for a duration of 30 seconds. A post- exposure bake was carried out at a temperature of 65 ^{o}C for 1 minute and then followed by 95 ^{o}C for 7 min, respectively, after UV exposure. Finally, the "Lub-tape" film was peeled off from the OHP substrate with mild heating. The peeled off Lub-tapes were stored in the desiccators before any further characterization.

Surface free energy was calculated for pristine SU-8 and SU-8 composites using water static contact angle measurements (WCAs). Geometric equation was used for calculation of surface free energy of the films, given below in equation (1).

$$(1+COS\theta_i)\gamma_i = 2\left(\sqrt{\gamma_i^d \gamma_s^d} + \sqrt{\gamma_i^p \gamma_s^p}\right) \quad (1)$$

where θ_i is the contact angle, γ_i^d and γ_i^p are dispersive and polar surface tensions of liquids respectively. γ_s^d and γ_s^p are the dispersive and polar surface energies of the surface, respectively, to be calculated. The surface free energy calculations were also performed inside the regions of wear track.

Tribological tests (friction and wear tests) were performed using UMT-2 (universal Micro Tribometer, CETR, USA) in a ball-on-disk setup. The typical number of sliding cycles vs coefficient of friction (COF) plot is outcome of the sliding tests, where COF values were derived with respect to the corresponding sliding cycles. Si_3N_4 balls of 4 mm diameter with a surface roughness of 5 nm were used as the counterface. From the sliding tests, an initial coefficient of friction (μ_i) was noted as an average of the first twenty sliding cycles. The steady-state coefficient of friction (μ_s) was measured as the average of all coefficients of friction from the point where the steady-state behavior (after the observation period of initial coefficient of friction) was observed until the end of the test or until the failure point, whichever was earlier [8].

The wear life for the tested conditions was taken as the number of sliding cycles after which the coefficient of friction exceeded 0.3 or a visible wear track was observed on the substrate with abnormally fluctuating friction values, whichever occurred earlier.

The surface morphologies of the wear track and the cross-section of pristine SU-8 and SU-8 composite films were studied using Field Emission Scanning Electron Microscopy (FESEM) (FESEM S-4300, Hitachi High-Technologies Inc, Canada). Prior to FESEM imaging, the samples were gold coated at 10 mA for 30 s using a JEOL, JFC-1200 Fine Coater. EDS attached to the FESEM was used to analyze the chemical elements of pristine SU-8 and SU-8 composites.

3. Results and Discussion:

The SU-8 based "Lub – Tape" films formed under the conditions provided in the experimental section have shown a thickness of ~180 μm. Figure 1 shows the low and high friction features of film and descriptions about them.

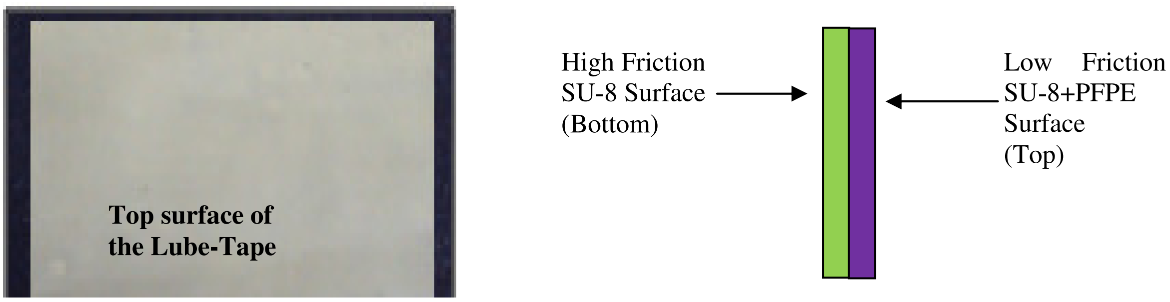
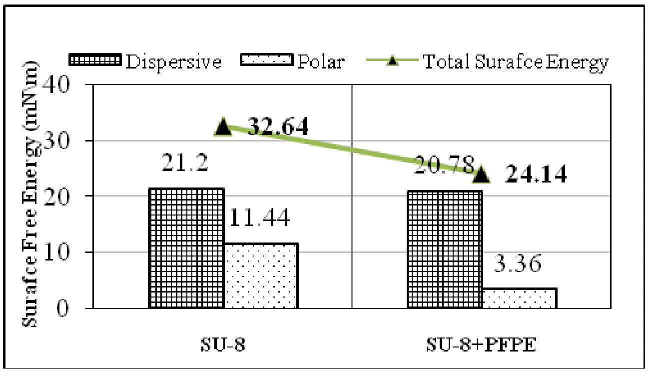


Figure 1: *Free standing SU-8 based "Lub-Tape" (left image) showing the top view. A graphical illustration of the cross section of the Lube-Tape (right image) showing different friction behavior of top surface and bottom surface, respectively.*

The top surface of lub-tape is shown in left image of Figure 1, which is the low friction SU-8+PFPE composite surface. The bottom layer is pristine SU-8 layer, which is the high friction layer and also can be easily stuck onto any surface.

3.1. Surface Free Energy Calculations on Fresh Surface:

Freshly spin-coated surfaces of pristine SU-8 and SU-8+PFPE composite sides were subjected to surface free energy calculations, as shown in Figure 2(a). Pristine SU-8 shows the highest surface free energy of 32.64 mN/m, hence it offers greater adhesion and friction, where as SU-8+PFPE shows the surface free energy of 24.14 mN/m. However, the pristine SU-8 shows the polar surface energy of 12 mN/m, which is four times higher than that of SU-8+PFPE. This high polar nature of pristine SU-8 makes the surface much more hydrophilic. Hence high polar component of the surface free energy may lead to high adhesion and friction [9].



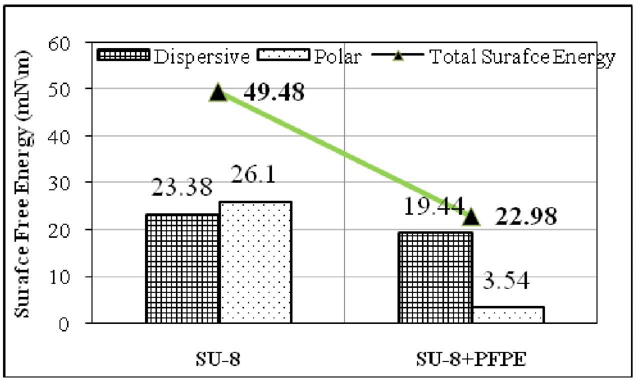


Figure 2: *Polar, dispersive and total Surface energies of pristine SU-8 side and SU-8+PFPE side of Lub-tape. (a) At fresh surfaces. (b) At worn surfaces (wear track).*

3.2. Tribological Characterization:

Table 1: *Tribological test results of SU-8 Lub-tape (initial coefficient of friction (μ_i), steady-state coefficient of friction (μ_s) and wear life (number of sliding cycles) of 10 and 5 wt% SU-8+PFPE lub-tapes, tested against 4 mm diameter Si_3N_4 ball at a different loads and a sliding speeds. (Both sides of the Lub-tape were tested, as indicated).*

Composite Description	Initial coefficient of friction, COF (μ_i)	Steady- state coefficient of friction, COF (μ_s)	Wear Life (Number of Cycles, N)
10wt% SU-8+PFPE Free Standing Lub-tape Film /Test Parameter: 300g, 2000 rpm			
High Friction Side (SU-8 alone)	0.62	0	~10
Low friction Side	0.08	0.12	Failed at 700000 cycles
5wt% SU-8+PFPE Free Standing Lub-tape Film /Test Parameter: 300g, 1000 rpm			
High Friction Side (SU-8 alone)	0.56	0	~10
Low friction Side	0.05	0.019	>500000
High Friction Side (SU-8 alone)	0.53	0	~10
Low friction Side	0.06	0.08	>500000

Table 1 shows the initial coefficient of friction (μ_i), the steady-state coefficient of friction (μ_s) and the wear life data for Lub-tape films (conducted at both sides i.e. high friction and low friction sides, respectively) with different PFPE concentrations and at different loads and rotational speeds, respectively. The tribological data summarized in Table 1 were obtained from typical coefficient of friction (μ) versus number of cycles (N) plots as shown in Figure.3. The tribological properties obtained at a normal load of 300 g and a rotational speed of 1000 rpm will be discussed in this section and for other results, Table 1(Top) can be referred. The high friction pristine SU-8 side has shown high friction properties (μ_i: 0.62,0.56 and μ_s: 0) and low wear life (n~10) when tested at a normal load of 300 g and at rotational speeds of 1000 rpm and 2000 rpm, respectively.

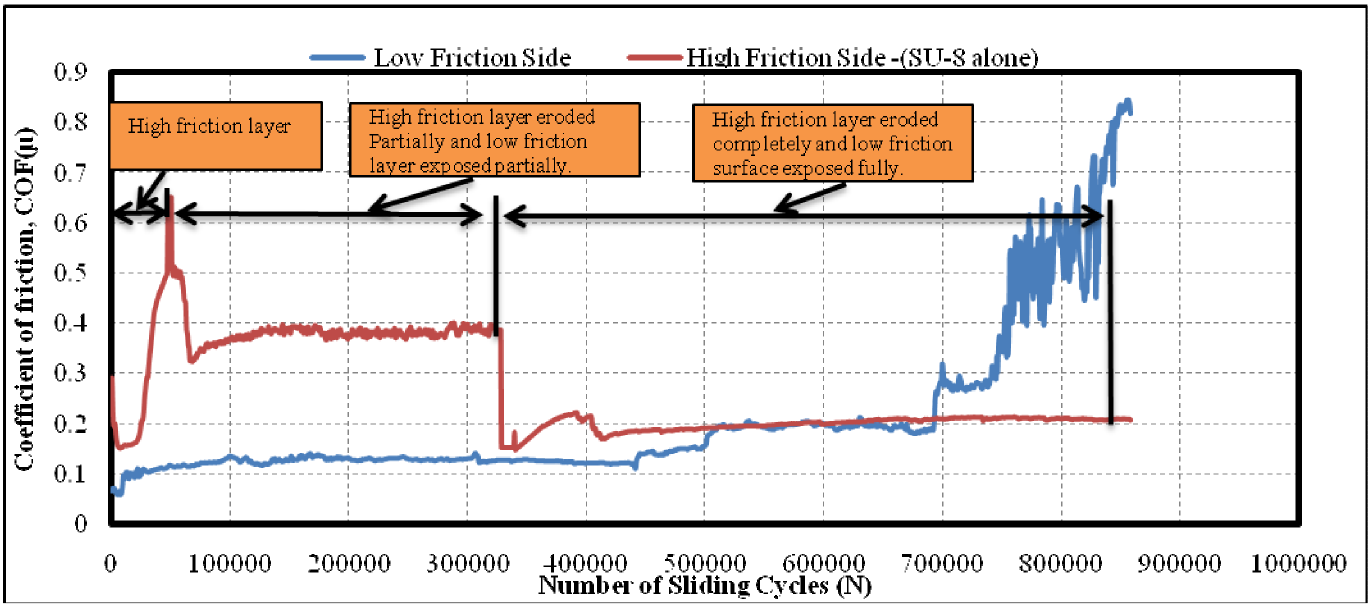


Figure 3: ***(a).*** *Typical coefficient of friction versus number of cycles plot for 10 wt% SU-8+PFPE composite based Lub-tape film obtained from the ball-on-disk sliding tests against 4 mm diameter Si_3N_4 ball at a normal load of 300 g and a sliding speed of 2000 rpm. The same trend was observed for 5 wt% SU-8+PFPE composite Lub-tape films, not presented here.*

Under the same loading conditions, SU-8+PFPE side has shown very low coefficients of friction (μ_i: 0.08 and μ_s: 0.12) and high wear life (n>500,000). Therefore, the composite of SU-8+PFPE present on the other side of the tape shows significant improvement in tribological properties (the μ_i has been reduced by ~8 times and the wear life has been improved by >250 times) when compared with the properties of high friction side (pristine SU-8). The high friction side of the Tape can be used to adhere to the surface of interest and apparently the SU8+PFPE layer will be exposed against the counterface material and can reduce the friction and increase the wear life. The PFPE concentration in the composites was increased from 5 wt% to 10 wt% and then the tribological behaviour was evaluated. An increase of PFPE concentration from 5 wt% to 10 wt% has shown an improvement in tribological properties by 30-40%. Therefore, the concentration of the PFPE has to be optimized depending on the application requirements and the operating conditions of the Lub-tape once it is placed in the application.

3.3. Surface Free Energy Calculations on Worn Surface:

Surface free energy measurements were performed on wear tracks of pristine SU-8 and SU-8+PFPE composite sides of lub-tape after enduring 500,000 sliding cycles (not necessarily for SU-8) at a normal load of 300g and sliding speed of 1000 rpm, shown in Figure. 2(b). Pristine SU-8 shows the highest surface energy of 49.48 mN/m. It also shows the highest polar contribution of 26.1 mN/m, which is 15 mN/m more than that of the fresh surface, indicating that unsatisfied broken bonds make it highly hydrophilic. However, SU-8+PFPE shows the very low surface energy of 22.98 mN/m, which is ~2 mN/m less than fresh surface, suggesting that proper surface coverage by PFPE lubricant.

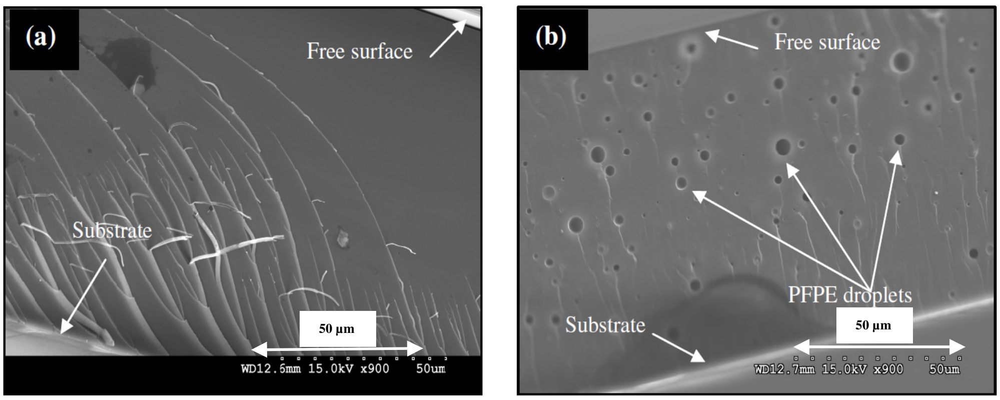
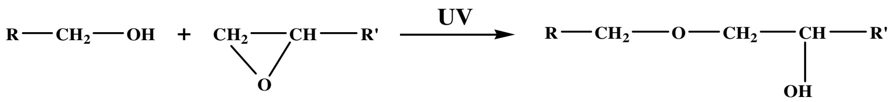


Figure 4: *SEM cross-sectional images of ~100 μm thick pristine SU-8 and SU-8+PFPE composite films. (a) Pristine SU- (b) SU-8+PFPE.* [10]

3.4. Boundary Layer Lubrication :

Figure 3 shows the cross-sectional images of pristine SU-8 and SU-8 composite films. It is necessary to find the source of lubrication for the prolonged wear life of SU-8+PFPE composites over pristine SU-8. Physical boundary layer lubrication also found responsible along with chemical bonding between SU-8 and PFPE molecules. Before curing and UV exposure, the composite resin is in the gluey state, where the SU-8 matrix has lubricant (PFPE) droplets of sizes ranging from few nm to µm dispersed throughout its matrix. After UV exposure and curing, the SU-8 undergoes cross-linking and becomes solid. As the lubricant remains unaffected by the UV radiation, the droplets remain trapped inside the solid SU-8 bulk. This trapped lubricant in tiny cavities gives an advantage of storing lubricants for self-regeneration and lubrication. The sectioned images are the measure of the lubricant dispersion and agglomeration within the composites. However, pristine SU-8 (Figure.4 (a)) shows plain surface without any surface features. SU-8+PFPE (Figure.4 (b)) shows uniformly dispersed round shaped droplets in greater numbers all across the film. Once the lubricant layer over the surface is worn away with counterface sliding, the lubricant droplets beneath the worn surface is released which forms the boundary layer to reduce the friction and wear and the same cycle repeats till the complete wear of the composite. This model also emphasizes that the tribological performance of composites depends on the uniform dispersion of lubricants and bonding of the lubricants with the surface. Hence, the effect of dispersion and bonding of the lubricant is vital in the wear durability of the SU-8+PFPE composites.

The significant improvement in tribological properties of SU-8 by the addition of PFPE can be attributed to the possible ether bond formation between the SU-8 and PFPE molecules [11, 12]. The possible etherification reaction is depicted in Equation.2. Perhaps, the -OH terminal groups in the PFPE polymer and the carbocations (C^+) in the SU-8 polymer (epoxide ring) undergoes the reaction, which breaks the existing bond and forms new linkage through ether bonds.



PFPE **SU8** **Crosslinked PFPE on SU8** (2)

The surface free energy calculations, tribological characterization and SEM images indicate the possibility of chemical reaction.

4. Conclusions:

Below listed are the major conclusions drawn from the current work:

1. SU-8+PFPE based lub-tape has reduced the initial coefficient of friction (μ_i) by ~7 times and enhanced wear life by five orders of magnitude at all lubricant concentrations.
2. Possible ether bond formation between SU-8 and PFPE molecules was also responsible for their superior tribological properties over pristine SU-8, verified by tribological characterization and surface free energy calculations.
3. This is novel use of SU-8 composite for reducing the coefficient of friction of any surface and the high friction surface will ensure that the tape sticks to the surface firmly.

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